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# Concurrent ATRP/RAFT of Styrene and Methyl Methacrylate with Dithioesters Catalyzed by Copper(I) Complexes

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**Introduction.** Controlled radical polymerization (CRP) became one of the robust and powerful techniques for polymer synthesis during the past decade because of the ability to employ the newly developed procedures to (co)polymerize a wide range of commercially available monomers to yield well-defined (co)polymers with designed architecture.[1,2] In addition to atom transfer radical polymerization (ATRP),[3−7] reversible addition−fragmentation chain transfer (RAFT) polymerization is one of the most efficient CRP techniques, with versatility, functional group compatibility, and very good architectural and molecular weight control.[8−10] A “standard” RAFT polymerization reaction requires presence of a monomer, a conventional radical initiator, and a chain transfer agent (CTA) in the reaction medium. The simplified mechanism involves a series of reversible addition−fragmentation chain transfer steps between the CTA and a radical as shown in Scheme 1a[8,11] as well as initiation, propagation, and termination steps, typical of a conventional radical polymerization. The exchange reaction (rate constant $k_{ex}$) and propagation process repeat themselves many times so 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, $In_2$ in Scheme 1a) to compensate for chain termination between propagating radicals that continuously occur. The radical initiators in the RAFT system produce new polymer chains and may also decrease chain end functionality[12,13] Therefore, it is difficult to prepare pure block copolymers as well as high molecular weight polymers, especially at higher radical initiator concentrations.

ATRP also allows the synthesis of well-defined block copolymers with predictable molecular weight, narrow molecular weight distribution, with a wide range of functionalities, a high degree of chain end-functionality, and controllable macromolecular architecture.[3−7] ATRP involves homolytic cleavage of an $P_x-Y$ bond by a lower oxidation state transition metal complex, such as $Cu^I/L$ (with a rate constant $k_a$), followed by propagation (with a rate constant $k_p$) and reversible deactivation of the propagating chain radical ($P_x^•$) (with a rate constant $k_{da}$) by the higher oxidation state catalyst complex, $YCu^{II}/L$ (Scheme 1b, left-hand side).[11] The reaction progresses by repetitive transfer of (pseudo)halogen atoms to and from the transition metal complex, resulting in the formation of low-polydispersity polymers. In contrast to RAFT, a typical ATRP process does not employ free radical initiators (except for continuous activator regeneration (ICAR) and simultaneous reverse and normal initiation (SRNI) ATRP[14,15] which require conventional initiator to activate the $Cu^{II}$ complex, since the majority of polymer chains grow from the $P_x-Y$ initiator rather than from the conventional radical initiator).

Recently, we reported ATRP systems based on pseudohalogen initiators, including alkyl dithiocarbamate (DC)[16] and trithiocarbonate (TTC),[17] that provide well-defined (co)polymers with narrow molecular weight distribution. We demonstrated that DC or TTC initiators were activated by the copper catalyst and generated carbon-centered radicals, as in a typical ATRP with halogen initiators. Herein, we extend the application of the pseudohalogen initiators used in ATRP to dithioester (DTE) initiators which can result in concurrent ATRP/RAFT as shown in Scheme 1b. As described above, termination occurs in both conventional RAFT and ATRP (as well as in concurrent ATRP/RAFT) systems, but there is no generation of new radical in concurrent ATRP/RAFT. Therefore, we successfully utilized ATRP/RAFT to prepare high molecular weight polymers and purer block copolymers, while properly maintaining chain end functionality.

**Results and Discussion.** *Concurrent ATRP/RAFT of St.* The reaction conditions and the results of St polymerization with a ratio of St/cumyl dithiobenzoate (CDB) = 200/1 and additional additive(s) are summarized in Table 1 (entries 1−7). All polymerizations were well-controlled, producing polymers with molecular weight ($M_{n,GPC}$) identical to the theoretical value ($M_{n,th}$) and maintaining a low PDI ($M_w/M_n$ < 1.1), regardless of variations in polymerization methods (RAFT/V-40 or RAFT/Cu(I)), type of ligand, or addition of a reducing agent, copper powder. Linear development of monomer conversion and gradual shift of molecular mass in GPC chromatograms to higher molecular weight were observed in all polymerizations (Figure S1-2 of the Supporting Information). However, there were significant differences in rate of polymerization ($R_p$) in each experiment. For example, thermal polymerization of St in the presence of CDB resulted only in 1.7% conversion and formation of an oligomer ($M_n$ = 400) after 21 h at 80 °C, as shown in entry 1. In the presence of CuBr/$Me_6$TREN (entry 4), the $R_p$ increased more than 7 times over that of entry 1 at the same reaction time and temperature. Furthermore, $R_p$ increased to 13 times its original value in the presence of Cu(0) because Cu(0) regenerated $Cu^I$ from $Cu^{II}$ formed via radical termination[18,19] and accelerated activation of CDB (entry 5). The $R_p$ in the presence of $Me_6$TREN/CuBr/Cu(0) was slightly faster than that with PMDETA/CuBr/Cu(0) (entry 5 vs entry 3). The $R_p$ increased ca. 3 times by increasing the temperature

