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A Simple and Efficient Synthesis of RAFT Chain Transfer Agents via Atom Transfer Radical Addition−Fragmentation

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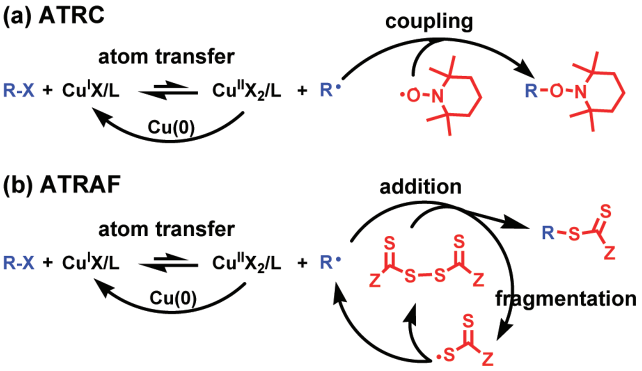
ABSTRACT: A simple, versatile, and one-step atom transfer radical addition−fragmentation (ATRAF) technique is reported for the synthesis of chain transfer agents (CTA) containing dithio groups (dithiobenzoate, dithiocarbamate, and xanthate), with various alkyl substituents, in the presence of copper catalyst, alkyl halide, and bis(thiocarbonyl) disulfide. The ATRAF procedure is efficient and selective, leading to almost quantitative conversion of alkyl halide initiators and formation of CTAs in high isolated yield under stoichiometric conditions as well as in the presence of catalytic amounts of copper(I) species. The CTAs synthesized by this process were used for reversible addition−fragmentation chain transfer (RAFT) polymerizations of styrene and methyl methacrylate without any further column purification, producing well-controlled polymers with low polydispersity, thereby demonstrating the effectiveness of ATRAF. Moreover, a simple one-pot, two-step RAFT polymerization was successful, starting from CTA synthesized in situ via ATRAF, followed directly by the addition of a monomer.

Introduction

Many initiators for controlled radical polymerization (CRP),[1−3] such as nitroxide-mediated polymerization[4−6] or reversible addition−fragmentation chain transfer (RAFT)[7−15] polymerization, are prepared from alkyl halides, used as initiators for atom transfer radical polymerization (ATRP).[16−20] We have previously reported the synthesis of various alkoxyamines from equimolar mixtures of alkyl halides and nitroxides in the presence of small amount of ATRP catalysts and Cu metal, as a reducing agent (Scheme 1a).[21,22] This atom transfer radical coupling (ATRC) process is a preferred way for preparation of high-purity alkoxyamines in high yields.[23−26] Herein, we report an extension of ATRC to the synthesis of various RAFT reagents, including dithioesters, dithiocarbamates, and xanthates. They were prepared in high yields via an atom transfer radical addition−fragmentation (ATRAF) process, using stoichiometric amounts of alkyl halides and bis(thiocarbonyl) disulfides in the presence of ATRP catalysts and, optionally, Cu metal as a reducing agent (Scheme 1b). Purity of RAFT reagents was sufficiently high that they could be successfully used in a RAFT process without any further purification.

RAFT polymerization requires monomer, conventional radical initiator, and chain transfer agent (CTA) in the reaction medium. The simplified RAFT mechanism involves a series of reversible addition−fragmentation chain transfer steps between the CTA and a radical, in addition to the initiation, propagation, and termination steps typical of a conventional radical polymerization.[7,27] The exchange reaction process repeats itself many times, such that every chain has a similar chance to grow. The RAFT process requires a continuous supply of new initiating radicals by the decomposition of radical initiators (such as AIBN), producing new polymer chains. However, this could be avoided by using copper-catalyzed RAFT polymerization (or dithioester-initiated ATRP), yielding purer block copolymers and higher molecular weight polymers.[28]

Scheme 1. (a) Atom Transfer Radical Coupling (ATRC) for Alkoxyamine Synthesis and (b) Atom Transfer Radical Addition−Fragmentation (ATRAF) for CTA Synthesis



The proper selection of the Z and R groups in the CTA (cf. Scheme 1b) for a particular monomer is crucial for a successful RAFT polymerization.[29,30] The selection of the R group should take into account the stability of the dormant species and the rate of addition of R$^•$ to a given monomer. Steric effects in RAFT are much more important than in ATRP,[8,11,31,32] and the order of the leaving ability of R groups reflects the significance of both steric and electronic effects.[2,33] The structure of the Z group is equally important and should be selected appropriately for various monomers. Thus, there is a need for a simple procedure to prepare various CTAs to properly control various RAFT systems.

