Articles

Dibromotrithiocarbonate Iniferter for Concurrent ATRP and RAFT Polymerization. Effect of Monomer, Catalyst, and Chain Transfer Agent Structure on the Polymerization Mechanism

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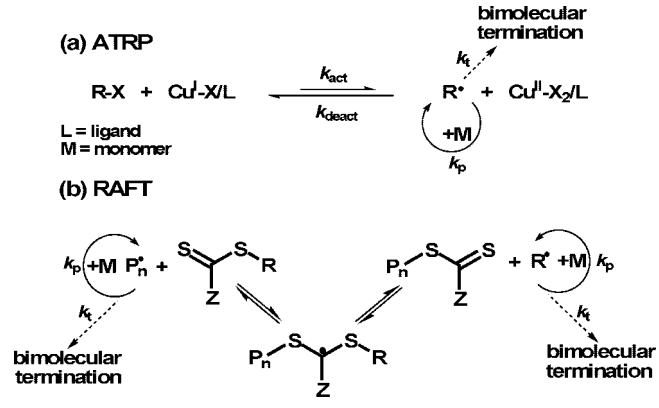
ABSTRACT: An iniferter comprising a trithiocarbonate (TTC) moiety and two bromine chain ends was prepared and used to successfully conduct, independently or concurrently, atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) polymerization. RAFT polymerization was carried out by self-initiation (styrene, (St)) or in the presence of a thermal initiator (acrylates) and yielded polymers with narrow molecular weight distribution ($M_w/M_n \leq 1.16$ (St) and $M_w/M_n \leq 1.15$ (acrylates)). Methyl methacrylate (MMA) polymerization under these conditions was poorly controlled. However, ATRP of MMA with the dibromotrithiocarbonate (DiBrTTC) iniferter was successful in the presence of copper catalysts formed with various nitrogen-based ligands. Polymers with narrow molecular weight distribution ($M_w/M_n < 1.27$) were obtained in every case. Depending on the ligand, polymerization proceeded only through the bromine chain ends or through both the bromine chain ends and the TTC moiety, providing the first example of an ATRP with a trithiocarbonate. ATRP and RAFT polymerization of St and *n*-butyl acrylate (*n*BA) were conducted concurrently using CuBr/PMDETA as catalytic system. Polymers with broad molecular weight distribution ($M_w/M_n \approx 1.6$) and polymodal size exclusion chromatography traces were obtained due to chain reshuffling through the TTC moiety. SEC analysis of the polymers after aminolysis or methanolysis showed that ATRP and RAFT occurred simultaneously, with good control, for each *n*BA and St ($M_w/M_n < 1.3$). Triblock, pentablock, or multiblock copolymers were prepared in two steps by appropriate selection of monomers and catalytic systems.

Introduction

Controlled/"living" radical polymerization (CRP) has emerged during the past decade as one of the most robust and powerful techniques for polymer synthesis,[1–6] as it combines some of the desirable attributes of traditional free radical systems (e.g., relative insensitivity to water and polar organic impurities, tolerance to a wide range of chemical functions) with the advantages of living ionic polymerization techniques (e.g., low polydispersity (PDI), preparation of chain-end-functionalized polymers and block copolymers).[1,3,7] CRP methods include nitroxide-mediated radical polymerization (NMP),[8,9] atom transfer radical polymerization (ATRP),[10–14] and degenerative chain transfer (i.e., iodine transfer polymerization,[15] reversible addition−fragmentation chain transfer (RAFT),[16–18] Te-, Sb-, and Bi-mediated radical polymerization,[19–23] quinone transfer radical polymerization,[24] and reversible chain transfer catalyzed polymerization[25]). All CRP techniques rely on a dynamic equilibrium between dormant species and propagating radicals via a reversible deactivation procedure. This equilibrium depends on several parameters which might differ from one CRP method to another.

ATRP[10–14] is one of the most advantageous methods for synthesizing polymers with well-defined architecture as it allows to control, under mild reaction conditions, molecular weight and molecular weight distribution (M_w/M_n) for a wide range of monomers, including styrenics,[26] (meth)acrylates,[27–30] and others.[12] ATRP generally requires an alkyl halide (R−X) or pseudohalide[31,32] as an initiator and a transition metal complex (Cu,[10] Ru,[11] or Fe,[33–36] for example) as a catalyst. ATRP involves homolytic cleavage of an R−X bond by a transition metal complex, for example Cu^I−X/L (with a rate constant k_{act}), followed by propagation (with a rate constant k_p) and reversible deactivation of the propagating chain radical ($R^\bullet$) (with a rate constant k_{deact}) by the higher oxidation state catalyst complex, $Cu^{II}-X_2$/L (Scheme 1a). The reactivity of ATRP initiators and dormant species depends reciprocally on the alkyl halide bond

Scheme 1. (a) ATRP Mechanism and (b) RAFT Polymerization Mechanism



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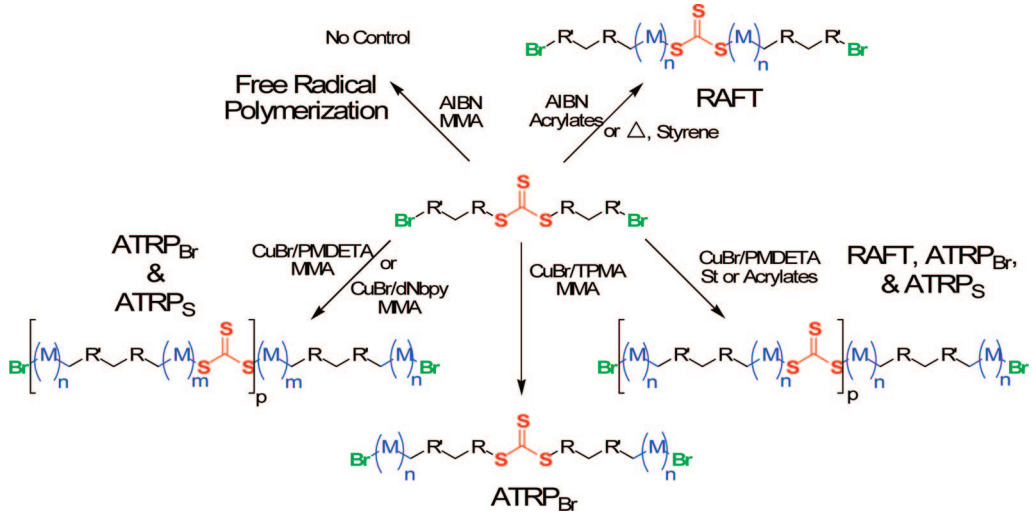
Scheme 2. Effect of Monomer and Catalyst on Polymerization Mechanism with DiBrTTC 3



dissociation energy (BDE).[37,38] Several rules pertaining to initiator structure that govern activation rate constants have emerged from recent studies and can be summed up as follows: (1) activity depends on the degree of initiator substitution (primary < secondary < tertiary), (2) on the leaving atom/group (for methyl 2-halopropionates: Cl < Br < I), and (3) on the radical stabilizing groups (−Ph ∼ −COOR ≪ −CN).[39]

RAFT polymerization is one of the other most successful CRP processes due to its applicability to a wider range of monomers. Various dithioesters, dithiocarbamates, trithiocarbonates, and xanthates have been effectively used as transfer agents to control molecular weights, molecular weight distribution, and molecular architecture of polymeric material prepared from a wide range of monomers.[16–18,40,41] Exchange reactions in this technique are fast, which leads to well-controlled systems. During the first stages of the polymerization the RAFT agent (ZC═SSR) is consumed by propagating radicals by an addition−fragmentation mechanism. The fragmented radical (R•) reinitiates polymerization, resulting in new propagating radicals which then take part in the equilibrium established between the dormant polymer and active chains (Scheme 1b). The equilibration process allows all chains to grow in a uniform manner, resulting in low-polydispersity polymers. The nature of the Z and R groups is crucial to the success of the polymerization, and successful application of the RAFT process requires the appropriate selection of a RAFT reagent for a particular monomer. The selection of the R group should take into account the stability of the dormant species and rate of addition of R• to a given monomer. The order of R group leaving ability reflects the importance of both steric and electronic effects.[38] Steric effects in RAFT are much more important than in ATRP. For example, the reactivity of secondary 2-bromopropionitrile in ATRP is higher than that of the tertiary 2-bromoisobutyrate.[5] However, the opposite trend in reactivity is observed in RAFT. Similarly, *tert*-butyl halides are inactive in ATRP but are more active than benzyl derivatives in RAFT. Additionally, acrylate derivatives are not very active in RAFT, in contrast to ATRP. The structure of the Z group is equally important.[17,42,43] Z groups such as −Ph and −Me are efficient in styrene and methacrylate polymerization, but they retard polymerization of acrylates and inhibit polymerization of vinyl esters. On the other hand, very weakly stabilizing groups, such as $-NR_2$ in dithiocarbamates or −OR in xanthates, are good for vinyl esters but inefficient for styrene.