**Scheme 1. General Mechanism for (a) RAFT and (b) Concurrent ATRP/RAFT**

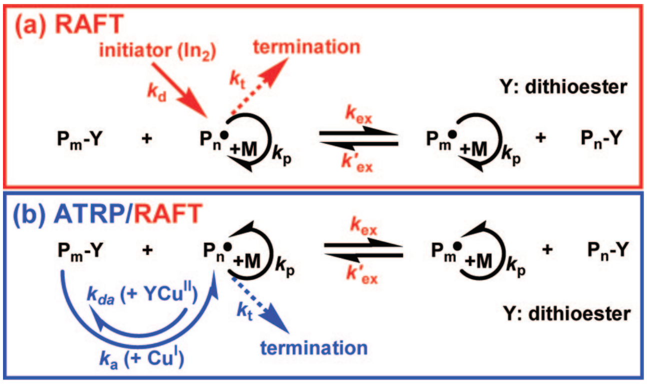

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**Table 1. Results for the Syntheses of PSt, PMMA, and PMMA-*b*-PSt in the Presence of Conventional Initiator (V-40) and Copper Catalyst**[a]

| entry | M | V-40 | CuBr | L[b] (equiv) | Cu(0) | $T$ (°C) | $t$ (h) | conv (%) | $M_{n,th}$[c] | $M_{n,GPC}$ | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | St | | | | | 80 | 21 | 1.7 | 560 | 400 | 1.05 |
| 2 | St | 0.5 | | | | 80 | 21 | 54.8 | 11370 | 10600 | 1.14 |
| 3 | St | | 1 | A (1.5) | 0.5 | 80 | 21 | 15.0 | 3120 | 2900 | 1.06 |
| 4 | St | | 1 | B (1.5) | | 80 | 21 | 12.0 | 2500 | 2200 | 1.06 |
| 5 | St | | 1 | B (1.5) | 0.5 | 80 | 21 | 21.4 | 4460 | 4100 | 1.05 |
| 6 | St | | 1 | B (1.5) | 0.5 | 100 | 21 | 53.9 | 11230 | 11800 | 1.06 |
| 7 | St | | 1 | B (1.5) | 0.5 | 100 | 48 | 73.4 | 15300 | 17400 | 1.08 |
| 8 | MMA | | 0.1 | B (0.1) | 1 | 80 | 17 | 64.5 | 129200 | 140800 | 1.11 |
| 9 | MMA | | 0.1 | B (0.1) | 1 | 80 | 13.5 | 39.0 | 390500 | 499500 | 1.36 |
| 10 | MMA | 0.5 | | | | 80 | 16.5 | 97.0 | 7800 | 8800 | 1.22 |
| 11 | MMA | | 2 | C (4.0) | | 80 | 16.5 | 93.2 | 7450 | 8300 | 1.23 |
| 12 | St | 2 | | | | 80 | 20 | 50.1 | 61000 | 40900 | 1.32 |
| 13 | St | | 20 | B (30) | 10 | 80 | 20 | 48.4 | 58700 | 50600 | 1.20 |

[a] All polymerizations were performed in 50% (v/v) anisole. Entries 1−7 (St homopolymerization): [St]/[CDB] = 200/1. Entries 8−9 (ARGET ATRP/RAFT): [MMA]/[CDB] = 2000/1 (entry 8); [MMA]/[CDB] = 10,000/1 (entry 9). Entries 10−11 (macroinitiator synthesis for entries 12 and 13, respectively): [MMA]/[CDB] = 80/1. Entries 12−13 (PMMA-*b*-PSt synthesis): [St]/[macroinitiator] = 1000/1. [b] A = PMDETA; B = $Me_6$TREN; C = bpy. [c] $M_{n,th}$ = [M]/[CDB] × conversion + $M_{n,CTA}$.