Low molar mass RAFT agents are synthesized in moderate-to-excellent yields by several methods: (1) reaction of carbodithioate salt with alkylating agent;[29,30,34−39] (2) addition of dithio acid across olefinic double bond;[29,35,40,41] (3) radical-induced decomposition of bis(thioacyl) disulfide;[37,42−44] (4) sulfuration of thioloester,[29,34] carboxylic acid with alcohol,[45] and treatment of carboxylic acid with P$_4$S$_{10}$;[46,47] (5) radical-induced ester exchange;[29,30,35,48] (6) reaction of thiocarbonylbisimidazole with thiol or alcohol.[49,50] However, all the methods reported above require a tedious purification process which adds cost to the final material. Thus, the search for a simple synthesis of RAFT agents in high yields and with high purity continues. Recently, an interesting approach was applied to the end-group transformation of ATRP polymers to dithioester and block copolymerization from the surfaces by converting polymeric alkyl halides to the corresponding RAFT reagents in the presence of bis(thioacyl) disulfide species.[51,52] A large excess

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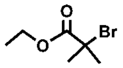
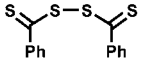
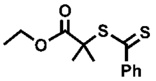
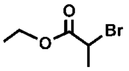
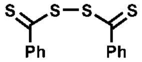
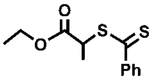
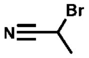
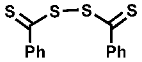
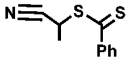
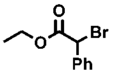
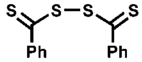
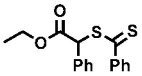
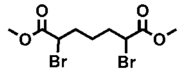
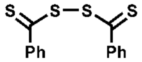
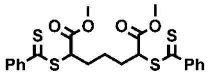
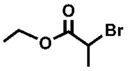
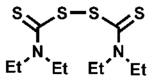
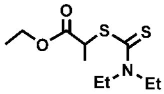
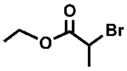
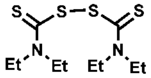
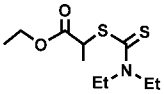
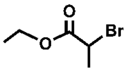
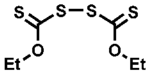
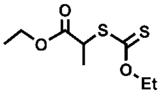
Table 1. Chain Transfer Agents Syntheses via ATRAF[a]

entry	R-X	disulfide	CTA	CTA label	yield (%)	purity (%)
1				**a**	92	99
2				**b**	91	99
3				**c**	89	99
4				**d**	92	99
5				**e**	82	93
6[b]				**f**	65	98
7[c]				**g**	58	99
8				**h**	43	99

[a] R−X/disulfide/CuBr/PMDETA/Cu(0) = 2 (164 mM)/1/0.5/1/2.5 in toluene at 80 °C for 6 h. Purity determined by ^{1}H NMR, yield based on isolated CTA. [b] Performed at 60 °C in acetone. [c] R−X/disulfide/CuBr/PMDETA/Cu(0) = 2 (1.10 M)/1/0.05/0.1/2.2 in acetone for 18 h at room temperature.

of bis(thioacyl) disulfide and copper catalyst over alkyl halides was used, and long reaction times were reported. Unfortunately, the efficiency of this transformation from ATRP to RAFT was not quantified.