ATRP has been recently extended to dithiocarbamate systems. Cuprous *N,N*-diethyldithiocarbamate has been used as a catalyst for normal and reverse ATRP of MMA.[44,45] PMMA with low polydispersities were obtained, but initiation efficiency and chain end functionality were low in the case of reverse ATRP. Various diethyldithiocarbamate iniferters have also been used as initiators for St and MMA ATRP with copper bromide and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA).[46–48] While control over molecular weight distribution was good, initiation efficiency was poor for MMA polymerization. Very recently, a series of new diethyldithiocarbamate were prepared and used for St and MMA polymerizations with copper bromide and different nitrogen-based ligands. The effect of iniferter and ligand structures was studied, and well-defined low PDI PSt and PMMA could be prepared with high initiation efficiency.[49]

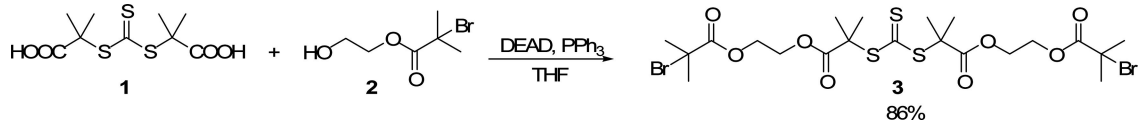
In this work we study the effect of monomer, catalyst, and chain transfer agent (CTA) structure on the "controlled/living" radical polymerization of St, acrylates, and MMA with a dibromotrithiocarbonate (DiBrTTC) iniferter. Appropriate selection of the monomer/catalyst couple allows polymerization exclusively through the trithiocarbonate moiety, exclusively through the bromine chain ends, or through both the trithiocarbonate and the bromine chain ends simultaneously (Scheme 2). In the latter case, depending on the monomer and catalyst, either ATRP or both RAFT and ATRP mechanisms are participating in polymer chain growth, yielding polymers with different molecular weight distributions (M_w/M_n).

Experimental Section

Materials. Methyl acrylate (MA, 99%), *n*-butyl acrylate (nBA, 99%), styrene (St, 99%), and methyl methacrylate (MMA, 99%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove the inhibitors or antioxidants. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) purchased from Aldrich was recrystallized from methanol and stored in a refrigerator prior to use. CuBr (98%, Acros) was purified using a modified literature procedure.[50] *S,S′*-Bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate[51] and tris[(2-pyridyl)methyl]amine[52] (TPMA) were synthesized according to procedures previously reported in the literature. All other reagents—anhydrous ethylene glycol, α-bromoisobutyryl bromide, diethyl azodicarboxylate (DEAD), 4,4′-dinonyl-2,2′-bipyridyne (dNbpy), ethylenediamine, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), sodium methoxide, triethylamine, triphenylphosphine, and $CuBr_2$—and solvents were purchased from Aldrich with the highest purity available and used as received without further purification.

Analyses. NMR spectra were recorded on a Bruker instrument operating at 300 MHz. Monomer conversions were determined on a Shimadzu GC 14-A gas chromatograph equipped with a FID

Scheme 3. Synthesis of Dibromotrithiocarbonate, DiBrTTC, 3



detector using a J&W Scientific 30 m WAX Megabore column and anisole or DMF as internal standard. Molecular weight and polydispersity were determined by size exclusion chromatography (SEC). The SEC analysis was conducted with a Waters 515 pump and Waters 410 differential refractometer using Polymer Standards Services (PSS) columns (Styrogel 10^5, 10^3, and 10^2 Å) in THF as eluent at 35 °C and at a flow rate of 1 mL/min. The apparent molecular weights ($M_{n,RI}$ and $M_{w,RI}$) and polydispersities (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (polyMMA) or polystyrene (polySt) standards.

Synthesis of Hydroxyethyl 2-Bromoisobutyrate. Anhydrous ethylene glycol (301.3 g, 4.85 mol) and triethylamine (28 mL, 200 mmol) were diluteded with dry tetrahydrofuran (100 mL). The reaction mixture was cooled in an ice−water bath, and a solution of α-bromoisobutyryl bromide (12 mL, 97.1 mmol) in dry tetrahydrofuran (50 mL) was slowly added while stirring. The mixture was stirred in the cooling bath for 1 h and then at room temperature for 16 h. The reaction mixture was then poured into water (800 mL) and extracted with dichloromethane (6 × 100 mL). The organic fractions were combined, washed with acidic water (pH = 4), dried over $MgSO_4$, and evaporated to dryness to afford 17.477 g (yield = 85.3%) of a very pale yellow liquid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.30−4.19 (m, 2H), 3.86−3.75 (m, 2H), 2.86−2.47 (broad peak, 1H, OH), 1.89 (s, 6H). ^{13}C NMR ($CDCl_3$, δ): 171.95, 67.40, 60.63, 55.89, 30.72.

Synthesis of *S*,*S*′-Bis[4-(6-bromoisobutyrate)ethyl isobutyrate]trithiocarbonate. A 100 mL round-bottomed flask equipped with a dropping funnel was charged with *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (2.115 g, 7.5 mmol), hydroxyethyl 2-bromoisobutyrate (5.065 g, 24 mmol), and triphenylphosphine (6.295 g, 24 mmol) and then purged with nitrogen. 40 mL of anhydrous tetrahydrofuran was then added. The flask was immersed in an ice bath, and diethyl azodicarboxylate (DEAD) (3.779 mL, 24 mmol) in 10 mL of dry THF was added dropwise at a rate such that the temperature of the reaction mixture is maintained below 10 °C. Upon completion of the addition, the flask was removed from the ice bath, and the solution was allowed to stir at room temperature overnight (16 h) and subsequently at 40 °C for 3 h. The reaction mixture was cooled to room temperature, diluted with 150 mL of dichloromethane, and washed twice with 25 mL portions of saturated aqueous sodium bicarbonate solution. The aqueous layers were combined and back-extracted with 100 mL of dichloromethane. The combined organic layers were dried over magnesium sulfate and concentrated under vacuum. The product was purified by column chromatography (eluent: hexanes/ethyl acetate: 9/1) to afford 4.309 g (yield = 85.9%) of a yellow solid. ^{1}H NMR ($CDCl_3$, δ, ppm): 4.40−4.29 (m, 8H), 1.92 (s, 12H), 1.66 (s, 12H). ^{13}C NMR ($CDCl_3$, δ): 218.82, 172.50, 171.49, 63.47, 63.24, 56.28, 55.50, 30.84, 25.21.

General Procedure for RAFT Polymerization of Acrylates or MMA. In a typical experiment, DiBrTTC (133.7 mg, 0.2 mmol), AIBN (1.64 mg, 0.01 mmol), and anisole (1 mL) were charged to a flask and bubbled with N_2 for 30 min. Deoxygenated MA (2 mL, 22.21 mmol) was added, and an initial sample was taken. The flask was placed in an oil bath thermostated at 70 °C for 2 h. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by gas chromatography (GC) and SEC, respectively. The polymerization was stopped by quenching the reaction in an ice bath (M_n = 8150 g/mol, M_w/M_n = 1.10, conversion = 91.8%).

General Procedure for RAFT Polymerization of St. In a typical experiment, DiBrTTC (97.2 mg, 1.455×10^{-1} mmol) and styrene (5 mL, 43.6 mmol) were charged to a flask and bubbled with N_2 for 30 min. The flask was placed in an oil bath thermostated at 130 °C for 11 h. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by gravimetry and SEC, respectively. The polymerization was stopped by quenching the reaction in an ice bath (M_n = 12 300 g/mol, M_w/M_n = 1.16, conversion = 39.3%).

General Procedure for Simultaneous ATRP and RAFT Polymerization of St and Acrylates. In a typical experiment, CuBr (51.6×10^{-3} g, 0.36 mmol) and $CuBr_2$ (8.9×10^{-3} g, 0.04 mmol) were charged to a flask and purged with N_2 for 30 min. Anisole (6 mL) and PMDETA (83.6×10^{-3} mL, 0.4 mmol) were added, and the solution turned green as complex formation occurred. A solution of DiBrTTC (133.7×10^{-3} g, 0.2 mmol) in styrene (11.46 mL, 100 mmol) was added, and an initial sample was taken. The flask was placed in an oil bath thermostated at 90 °C for 19 h. At timed intervals, samples were withdrawn via a syringe for measurement of monomer conversion and polymer molecular weight by GC and SEC, respectively. The polymerization was stopped via exposure to air and dilution in THF (M_n = 36 750 g/mol, M_w/M_n = 1.63, conversion = 68.1%).

General Procedure for ATRP of MMA. In a typical experiment, CuBr (10.8 mg, 0.075 mmol), $CuBr_2$ (1.7 mg, 7.5×10^{-3} mmol), 4,4′-dinonyl-2,2′-bipyridyne (67.4 mg, 0.165 mmol), and DiBrTTC (50.1 mg, 0.075 mmol) were charged to a flask and purged with N_2 for 30 min. Anisole (4 mL) and MMA (4 mL, 37.4 mmol) were added, and the solution turned brown as complex formation occurred. An initial sample was taken, and the flask was placed in an oil bath thermostated at 90 °C for 3 h. At timed intervals, samples were withdrawn via a syringe for measurements of monomer conversions and polymer molecular weights by GC and SEC, respectively. The polymerization was stopped via exposure to air and dilution in THF (M_n = 41 300 g/mol, M_w/M_n = 1.21, conversion = 82.3%).

General Procedure for Polymer Aminolysis. In a typical experiment, polystyrene (M_n = 36 750 g/mol, M_w/M_n = 1.63, 92 mg, 2.5×10^{-3} mmol) was dissolved in a solution of ethylenediamine (0.17 mL, 2.5 mmol), triethylamine (1.4 μL, 0.01 mmol), and tetrahydrofuran (10 mL). The solution was stirred at room temperature for 72 h, and the polymer was analyzed by SEC without purification (M_n = 18 500 g/mol, M_w/M_n = 1.28).