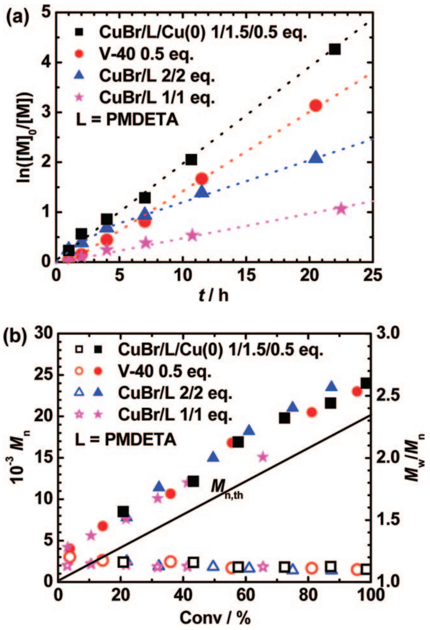

**Figure 1.** (a) Kinetic plot of monomer conversion and (b) dependence of $M_n$ (filled symbols) and $M_w/M_n$ (open symbols) vs percent conversion for the MMA polymerization at 80 °C: all polymerizations were performed with a ratio of MMA/CDB = 200/1 with additional CuBr/PMDETA/Cu(0) = 1/1.5/0.5 equiv (■ and □), V-40 = 0.5 equiv (● and ○), CuBr/PMDETA = 2/2 equiv (▲ and △), or CuBr/PMDETA = 1/1 equiv (★ and ☆) in 50% (v/v) anisole.

from 80 to 100 °C under the same conditions (entry 5 vs entries 6, 7), which was comparable to that of polymerization in the presence of V-40 (entry 2).

*Concurrent ATRP/RAFT of MMA.* The initial attempt to polymerize MMA in 50% (v/v) anisole only with CDB (no radical initiator) carried out at 80 °C with a ratio of MMA/CDB = 200/1 resulted in no polymer over a 40 h reaction period due to the lack of a radical source in the system. Next, RAFT polymerizations of MMA in the presence of either V-40 or Cu(I) complexes at 80 °C with a ratio of MMA/CDB = 200/1 and additional additive(s), as indicated in Figure 1, resulted in a controlled reaction. Figure 1a shows the kinetic plot of monomer conversion. Linear development of monomer conversion was observed in the polymerization with V-40, 1/1 equiv of CuBr/PMDETA, and 1/1.5/1 equiv of CuBr/PMDETA/Cu(0). A polymerization with 2/2 equiv of CuBr/PMDETA was ca. 2 times faster than that with 1/1 equiv, but the plot showed curvature, which indicated chain termination at the early stage of the polymerization due to the presence of a too large amount of the activator Cu(I). When 0.5 equiv of Cu(0) was introduced, the polymerization rate increased 4 times, as compared to the polymerization with equivalent ratio of reagents without Cu(0). Figure 1b shows the evolution of $M_n$ and $M_w/M_n$ for these systems. All polymerizations appear to be well controlled. The molecular weights of PMMA increased linearly with conversion, although they were slightly higher than theoretical values ($M_{n,th}$), and low PDI ($M_w/M_n < 1.20$) were observed. A similar increase of molecular weights in all polymerizations indicates that the molecular weights of the polymers were determined by the ratio of consumed monomer to CDB as in conventional RAFT polymerization.

*High Molecular Weight PMMA Prepared by Concurrent ATRP/RAFT.* In contrast to polyacrylates,[19,20] preparation of high molecular weight polystyrene and poly(methyl methacrylate) by CRP methods is still a challenge, although there are some reports on the successful preparation of high molecular weight polymers under high-pressure conditions.[21−23] The concurrent ATRP/RAFT provides some advantages over conventional RAFT and ATRP. (1) The formation of new chains is suppressed by generating the initiating radicals directly from the CTA in the presence of copper catalyst, without adding an extra amount of radicals, that produce new chains. (2) Synthesis of high molecular weight polymers can be accomplished by activators regenerated by electron transfer (ARGET) ATRP, but low polydispersities require the presence of a minimum amount of rapidly deactivating $Cu^{II}$ complex. The presence of CTA should facilitate formation a polymer with a lower PDI because of the very high chain transfer constant ($C_{ex}$ = 6000 ± 2000 at 40 °C).[24]