Herein, we report the synthesis of a variety of low molar mass RAFT agents with dithiobenzoates, dithiocarbamates, and xanthates as Z groups and with various R groups generated from commercially available alkyl halides. RAFT agents were prepared via ATRAF using a stoichiometric amount of bis(thiocarbonyl) disulfides and alkyl halides in the presence of copper(I) species. The ATRAF process was carried out by mimicking ATRC (Scheme 1a) and replacing a nitroxide with a bis(thiocarbonyl) disulfide, as shown in Scheme 1b. The presence of copper metal, as reducing agent, shifted the equilibrium to the right by regenerating the activator, Cu(I), from the deactivator, Cu(II). The aim of this report is not only to validate the selectivity and efficiency of ATRAF but also to demonstrate the high purity of RAFT reagents prepared by ATRAF. Their purity was sufficient for their direct use in a one-pot, two-step RAFT process, without any further purification.

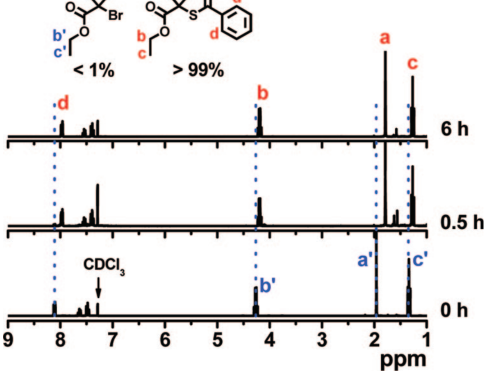


Figure 1. ^{1}H NMR spectra in $CDCl_3$ of the mixture of EBiB (164 mM), BTBD, CuBr, PMDETA, and Cu(0) with a molar ratio of 2/1/0.5/1/2.5 in toluene before and after heating at 80 °C. Note that samples were passed through a short alumina column to remove copper catalyst, followed by removal of the solvent.

Experimental Section

Chemicals. Styrene (St, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were passed through a column filled with

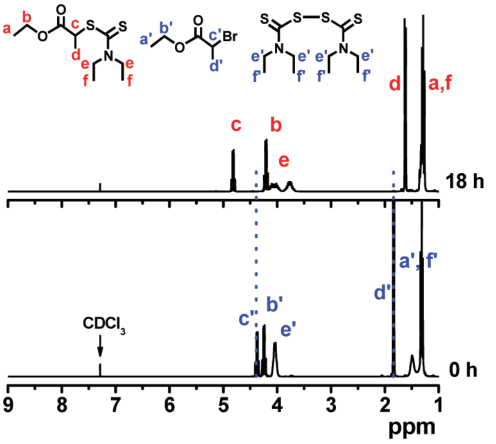


Figure 2. ^{1}H NMR spectra in $CDCl_3$ of the mixture of EBP (1.10 M), TETD, CuBr, PMDETA, and Cu(0) with a molar ratio of 2/1/0.05/0.1/2.2 in acetone before and after reaction at room temperature.

Table 2. Result of RAFT Polymerization of St and MMA with CTAs[a]

monomer	CTA	*t*/h	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n	conv/%
St[b]	**a**	15	6040	5900	1.26	29.0
St	**d**	7.5	2560	2500	1.10	13.4
		19	6170	5800	1.14	29.6
MMA	**d**	7.5	12400	18700	1.22	62.0
		19	20000	22800	1.24	>99

[a] St (or MMA)/**d**/AIBN = 200/1/0.5 in 50% (v/v) anisole at 60 °C. [b] St/**a**/AIBN = 200/1/1 in 50% (v/v) anisole at 60 °C.

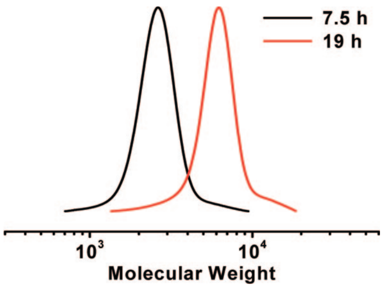


Figure 3. GPC chromatogram of PSt prepared with **d** at 60 °C: St/**d**/AIBN = 200/1/0.5 in 50% (v/v) anisole.