General Procedure for Polymer Methanolysis. An oven-dried 10 mL Schlenk flask equipped with a condenser was charged with poly(methyl methacrylate) (M_n = 41 300 g/mol, M_w/M_n = 1.21, 41.3 mg, 1×10^{-3} mmol) and deoxygenated for 25 min with nitrogen. Anhydrous tetrahydrofuran (4 mL) and sodium methoxide solution 25 wt % in methanol (2 mL, 8.75 mmol) were added, and the solution was refluxed for 16 h. The reaction mixture was cooled and 10 mL of 1 M HCl was added. The organic phase was washed with water (until it became acid-free) and dried over $MgSO_4$, and the solvent was evaporated. The crude product was redissolved in THF and analyzed by SEC (M_n = 11 525 g/mol, M_w/M_n = 1.29).

Results and Discussion

RAFT Polymerization of Acrylates and Styrene with the DiBrTTC Iniferter 3. It has been previously reported that the dicarboxytrithiocarbonate CTA, **1**, used to prepare the DiBrTTC iniferter **3** (Scheme 3) efficiently mediates the polymerization of various monomers such as acrylates, acrylamides, acrylic acid, and styrene.[51] We thus anticipated **3** to be a good CTA for the RAFT polymerization of acrylates and styrene.

The effectiveness of **3** for the RAFT polymerization of acrylates was evaluated by polymerizing *n*BA in 33% anisole

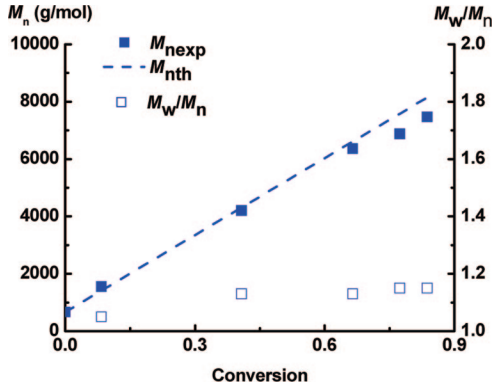


Figure 1. Plot of M_n and M_w/M_n vs conversion for *n*BA polymerization with **3** in 33% anisole solution at 70 °C with a ratio $[n\text{BA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 70/1/0.05.

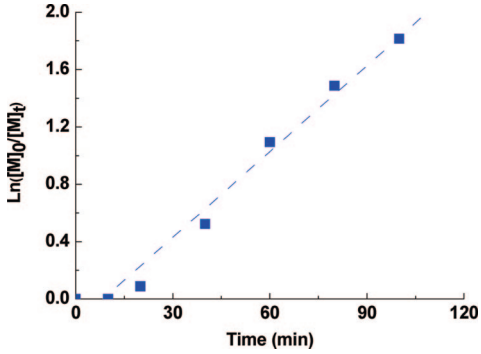


Figure 2. Kinetic plot for *n*BA polymerization with **3** in 33% anisole solution at 70 °C with a ratio $[n\text{BA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 70/1/0.05.

solution at 70 °C with a ratio $[n\text{BA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 70/1/0.05. After 100 min, poly(*n*-butyl acrylate) with $M_n = 7450$ g/mol ($M_{nth} = 8150$ g/mol) and $M_w/M_n = 1.15$ was obtained. Good control was achieved up to high conversion. A linear increase of the molecular weight with conversion as well as low PDIs was observed (Figure 1). A linear relationship between $\ln([M]_0/[M]_t)$ vs time was observed, indicating that no detectable termination occurred in this system (Figure 2). A small induction period of ca. 10 min was observed, a phenomenon that was also reported for *n*BA polymerization with CTA **1**.[53]

The effectiveness of **3** for the RAFT polymerization of styrene was evaluated at 130 °C under bulk conditions. Using 29.1 mmol/L of **3**, polystyrene with $M_n = 12\,300$ g/mol ($M_{nth} = 12\,950$ g/mol) and $M_w/M_n = 1.16$ was obtained after 11 h (Figure 3).

RAFT Polymerization of Methyl Methacrylate with the DiBrTTC Iniferter 3. According to the literature, only asymmetrical trithiocarbonate CTA with an alkyl chain on one side and 2-methylpropionitrile,[42,54] 4-cyano-4-pentanoic acid,[17,55] or 2-benzyl cyanide[18] substituents on the other side were used successfully to polymerize MMA by RAFT with a trithiocarbonate. The leaving group R should be more stabilized than the propagating PMMA radical for all these trithiocarbonates, leading to efficient fragmentation and reinitiation. In the case of the DiBrTTC **3**, the leaving group R is an isobutyrate derivative and is not expected to be an efficient leaving group for MMA polymerization since in the RAFT polymerization of MMA with dithiobenzoates (S=C(Ph)SR), only RAFT reagents with $C(Alkyl)_2CN$ or $C(Alkyl)_2Ph$ substituents as leaving group were successfully used to prepare well-defined PMMA.[56]

The effectiveness of **3** for the RAFT polymerization of MMA was evaluated by conducting polymerization in 50% anisole

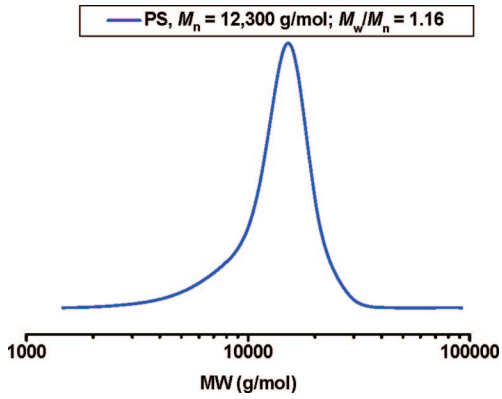


Figure 3. SEC trace of polystyrene obtained after 11 h of polymerization at 130 °C with **3**. Experimental conditions: $[\text{St}]_0/[\text{DiBrTTC}]_0 = 300$; in bulk; $T = 130$ °C.

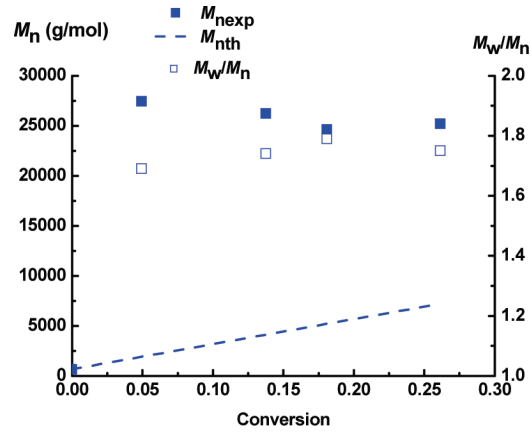


Figure 4. Plot of M_n and M_w/M_n vs conversion for MMA polymerization with **3** in 50% anisole solution at 70 °C with a ratio $[\text{MMA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 250/1/0.05.

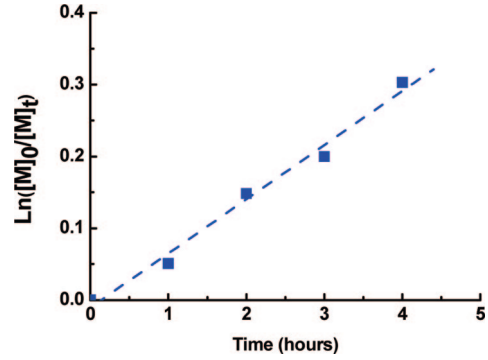


Figure 5. Kinetic plot for MMA polymerization with **3** in 50% anisole solution at 70 °C with a ratio $[\text{MMA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 250/1/0.05.

solution at 70 °C with a ratio $[\text{MMA}]_0/[\text{DiBrTTC}]_0/[\text{AIBN}]_0$ of 250/1/0.05. After 4 h, poly(methyl methacrylate) with $M_n = 25\,200$ g/mol ($M_{nth} = 7200$ g/mol) and $M_w/M_n = 1.75$ was obtained. Molecular weight did not increase with conversion and remained constant during the polymerization reaction. Molecular weight distribution (M_w/M_n) did not decrease with increasing conversion and remained around 1.75 (Figure 4). A linear relationship between $\ln([M]_0/[M]_t)$ vs time was observed, indicating a constant radical concentration during the span of the reaction (Figure 5). All these features combined are characteristic of a conventional free radical process and indicate that **3** is an inefficient chain transfer agent for RAFT polymerization of MMA.

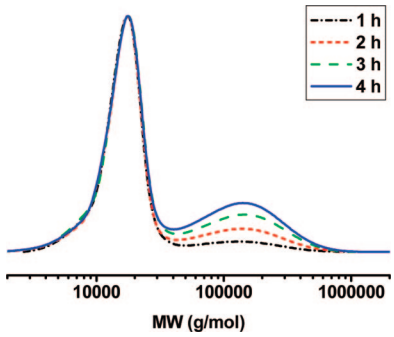


Figure 6. Evolution of SEC traces during MMA polymerization with a polystyrene macro-CTA. Polymerization conditions: $[MMA]_0/[PS\text{-}CTA]_0/[AIBN]_0 = 500/1/0.05$ in anisole 50% by volume, 4 h at 70 °C.