Well-controlled PMMA with higher molecular weight was prepared by ARGET ATRP/RAFT polymerization (entries 8 and 9 in Table 1). A molar ratio of 2000 and 10 000 equiv of MMA to CDB was used in entries 8 and 9, respectively, with 0.1 equiv of CuBr/$Me_6$TREN complex (25 and 5 ppm of CuBr in entries 8 and 9, respectively). Furthermore, 1 equiv of Cu(0) was used to return accumulating deactivator $Cu^{II}$ to activator $Cu^I$ and to constantly reactivate the system. Well-controlled PMMAs with high molecular weight ($M_n$ = 140 800, $M_w/M_n$ = 1.11 in entry 8 and $M_n$ = 499 500, $M_w/M_n$ = 1.36 in entry 9) were obtained after 17 and 13.5 h reactions, at 64.5% and 39% conversion in entries 8 and 9, respectively. Polymerization was stopped at relatively low conversion due to the high viscosity

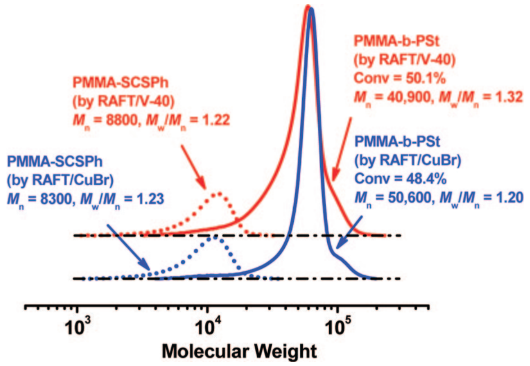

**Figure 2.** Molecular weight distribution of PMMA−SCSPh macroinitiators before (left side, broken lines) and after chain extension with St (right side, solid lines). See entries 10−13 in Table 1 for experimental conditions.

of the reaction medium under these conditions (in 50% (v/v) anisole).

*Synthesis of PMMA-b-PSt via Conventional RAFT and Concurrent ATRP/RAFT.* PMMA macroinitiators (MI) were synthesized under RAFT conditions with either V-40 or Cu(I), providing polymers with similar molecular weight. The amount of an initiator and catalyst was adjusted to reach the same conversion after exactly the same reaction time (16.5 h) at the same temperature (80 °C) (entries 10 and 11 in Table 1). Both PMMA MIs were chain extended with St under either RAFT/V-40 or ATRP/RAFT with CuBr/Me$_6$TREN conditions, as described in Table 1 (entries 12 and 13). 1000 equiv of styrene vs MI was used for PMMA-*b*-PSt synthesis, with 2 equiv of V-40 (entry 12) and 20/30/10 equiv of CuBr/Me$_6$TREN/Cu(0) (entry 13). The reason for introducing such an excess of CuBr/Me$_6$TREN/Cu(0) in the latter case was to reach the same rate of radical generation, i.e., the same $R_p$ (and consequently the same amount of termination), as in the former reaction, which resulted in 50.1% and 48.4% conversion under RAFT/V-40 and ATRP/RAFT conditions, respectively, after 20 h polymerization at 80 °C. It can be seen in Figure 2 that under standard RAFT/V-40 conditions there is a long tail toward the low molecular weight area resulting in a slightly higher PDI ($M_w/M_n = 1.32$). This indicates continuous initiation, chain termination, and lower chain end functionality (ca. 75%). On the other hand, under ATRP/RAFT conditions, a cleaner shift of the GPC traces to a higher molecular weight occurred, retaining a lower PDI ($M_w/M_n = 1.20$) and a monomodal shape. In addition, chain end functionality of this MI improved to 93 ± 3%. The above results indicate that a purer block copolymer was prepared using the copper activated RAFT system than the conventional RAFT system.

**Conclusions.** A concurrent ATRP/RAFT with dithioesters acting as initiators/dormant species for ATRP and also as chain transfer agents for RAFT was successfully applied to well-controlled polymerizations of both St and MMA. The polymerization rate followed first-order kinetics with respect to monomer conversion, and molecular weights increased linearly up to high conversion. Increasing amounts of CuBr/L in the system resulted in faster polymerization. The rate of polymerization ($R_p$) with CuBr/Me$_6$TREN was faster than with CuBr/PMDETA. The $R_p$ was further increased by adding a reducing agent, copper powder. High molecular weight PMMA, up to half-million with narrow molecular weight distribution, was successfully prepared by ARGET ATRP/RAFT. Purer block copolymers PMMA-*b*-PSt were synthesized by concurrent ATRP/RAFT than by conventional RAFT. This demonstrates that the control in ATRP/RAFT can be improved in comparison with conventional RAFT polymerization.

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**Supporting Information Available:** Experimental procedures, analytical methods, and detailed results of St polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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