basic alumina, dried over calcium hydride, and distilled under reduced pressure prior to use. Bis(thiobenzoyl) disulfide (BTBD, 99%) was synthesized according to procedures previously reported in the literature.[30,42,44,51] BTBD was purified by triple recrystallization from ethanol to increase purity, obtained as red flakes (34% yield and >99% purity). α,α′-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was purified by recrystallization from methanol. Bis(ethylxanthogen) (97%, Pfaltz & Bauer) was purified by distillation under reduced pressure. Copper(I) bromide (99.999%, Aldrich), copper powder (<425 μm, 99.5%, Aldrich), carbon disulfide (anhydrous, > 99%, Aldrich), ethyl α-bromoisobutyrate (EBiB, 98%, Aldrich), ethyl 2-bromopropionate (EBP, 99%, Aldrich), ethyl α-bromophenylacetate (EBPA, 97%, Aldrich), dimethyl 2,6-dibromoheptanedioate (97%, Aldrich), tetraethylthiuram disulfide (TETD, 97%, Aldrich), and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) were used as received. All the other reagents and solvents were used as received.

Analyses. Molecular weight and polydispersity were determined by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) in tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min (35 °C). The column system was calibrated with linear polystyrene (PSt) and poly(methyl methacrylate) (PMMA) standards. Conversions of all monomers were determined with known concentrations of polymers in THF. ^{1}H NMR spectra were recorded in $CDCl_3$ as a solvent using a Bruker 300 MHz spectrometer with a delay time of 1 s.

Typical Procedure for CTA Syntheses. (**a**) CuBr (23.4 mg, 41 mM) and Cu(0) (425 μm, 51.9 mg, 205 mM) were added to a dried Schlenk flask equipped with a stir bar. The flask was degassed and backfilled with nitrogen (N_2) five times and then left under N_2. Subsequently, a mixture of BTBD (100 mg, 82 mM), EBiB (127.5 mg, 164 mM), PMDETA (56.6 mg, 82 mM), and toluene (4 mL) was added to a glass vial and degassed by three freeze−pump−thaw cycles. This solution was then transferred to the Schlenk flask, which was placed in a thermostated oil bath at 80 °C. Samples were taken periodically under a N_2 atmosphere using a N_2-purged syringe, passed through a 1 in. column filled with neutral alumina to remove the copper complex, and analyzed by ^{1}H NMR after removing solvent.

General Polymerization Procedures. RAFT agent (**d** in Table 1, 22.9 mg), AIBN (6.0 mg), and St (1.50 g) in anisole (50% (v/v) of total volume) was added to a dried Schlenk flask equipped with a stir bar. The flask was degassed by three freeze−pump−thaw cycles and was placed in a thermostated oil bath at the desired temperature. Samples were taken periodically under N_2 atmosphere using a N_2-purged syringe, mixed with THF, passed through a column filled with neutral alumina to remove the copper complex, and analyzed by GPC.

One-Pot Two-Step Polymerization of MMA. BTBD (17.5 mg, 0.057 mmol), Cu(0) (10.9 mg, 0.17 mmol), and CuBr (4.1 mg, 0.0285 mmol) were added to a dried Schlenk flask equipped with a stir bar. The flask was degassed and backfilled with nitrogen (N_2) five times and then left under N_2. Degassed anisole (1.0 mL) and PMDETA (9.0 μL, 0.043 mmol) were added to the flask. After 10 min, EBPA (20 μL, 0.114 mmol) was introduced, and the flask was placed in a thermostated oil bath at 80 °C, followed by the addition of degassed MMA (5.0 mL, 46.9 mmol) and anisole (4.0 mL) after 45 min. Samples were taken periodically under N_2 atmosphere using a N_2-purged syringe, mixed with THF, passed through a column filled with neutral alumina to remove the copper complex, and analyzed by GPC.