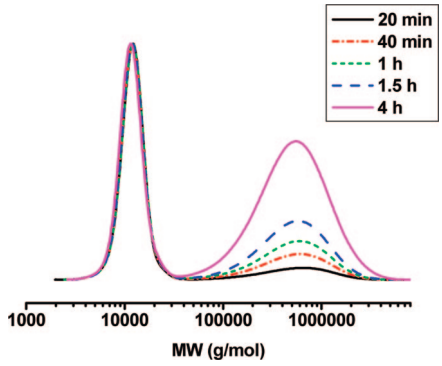


Figure 7. Evolution of SEC traces during MMA polymerization with a poly(*n*-butyl acrylate) macro-CTA. Polymerization conditions: $[MMA]_0/[PnBA\text{-}CTA]_0/[AIBN]_0 = 250/1/0.05$ in anisole 50% by volume, 4 h at 70 °C.

In regards to the already well established reactivity order of leaving group R for RAFT polymerization,[5,17,41] polystyrene and polyacrylates macro-CTA are expected to be even less efficient transfer agent for MMA polymerization. This assumption was confirmed by polymerizing MMA with a polystyrene or a poly(*n*-butyl acrylate) macro-CTA. For example, MMA polymerization was conducted in 50% anisole solution at 70 °C with a polystyrene macro-CTA (M_n = 12 300 g/mol and $M_w/M_n = 1.16$) and a ratio $[MMA]_0/[macro\text{-}TTC]_0/[AIBN]_0$ of 500/1/0.05. Using 9.4 mmol/L of polystyrene macro-CTA, two different polymer populations were obtained after 4 h of polymerization. The first population corresponded to the unreacted polystyrene macro-CTA, and the second population corresponded to PMMA obtained by free radical polymerization. The molecular weight of both populations did not change during the course of the polymerization, while the relative amount of the PMMA population increased (Figure 6). Comparable results were received when using similar polymerization conditions with a poly(*n*-butyl acrylate) macro-CTA (M_n = 7450 g/mol and $M_w/M_n = 1.15$) (Figure 7).

$ATRP_{Br}$ of MMA with the DiBrTTC Iniferter 3. The DiBrTTC iniferter **3** being an inactive CTA for RAFT polymerization of MMA, **3** can be used to polymerize MMA by ATRP through the bromine chain ends only (Scheme 2).

The effectiveness of **3** for the ATRP of MMA was evaluated by polymerizing MMA in 50% anisole solution at 25 °C with a ratio $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[TPMA]_0$ of 500/1/1.7/0.3/2. After 6 h, poly(methyl acrylate) with M_n = 34 500 g/mol (M_{nth} = 23 500 g/mol) and $M_w/M_n = 1.23$ was obtained. Molecular weight increased linearly with conversion, and polymers with low M_w/M_n were obtained (Figure 8). However, a significant discrepancy between theoretical and experimental

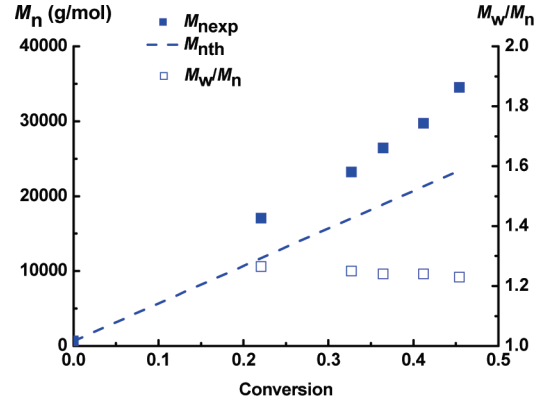


Figure 8. Plot of M_n and M_w/M_n vs conversion for MMA polymerization with **3** in 50% anisole solution at 25 °C with a ratio $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[TPMA]_0$ of 500/1/1.7/0.3/2.

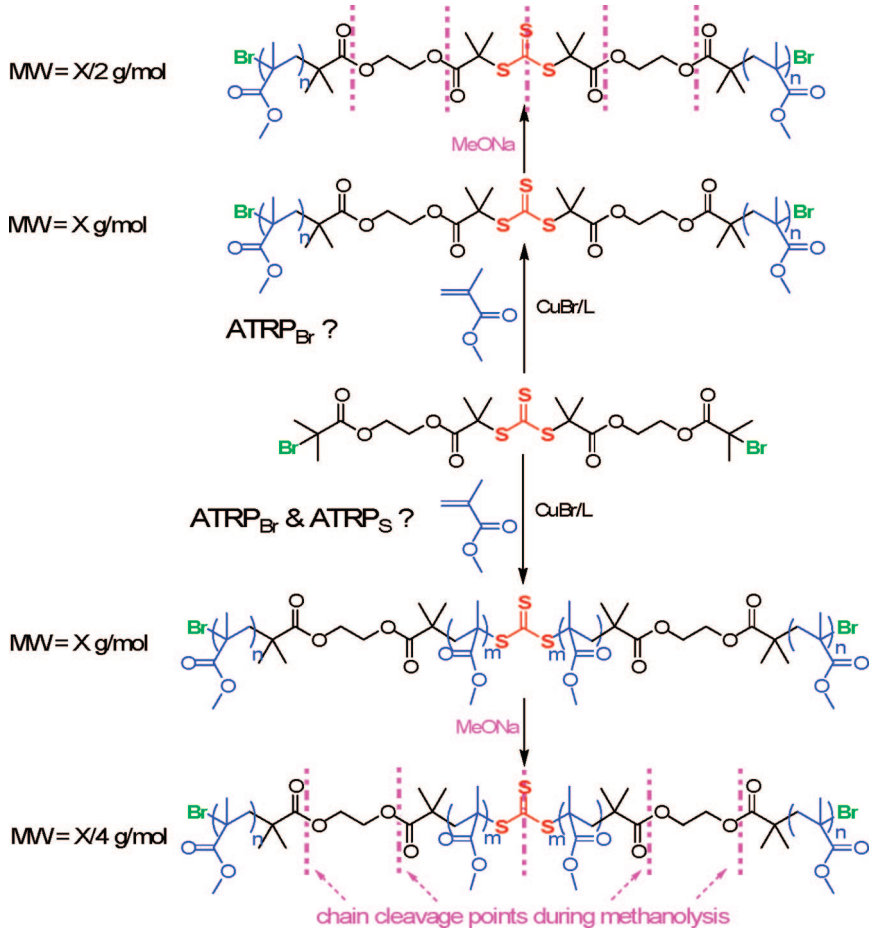
molecular weight was observed, revealing a poor initiation efficiency or bimolecular termination. Indeed, CuBr/TPMA is among the most active ATRP catalysts.[57,58] However, CuBr/TPMA was intentionally used to avoid activation of the TTC moiety by copper, i.e., $ATRP_S$ (Scheme 4). The curvature observed on $\ln([M]_0/[M]_t)$ vs time plot indicates a decrease of radical concentration with time, which is consistent with the occurrence of radical termination (Figure 9).

To confirm that polymerization occurred only through the bromine chain ends, PMMA prepared by ATRP with CuBr/TPMA as catalyst was cleaved by methanolysis. If polymerization occurs only through the bromine chain ends ($ATRP_{Br}$), the molecular weight should be twice lower after methanolysis while it should be 4 times lower if polymerization occurs through both the bromine chain ends and the TTC moiety ($ATRP_{Br}$ and $ATRP_S$) (Scheme 4). PMMA methanolysis was achieved by refluxing for 16 h 1×10^{-3} mmol of PMMA (M_n = 34 500 g/mol and $M_w/M_n = 1.23$), prepared by ATRP with CuBr/TPMA, and 8.75 mmol of sodium methoxide in 6 mL of a 2/1 THF/MeOH solution. The SEC analysis of the polymer after cleavage confirmed that polymerization occurred only through the bromine chain ends as the molecular weight was half the original value (Figure 10).

In order to study the influence of the trithiocarbonate structure during the polymerization of MMA with CuBr/TPMA, a dibromotrithiocarbonate polystyrene macroiniferter was used to polymerize MMA. The dibromotrithiocarbonate polystyrene macroiniferter (M_n = 12 300 g/mol and $M_w/M_n = 1.16$) was prepared by polymerizing styrene in bulk at 130 °C with **3**. This macroiniferter was subsequently used to polymerize MMA in 50% anisole solution at 25 °C with a ratio $[MMA]_0/[DiBrTTC\text{-}PS]_0/[CuBr]_0/[CuBr_2]_0/[TPMA]_0$ of 1000/1/1.7/0.3/2. After 6 h monomer conversion was 34.5%, and a PMMA-*b*-PS-*b*-PMMA with M_n = 58 550 g/mol (M_{nth} = 48 800 g/mol) and M_w/M_n = 1.40 was obtained. In order to determine whether the polymerization took place only through the bromine chain ends, the block copolymer was subsequently cleaved by methanolysis. Methanolysis was achieved by refluxing for 16 h 1×10^{-3} mmol of PMMA-*b*-PS-*b*-PMMA and 8.75 mmol of sodium methoxide in 6 mL of a 2/1 THF/MeOH solution. The molecular weight of the final polymer was 13 700 g/mol, ~4 times lower than the initial block copolymer, and M_w/M_n was 2.03. A decrease of the molecular weight by 4 after methanolysis is consistent with a first block obtained by pure RAFT (growth via the central trithiocarbonate moiety) and a second step with growth of PMMA via the bromine chain ends (Scheme 5).