Results and Discussion

Alkyl Dithiobenzoate Synthesis. A typical experiment was performed with a ratio of [EBiB]/[BTBD]/[CuBr]/[PMDETA]/[Cu(0)] = 164/82/41/82/205 mM in toluene at 80 °C. Before starting the reaction with only EBiB and BTBD, peaks were observed by ^{1}H NMR at 8.1 ppm from ortho protons of BTBD and 4.3 (2H, **b′**), 1.95 (6H, **a′**), and 1.35 (3H, **c′**) ppm from EBiB (Figure 1). After 30 min, a small portion of the reaction mixture was passed through a short alumina column to remove the copper complex, followed by removal of the solvent. The compound obtained was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR. All peaks from the initiator (EBiB) completely disappeared, and new peaks corresponding to 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate at 7.95 (2H, **d**), 4.2 (2H, **b**), 1.8 (6H, **a**), and 1.27 (3H, **c**) ppm appeared, as shown in Figure 1. No noticeable side reactions were observed, and in many cases essentially quantitative conversion of alkyl halides was observed. Further heating for 6 h resulted in the same ^{1}H NMR spectrum as after 30 min. The CTA was obtained in isolated yield 92%, and the purity was ca. 99% (^{1}H NMR) after a 6 h reaction (entry 1 in Table 1). This result clearly demonstrates that ATRAF is a simple, efficient, and selective method to synthesize a RAFT agent. This technique can be used to replace the halogen in many alkyl halides (ATRP initiators) by a “RAFT” group via ATRAF reaction. For example, EBP (entry 2), BrPN (entry 3), and one of the most active initiators for ATRP, EBPA (entry 4) were successfully used in an ATRAF reaction, resulting in CTAs **b**, **c**, and **d** in high yields (ca. 90%) (Figures S1−3). Furthermore, a difunctional initiator such as dimethyl 2,6-dibromoheptanedioate (entry 5) was employed to synthesize a difunctional RAFT agent in high yield (82%) (Figure S4).

Alkyl Dithiocarbamate and Xanthate Synthesis. The aforementioned dithioesters are efficient CTAs for St, MMA, and methyl acrylate polymerization due to the presence of a stabilizing phenyl Z group. However, these RAFT agents are poor CTAs for less reactive monomers, such as *N*-vinyl 2-pyrrolidone (NVP) or vinyl acetate (VAc). They are better controlled with dithiocarbamates or xanthates as CTAs. Therefore, we subsequently applied the ATRAF technique to synthesize dithiocarbamates and xanthates. Entry 6 shows the result of a dithiocarbamate synthesis under conditions similar to the synthesis of dithiobenzoate but with TETD, producing **f** in 65% yield with a high purity (98%, Figure S5). Xanthate synthesis using ATRAF was also successful under conditions similar to those of the dithiobenzoate synthesis, giving xanthate **h** in 43% yield with a high purity (99%, Figure S6).

Furthermore, ATRAF could be applied successfully at low temperature and with a reduced amount of copper(I) catalyst (5% relative to halide initiator). Figure 2 shows the ^{1}H NMR of dithiocarbamate synthesis via ATRAF with a ratio of [R−X]/[disulfide]/[CuBr]/[PMDETA]/[Cu(0)] = 1.1/0.55/0.027/0.055/

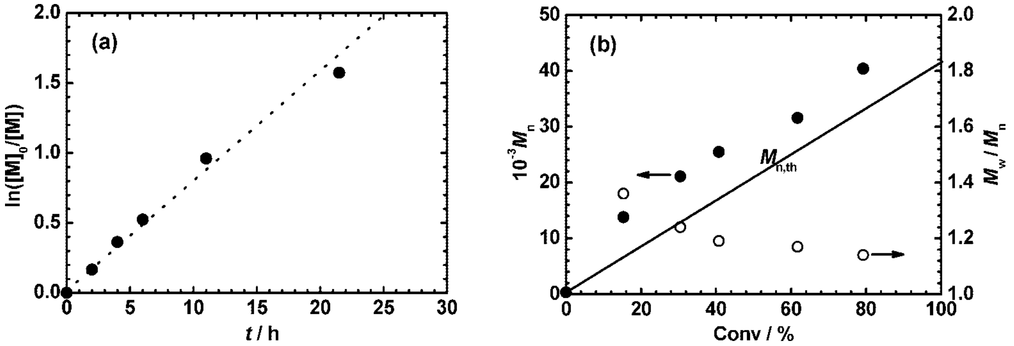


Figure 4. (a) Kinetic plot of monomer conversion and (b) dependence of M_n (●) and M_w/M_n (○) vs percent conversion for the MMA polymerization at 80 °C: [MMA]/[EBPA]/[BTBD]/[CuBr]/[PMDETA]/[Cu(0)] = 820/2/1/0.5/0.75/3 in 50% (v/v) anisole. Note that this is the result of a one-pot, two-step RAFT process.

1.21 M in acetone at room temperature for 18 h, which indicated a complete shift of reactant peaks (a′−f′) to RAFT agent (**g**) peaks (a−f) resulting in 58% yield with 99% purity. This result shows that the CTA synthesis via ATRAF, at room temperature and with a catalytic amount of copper(I)/L, was efficient and successful.

RAFT Polymerization of St and MMA. In order to examine the effectiveness of CTAs prepared by ATRAF (without further column purification process, only a simple filtration to remove copper species), RAFT polymerizations of St and MMA were carried out at 60 °C. Since CTA **d** was reported to control both St and MMA polymerizations, it was chosen for both polymerizations with a ratio of M/**d**/AIBN = 200/1/0.5 in 50% (v/v) anisole at 60 °C. As shown in Table 2, both the polymerization of St and MMA were well-controlled. Conversion and molecular weights increased with time, observed molecular weights ($M_{n,GPC}$) were very close to the theoretical values ($M_{n,th}$), and polydispersities (M_w/M_n) were low. The GPC chromatogram of St polymerization with RAFT agent **d** shows monomodal shape and gradual shift of molecular weight to higher values with time (Figure 3). CTA **a** also resulted in a well-controlled St polymerization under similar conditions (Table 2). These aforementioned results clearly indicate that the CTAs prepared by ATRAF can be used for well-controlled RAFT polymerization without any further purification.

One-Pot Two-Step Polymerization. As demonstrated above, ATRAF is highly selective and efficient, resulting in high-purity RAFT CTAs. Each CTA can be subsequently used for a successful RAFT polymerization without further purification step. Because of the high efficiency of the ATRAF process, a one-pot, two-step polymerization was applied: (1) RAFT agent synthesis with a ratio of [EBPA]/[BTBD]/[CuBr]/[PMDETA]/[Cu(0)] = 57/114/28.5/43/170 mM in 1.00 mL of anisole at 80 °C. (2) Addition of MMA (820 equiv compared to BTBD) to the reaction flask after 45 min. Figure 4a shows the linear semilogarithmic kinetic plot of monomer conversion, suggesting that a constant radical concentration was maintained. Figure 4b shows the evolution of M_n and M_w/M_n with conversion. The polymerization was well controlled; the molecular weights of PMMA increased linearly with conversion, agreeing well with the theoretical values ($M_{n,th}$), and low values of M_w/M_n (<1.20 at higher conversion) were observed. These results clearly demonstrate that the RAFT agent synthesis followed by polymerization in one pot was successful.

RAFT polymerization has been previously initiated by CTA prepared in situ from bis(thioaryl) disulfide or bis(alkyl) disulfide and AIBN.[53−55] However, control of polymerization was limited, since the efficiency of CTA formation was low, varying between 0.47 and 0.7, depending on the systems.[54,55]

Conclusions

In summary, a simple, versatile, and one-step method involving atom transfer radical addition−fragmentation (ATRAF) in the presence of an alkyl halide (ATRP initiator), copper catalyst, and bis(thiocarbonyl) disulfide was developed to prepare various chain transfer agents (CTA) for RAFT polymerization. The reaction is selective and efficient, producing high-purity CTAs in high yields. Various alkyl halides ATRP initiators were applied to prepare dithiobenzoates, dithiocarbamates, and xanthates. The CTA **g** was prepared in good yield at room temperature, using a small amount of copper(I) catalyst and Cu(0) as a reducing agent. CTAs prepared via ATRAF were used for RAFT polymerizations of St and MMA without further column purification, generating well-controlled polymers with low polydispersity. A simple one-pot, two-step polymerization starting with RAFT agent synthesized via ATRAF, followed by polymerization was also successful. This technique provides a new route to selective and efficient synthesis of multifunctional RAFT reagents useful, not only for linear polymers but also for (co)polymers with a more complex architecture.

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Supporting Information Available: Experimental results and ^{1}H NMR spectra for CTAs. This material is available free of charge via the Internet at http://pubs.acs.org.

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