The SEC trace of the cleaved polymer shows two different polymer populations (Figure 11). The low molecular weight population corresponds to PS; the peak value of this population

Scheme 4. Structure Dependence on ATRP Mechanism for MMA Polymerization with DiBrTTC Iniferter 3 in the Presence of CuBr/L



is 2 times smaller than the peak value of the PS initially prepared by RAFT. The high molecular weight population corresponds to PMMA grown through the bromine chain ends in the second step.

ATRP$_{Br}$ and ATRP$_{S}$ of MMA with the DiBrTTC Iniferter 3. Various diethyldithiocarbamate iniferters have been very recently used for ATRP, with CuBr/PMDETA and CuBr/bpy as catalytic systems, providing well-defined PS and PMMA with low PDI (M_w/M_n).[48,49] We were therefore particularly interested to test whether trithiocarbonates, a very common group of chain transfer agents for RAFT polymerization,[5,17,18,41] could be activated by complexes of CuBr with various nitrogen-based ligands. Activation of RAFT CTA by copper complexes is of interest as it will allow preparation of high molecular weight polymers or pure block copolymers without using an external source of radicals.

MMA polymerization mediated with **3** was conducted in 50% acetone solution at 50 °C with a ratio $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ of 500/1/1.4/0.6/2. After 6 h, PMMA with M_n = 30 700 g/mol (M_{nth} = 29 400 g/mol) and M_w/M_n = 1.27 was obtained. A linear increase of the molecular weight with conversion as well as polymers with low PDIs was observed (Figure 12). The $\ln([M]_0/[M]_t)$ vs time plot was slightly curved due to bimolecular termination, which indicates that the

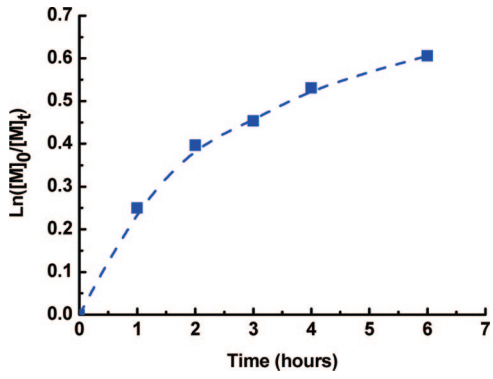


Figure 9. Kinetic plot for MMA polymerization with **3** in 50% anisole solution at 70 °C with a ratio $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[TPMA]_0$ of 500/1/1.7/0.3/2.

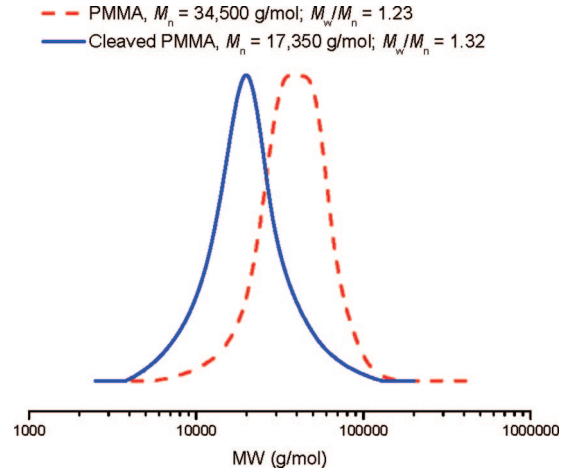
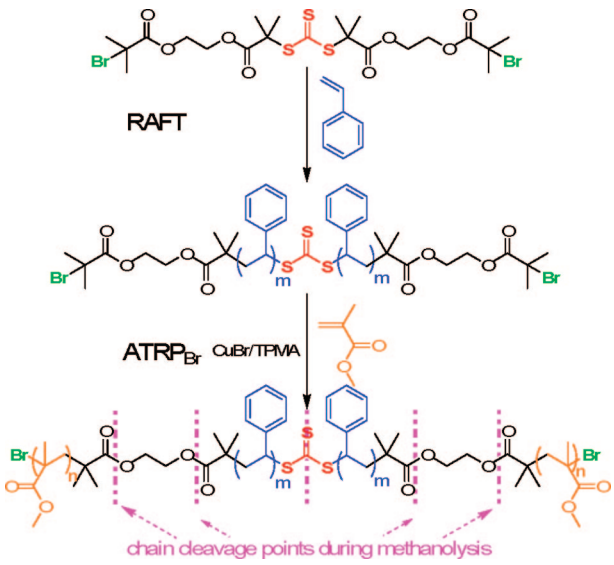


Figure 10. SEC traces of PMMA prepared by ATRP with CuBr/TPMA before and after methanolysis with sodium methoxide.

Scheme 5. Synthesis of ABA Triblock Copolymer by Successive RAFT Polymerization of St and ATRP of MMA with DiBrTTC Iniferter 3 and CuBr/TPMA as Catalyst



system could be too active (Figure 13). PMDETA is also a very active ligand for normal ATRP of MMA with CuBr due to a high activation rate constant, k_{act}, and a high equilibrium constant, K_{ATRP}.[39,52,57]

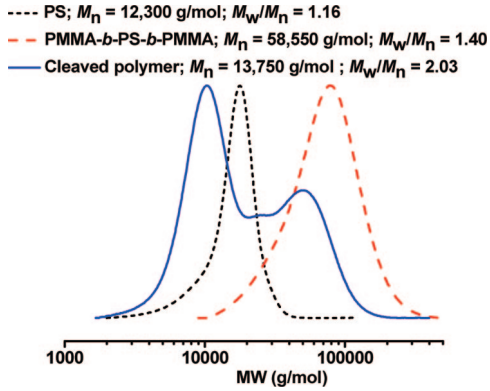


Figure 11. SEC traces of PS prepared by RAFT polymerization of St, PMMA-*b*-PS-*b*-PMMA obtained by ATRP of MMA with the PS macroinitiator and CuBr/TPMA as catalyst, and the resulting polymer after methanolysis with sodium methoxide.

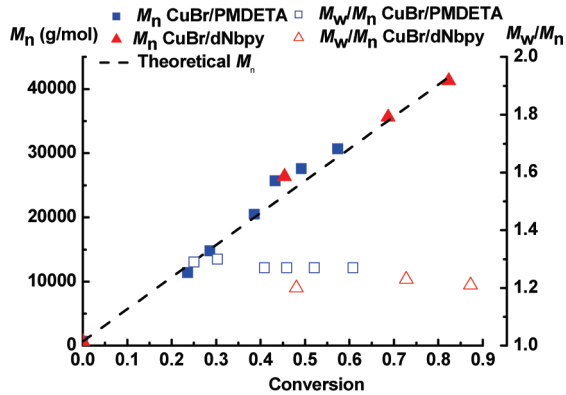


Figure 12. Plot of M_n and M_w/M_n vs conversion for MMA polymerization with **3**. Polymerization conditions: (blue) $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.4/0.6/2$ in acetone 50% by volume, 6 h at 50 °C; (red) $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[dNbpy]_0 = 500/1/1/0.1/2.2$ in anisole 50% by volume, 3 h at 90 °C.

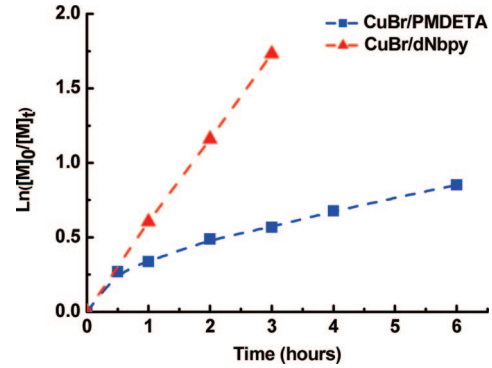


Figure 13. Kinetic plot for MMA polymerization with **3**. Polymerization conditions: (blue) $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.4/0.6/2$ in acetone 50% by volume, 6 h at 50 °C; (red) $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[dNbpy]_0 = 500/1/1/0.1/2.2$ in anisole 50% by volume, 3 h at 90 °C.

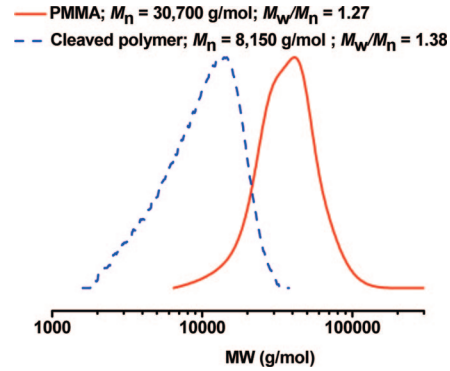


Figure 14. SEC traces of PMMA prepared by ATRP with CuBr/PMDETA before and after methanolysis with sodium methoxide.

MMA polymerization was also conducted using dNbpy, a less active ligand for ATRP.[52] Polymerization at 90 °C in 50% anisole solution with a ratio $[MMA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[dNbpy]_0$ of 500/1/1/0.1/2.2 gave a PMMA with M_n = 41 300 g/mol (M_{nth} = 41 850 g/mol) and M_w/M_n = 1.21 after 3 h. Molecular weight increased linearly with conversion while M_w/M_n remained below 1.25 (Figure 12). A linear relationship between $\ln([M]_0/[M]_t)$ vs time was observed, indicating that no detectable termination occurred in this system (Figure 13).

To confirm that polymerization occurred through both the bromine chain ends and the trithiocarbonate moiety, the PMMA prepared by ATRP with CuBr/PMDETA and CuBr/dNbpy as catalyst was cleaved by methanolysis. If polymerization occurred through both the bromine chain ends and the TTC moiety, the molecular weight should be 4 times lower after methanolysis (Scheme 4). PMMA methanolysis was achieved by refluxing for 16 h 1×10^{-3} mmol of PMMA prepared by ATRP with CuBr/PMDETA or CuBr/dNbpy and 8.75 mmol of sodium methoxide in 6 mL of a 2/1 THF/MeOH solution. In both cases the final molecular weight was reduced ~4 times after methanolysis, decreasing from M_n = 30 700 g/mol (M_w/M_n = 1.27) to M_n = 8150 g/mol (M_w/M_n = 1.38) and from M_n = 41 300 g/mol (M_w/M_n = 1.21) to M_n = 11 500 g/mol (M_w/M_n = 1.29) for PMMA prepared by ATRP with CuBr/PMDETA and CuBr/dNbpy, respectively (Figures 14 and 15).

These results, combined with the fact that **3** is an inefficient chain transfer agent for the RAFT polymerization of MMA, indicate that, like diethyldithiocarbamates, trithiocarbonates can be activated by a complex of copper bromide with various amine ligands.[46,48,49] It is interesting to note that the molecular weight distribution of the PMMA segments after methanolysis is quite low. There is, indeed, no reason for the bromine and the

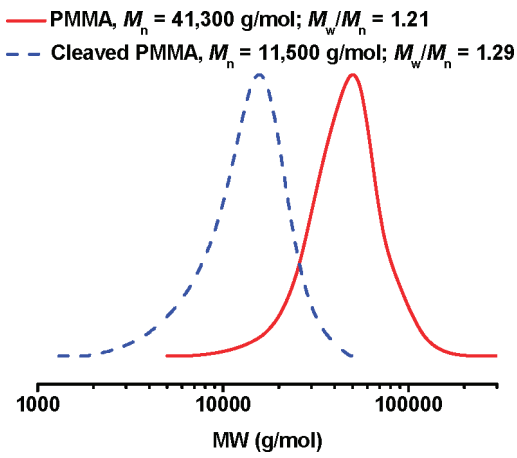
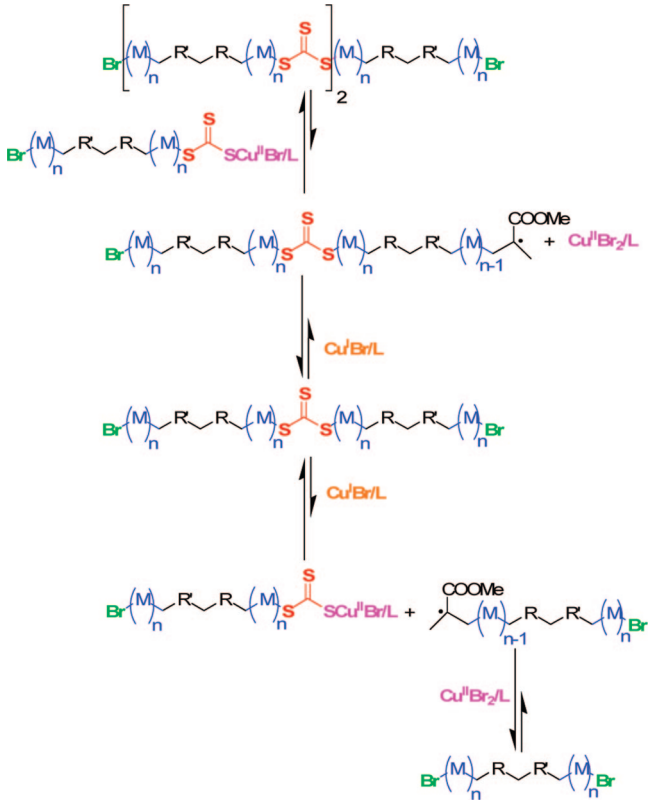


Figure 15. SEC traces of PMMA prepared by ATRP with CuBr/dNbpy before and after methanolysis with sodium methoxide.

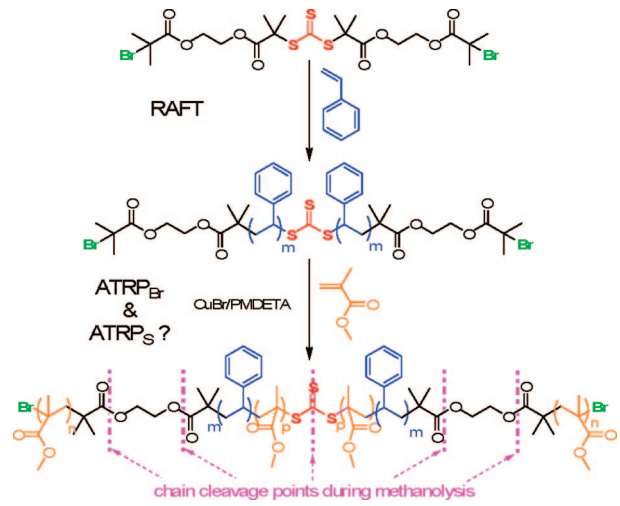
Scheme 6. Chain-End Interchange during MMA Polymerization with DiBrTTC 3 in the Presence of CuBr/PMDETA or CuBr/dNbpy



trithiocarbonate end-capped PMMA to have the same activation rate constant, k_{act}. The low molecular weight distribution of the PMMA segments after methanolysis reflects the interchange that take place between the bromine and the trithiocarbonate chain end (Scheme 6).

The influence of the trithiocarbonate structure on ATRP activation was investigated by polymerizing MMA with a dibromotrithiocarbonate polystyrene macroiniferter. A dibromotrithiocarbonate polystyrene macroiniferter (M_n = 12 300 g/mol and M_w/M_n = 1.16) prepared by RAFT polymerization of styrene with **3** was used to polymerize MMA in 50% anisole solution at 60 °C with a ratio $[MMA]_0/[DiBrTTC\text{-}PS]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ of 1000/1/1.4/0.6/2. After 4 h monomer conversion was 42%, and a block copolymer with M_n = 60 750 g/mol (M_{nth} = 56 400 g/mol) and M_w/M_n = 1.30 was obtained.

Scheme 7. Synthesis of Block Copolymer by Successive RAFT Polymerization of St and ATRP of MMA with DiBrTTC Iniferter 3 and CuBr/PMDETA as Catalyst



In order to know whether the polymerization took place only through the bromine chain ends or through both the bromine chain ends and the trithiocarbonate moiety, the block copolymer was subsequently cleaved by methanolysis. Methanolysis was achieved by refluxing 1×10^{-3} mmol of block copolymer and 8.75 mmol of sodium methoxide in 6 mL of a 2/1 THF/MeOH solution for 16 h. The molecular weight of the final polymer was 14 800 g/mol, ~4 times lower than that of the initial block copolymer, and M_w/M_n was 1.75. A 4-fold decrease of the molecular weight after methanolysis is consistent with a first block obtained by pure RAFT (growth via the central trithiocarbonate moiety) and a second step with growth of PMMA via the bromine chain ends or via both the bromine chain ends and the trithiocarbonate moiety (Scheme 7).

The SEC trace of the cleaved polymer shows three different polymer populations (Figure 16). The high molecular weight population corresponds to a PS-*b*-PMMA block copolymer obtained through the TTC moiety. The intermediate molecular weight population corresponds to PMMA obtained by ATRP via the bromine chain ends. The low molecular weight population corresponds to PS, the peak value of this population being 2 times smaller than the peak value of the PS initially prepared by RAFT. The presence of pure PS after cleavage indicates poor initiation efficiency when extending a polystyrene block to poly(methyl methacrylate) by ATRP through the trithiocarbonate moiety. This phenomenon is also typical of halogen end-capped

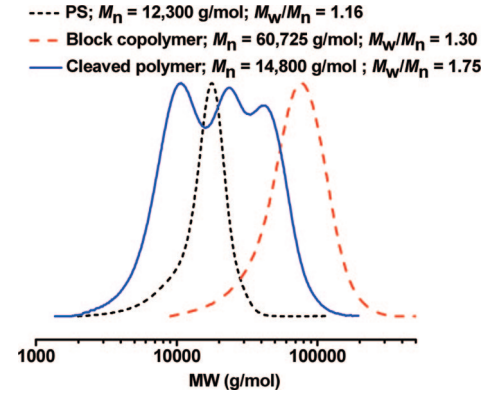
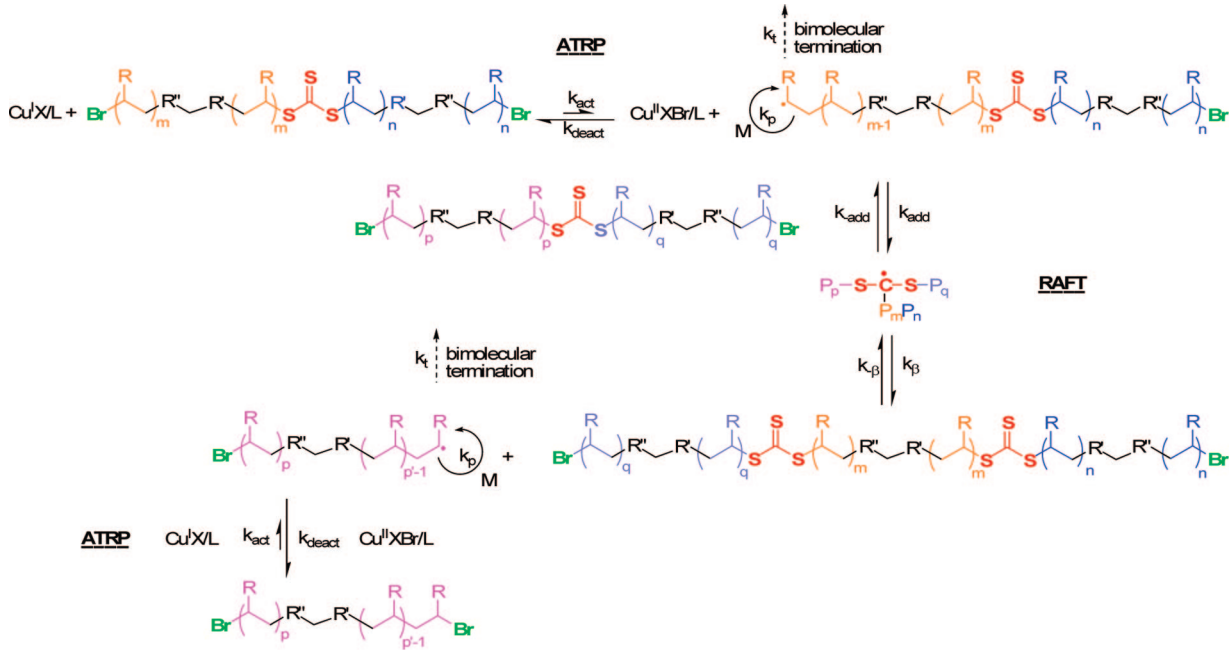


Figure 16. SEC traces of PS prepared by RAFT polymerization of St, block copolymer obtained by ATRP of MMA with the PS macroinitiator and CuBr/PMDETA as catalyst, and the resulting polymer after methanolysis with sodium methoxide.

Scheme 8. Simultaneous ATRP and RAFT Polymerization of Acrylates or Styrene with 3 in the Presence of Cu^{I}/L Complex



polymers and has been reported in the literature.[59–62]

A very important condition to obtain well-defined block copolymers is that the apparent rate constant of initiation should be greater than that of propagation if the system is fully equilibrated, i.e., $K_{ATRP}^{initiator}k_i > K_{ATRP}^{monomer}k_p$, where k_i and k_p are the rate constants for reinitiation (cross-propagation) and propagation, respectively, and $K_{ATRP} = k_{act}/k_{deact}$.[59,63,64] This condition is not met in the ATRP of methacrylate monomers from acrylate or styrene-based (macro)initiators ($K_{ATRP}^{initiator}k_i < K_{ATRP}^{monomer}k_p$), leading to poor initiation efficiency. At the beginning of such a block copolymerization, a small fraction of polyacrylate or polystyrene macroinitiator terminal halogens are activated, methacrylate monomer is added, and then the chain is deactivated again to be capped with a halogen. The resulting dormant chain is much more likely to reactivate, as compared to the remaining unactivated polyacrylate or polystyrene macroinitiator. This leads to an inefficient extension of the macroinitiator, and a product with a bimodal distribution of molecular weights is obtained.

Concurrent $ATRP_{Br}$, $ATRP_S$, and RAFT Polymerization of Acrylates and Styrene with the DiBrTTC Iniferter 3. Polymerization of acrylates and styrene with **3** in the presence of Cu^{I}/L complex can occur via $ATRP_{Br}$, $ATRP_S$, and RAFT mechanisms. The bromine chain ends are activated by the Cu^{I}/L complex to generate an organic radical, R•, and the corresponding higher oxidation state metal halide, $Cu^{II}Br$/L. R• can then propagate with vinyl monomer, terminate as in conventional free radical polymerization, be reversibly deactivated by the $Cu^{II}Br$/L complex, or add to the carbon−sulfur double bond of a RAFT reagent, which will release another initiating/propagating radical after β-scission of the radical adduct. As a result, during the polymerization of acrylates and styrene with **3** in the presence of Cu^{I}/L complex, the polymer chains can reshuffle, and the final product should be a mixture of polymer chains with various number of trithiocarbonate moieties in their backbone (Scheme 8).

The simultaneous ATRP and RAFT polymerization of St was conducted in 33% anisole solution using CuBr/PMDETA as catalytic system, with a ratio $[St]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0$ of 500/1/1.8/0.2. After 19 h at 90 °C, polystyrene with M_n = 36 750 g/mol (M_{nth} = 36 130 g/mol) and M_w/M_n = 1.63 was obtained. A linear relationship between $\ln([M]_0/[M]_t)$ vs time was observed, indicating that no detectable termination occurred in this system (Figure 17). A linear increase of the molecular weight with conversion and a good agreement between theoretical and experimental molecular weights were observed. Because of chain reshuffling, polymers with PDIs around 1.6 and polymodal SEC traces were obtained (Figures 18 and 19).

The simultaneous ATRP and RAFT polymerization of *n*BA with **3** was achieved in 33% DMF at 60 °C with a ratio $[nBA]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ of 488/1/1.9/0.1/2. After 7 h, poly(*n*-butyl acrylate) with M_n = 17 100 g/mol (M_{nth} = 16 300 g/mol) and M_w/M_n = 1.58 was obtained.

In order to asses the degree of control during concurrent ATRP and RAFT polymerization with **3**, the polymers were cleaved after the polymerization. The most widely used reagents to cleave thiocarbonylthio groups are nucleophiles, such as primary or secondary amines,[16,65–68] hydroxides,[68–70] or ionic reducing agents, such as borohydrides.[68,71–73] The polymers were cleaved either by aminolysis of the trithiocarbonate moiety or by methanolysis of both the trithiocarbonate and ester functions present in the backbone of the polymers. Aminolysis was achieved by stirring a mixture of 2.5×10^{-3} mmol of polystyrene or poly(*n*-butyl acrylate), 2.5 mmol of ethylenediamine, and 0.01 mmol of triethylamine in 10 mL of tetrahy-

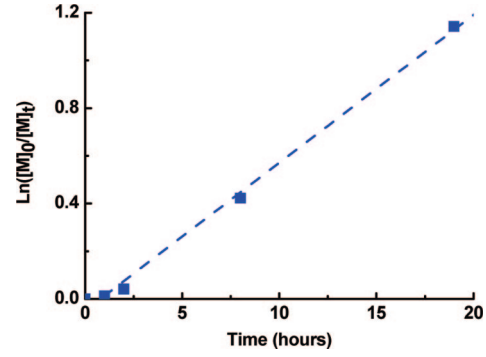


Figure 17. Kinetic plot for St polymerization with **3** in 33% anisole solution at 90 °C with a ratio $[St]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ of 500/1/1.8/0.2/2.

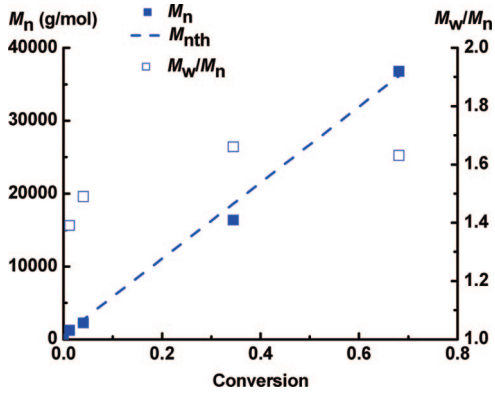


Figure 18. Plot of M_n and M_w/M_n vs conversion for St polymerization with **3** in 33% anisole solution at 90 °C with a ratio $[St]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ of 500/1/1.8/0.2/2.

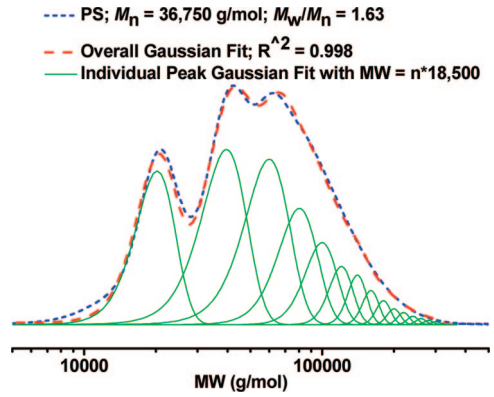


Figure 19. SEC trace and Gaussian fitting of polystyrene prepared by concurrent ATRP and RAFT with **3**. Experimental conditions: $[St]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.8/0.2/2$ in anisole 33% by volume; 90 °C for 19 h.

Table 1. Product of Aminolysis and Methanolysis of Polystyrene and Poly(*n*-butyl acrylate) Prepared by Concurrent ATRP and RAFT Polymerization with DiBrTTC 3

original polymer M_n (g/mol); M_w/M_n	aminolysis product M_n (g/mol); M_w/M_n	methanolysis product M_n (g/mol); M_w/M_n
PS:[a] 36750; 1.63	18500; 1.28	8950; 1.17
P*n*BA:[b] 17100; 1.58	9250; 1.23	

[a] Polystyrene prepared by concurrent ATRP and RAFT polymerization with **3**. Experimental conditions: $[St]_0/[DiBrTTC]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.8/0.2/2$ in anisole 33% by volume; 90 °C for 19 h. [b] Pol(*n*-butyl acrylate) prepared by concurrent ATRP and RAFT with **3**. Experimental conditions: $[nBA]_0/[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.9/0.1/2$ in DMF 33% by volume; 60 °C for 7 h.

drofuran for 72 h at room temperature. The product of aminolysis is a polymer with a molecular weight that is equal to the interval between each population of the polymodal polymer obtained by concurrent ATRP and RAFT polymerization (Schemes 2 and 8) (Table 1). Methanolysis of polystyrene was achieved by refluxing 1×10^{-3} mmol of polymer and 8.75 mmol of sodium methoxide in 6 mL of a 2/1 THF/MeOH solution for 16 h. Methanolysis of the final polystyrene gives information on the length of the segments grown by ATRP and RAFT polymerization.

Polymers prepared with **3** should have one trithiocarbonate moiety per polymeric chain on average, as the number of chains during concurrent ATRP and RAFT polymerization with **3** is equal to the initial number of DiBrTTC **3** molecules added (Scheme 8). Thus, the product of aminolysis should have half the molecular weight of the initial polymer. As expected, both polystyrene and poly(*n*-butyl acrylate) prepared by concurrent ATRP and RAFT had their molecular weight reduced by a factor of 2 after aminolysis (Table 1). More importantly the molecular weight distributions of the polymers after aminolysis were low for both PS and P*n*BA, 1.28 and 1.23, respectively, indicating that both polymerizations occurred with good control. Polystyrene prepared by concurrent ATRP and RAFT polymerization was also cleaved by methanolysis in order to assess whether blocks grown by ATRP through the bromine chain ends and blocks grown by RAFT through the trithiocarbonate moiety have the same chain length. The molecular weight of the polymer was reduced by a factor of 4 after methanolysis, as expected, and the molecular weight distribution of the cleaved polymer was 1.17, indicating that all blocks have the same chain length. This result was expected as every block should have an equal chance to grow by ATRP and RAFT during concurrent ATRP and RAFT polymerization with **3**. Because of chain reshuffling, a block initially end-capped with a bromine atom can be converted to trithiocarbonate end-capped block, and vice versa (Scheme 8). As a result, the population of polymers with one trithiocarbonate moiety decreases and leads to formation of polymers without TTC moiety and polymers with multiple TTC moieties.

The SEC trace of the final polystyrene was deconvoluted with a Gaussian fitting ($R^2 = 0.998$) using 18 500 g/mol as repeating unit (Table 1). From the deconvolution, the number distribution for populations with 0, 1, 2,..., 12 trithiocarbonate moieties was estimated (eq 1) to be 41.3%, 27.1%, 16.8%, 7.7%, 3.6%, 1.6%, 0.9%, 0.5%, 0.3%, 0.2%, 0.09%, 0.05%, 0.03%, 0.02%, and 0.01% for populations with 0, 1, 2,..., 14 trithiocarbonate moieties, respectively (Figure 19).

$$\% \, n_i = \frac{A_i/(M_{wi}^{\,2})}{\sum A_i/(M_{wi}^{\,2})} \qquad (1)$$

In eq 1, A_i and M_{wi} are the peak area and the weight-average molecular weight, respectively, of a polymer population, n_i, with i trithiocarbonate moieties. The formation of polymers with multiple trithiocarbonate functions requires polymers without TTC moiety to be formed simultaneously, in order to keep the balance between trithiocarbonate functions and chain ends constant (Scheme 9).

As a result, the population of polymers without TTC moiety, n_0, can be expressed, without taking into account termination, as a function of all the populations of polymers comprising two or more TTC moieties (eq 2).

$$n_0 = \sum n_i^*(i-1); \quad \text{for } i \geq 1 \qquad (2)$$

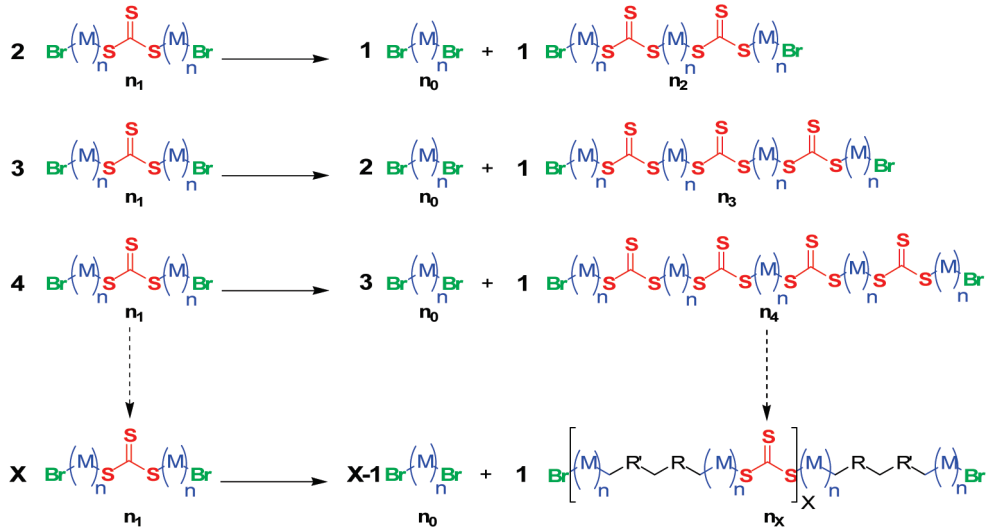
From the deconvolution, n_0 and $\sum n_i^*(i-1)$ were estimated to be 0.413 and 0.617, respectively. The discrepancy between predicted ratios of the different populations and experimentally determined values can be ascribed to small proportion of chains terminated by coupling. The terminated chains contribute exclusively to the high molecular weight population.

Therefore, it was interesting to make a similar analysis for poly(*n*-butyl acrylate), in which contribution of termination should be really small. The SEC trace of the final poly(*n*-butyl acrylate) was also deconvoluted with a Gaussian fitting ($R^2 = 0.996$) using 8500 g/mol as repeating unit. From the deconvolution, the number distribution for populations with 0, 1, 2,..., 9 trithiocarbonate moieties was estimated (eq 1) to be 38.5%, 36.3%, 16.4%, 5.7%, 1.8%, 0.9%, 0.3%, 0.2%, 0.05, and 0.02%, respectively (Figure 20). From the deconvolution, n_0 and $\sum n_i^*(i-1)$ were estimated to be 0.385 and 0.396, respectively, showing an excellent agreement between estimated values of the different polymer populations and eq 2.

Conclusion

The DiBrTTC iniferter **3** has been successfully used to conduct, independently or concurrently, ATRP and RAFT

Scheme 9. Redistribution of Polymer Populations during Concurrent ATRP and RAFT Polymerization with the DiBrTTC Iniferter 3



polymerization. The RAFT polymerization of *n*-butyl acrylate and styrene yielded polymers with low PDIs 1.15 and 1.16, respectively. The influence of the trithiocarbonate structure on the RAFT polymerization of methyl methacrylate was studied. Polymerization of MMA in the presence of DiBrTTC with methacrylate, styrene, or acrylate substituents proceeded by a free radical polymerization procedure, yielding polymer with broad molecular weight distribution and no control over molecular weight. Polymerization of MMA in the presence of the CuBr/TPMA complex proceeded by ATRP exclusively through the bromine chain ends, yielding polymer with low molecular weight distribution, 1.23. Polymerization of MMA in the presence of CuBr/PMDETA or CuBr/dNbpy complex proceeded by ATRP through the bromine chain ends and the trithiocarbonate function, yielding polymer with low molecular weight distribution, 1.27 and 1.21, respectively. The influence of the trithiocarbonate structure on the ATRP through transfer of the trithiocarbonate moiety was studied. Chain extension of a trithiocarbonate end-capped polystyrene macroiniferter with MMA in the presence of CuBr/PMDETA complex gave poor initiation efficiency, showing the same reactivity trend as normal ATRP. Concurrent ATRP and RAFT polymerization of styrene and *n*-butyl acrylate was conducted using CuBr/PMDETA as the catalytic system. Polymers with broad molecular weight distribution ($M_w/M_n \approx 1.6$) and polymodal size exclusion chromatography traces were obtained due to chain reshuffling through the TTC moiety. SEC analysis of the polymers after aminolysis or methanolysis showed that concurrent ATRP and RAFT occurred with good control for both *n*-butyl acrylate and styrene ($M_w/M_n < 1.3$). This work provides the first example of ATRP with a trithiocarbonate, a common chain transfer agent for RAFT polymerization. Mechanistic studies to correlate structure and ATRP reactivity of various RAFT chain transfer agents are currently in progress.

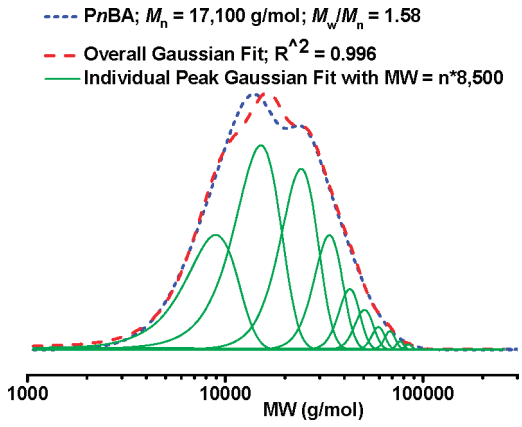


Figure 20. SEC trace and Gaussian fitting of pol(*n*-butyl acrylate) prepared by concurrent ATRP and RAFT with **3**. Experimental conditions: $[nBA]_0/[I]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 500/1/1.9/0.1/2$ in DMF 33% by volume; 60 °C for 7 h.

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