Novel Difunctional Reversible Addition Fragmentation Chain Transfer (RAFT) Agent for the Synthesis of Telechelic and ABA Triblock Methacrylate and Acrylate Copolymers

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ABSTRACT: The design of a novel difunctional chain transfer agent (CTA) based on the propagating core (R group) approach is detailed. Successful synthesis of ABA block copolymers of poly(butyl methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl methacrylate) and poly(butyl acrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl acrylate) with targeted molecular weight and polydisperity indices in the range 1.2−1.4 is reported. The effect of free radical initiator concentration with respect to CTA concentration on block efficiency is investigated and lower concentrations were found to increase reaction time, but significantly reduce termination reactions. The consequence of difunctionality on homo and block extension polymerizations is discussed, with the polymerization of methyl and butyl methacrylate being more controlled than butyl acrylate.

Introduction

Triblock copolymers consisting of a central block of type B surrounded by outer blocks of type A, find uses as dispersing agents,[1,2] adhesives,[3] elastomers,[4] thermoresponsive materials,[5] and liquid crystal displays[6] and for drug delivery systems.[7] The driving force behind much of the latest research into ABA triblock copolymers stems from the unique morphologies they are capable of adopting. The majority of triblock copolymers have been synthesized by traditional living polymerizations, with living anionic polymerization[4] being the most popular. An alternative synthetic route focuses on the use of living radical polymerization (LRP) techniques, based on radical chemistry, which permits to avoid the traditional issues encountered when using ionic polymerizations (e.g., complex experimental procedures, extreme reaction conditions, stringent monomer purification and/or limited range of suitable monomers). Among LRP techniques, reversible addition−fragmentation chain transfer (RAFT) polymerization is one of the most versatile processes, and it offers the potential to synthesize many new materials.[8,9] Strategies to date for the synthesis of ABA copolymers by RAFT include the conversion of α,ω-telechelic homopolymers into macro CTAs,[10−12] the use of a symmetrical trithiocarbonate,[13] the sequential addition of monomer mediated by a monofunctional CTA,[14] and the use of a difunctional CTA.[9,12,15−20] The synthesis of thiol functionalized α,ω-telechelic polymers has also been achieved using a difunctional CTA.[21] Transforming α,ω-telechelic polymers into macroCTAs typically requires the use of a homopolymer containing hydroxy, carboxylic acid, thiol, or halo chain-end functionality. Quantitative yields and a high degree of purity are required, as shown by the very few examples reported to date. Sequential monomer addition from a monofunctional CTA has been successful, but it requires three reaction steps and is limited to monomers of the same reactivity.

Difunctional CTAs can be classified into two types: CTAs where propagation occurs from the core, with thiocarbonyl thio groups remaining on the outside, and CTAs in which the polymer chains grow away from the core before adding back onto the thiocarbonyl thio group, which remains in the center of the polymeric chain. The latter type has the advantage of a dormant core during polymerization, which avoids core−core coupling, a key feature when using CTAs of functionality >2, e.g., for star polymer synthesis.[22,23] CTAs that propagate from the core are advantageous in that they yield polymers that do not contain thermally labile thiocarbonyl thio bonds at their center, and produce polymers with α,ω-chain end functionality. Thiocarbonyl thio chain ends are capable of undergoing numerous transformations by reduction, hydrolysis, irradiation, thermolysis[13,24−26] as well as radical induced substitution reactions.[27] The use of such CTAs is therefore one of the most versatile approaches in the synthesis of ABA block copolymers, although only few examples can be found in the literature. For instance, the CSIRO group used a bis(dithioester) CTA to synthesize thermoplastic type materials: poly(styrene)-*b*-poly(*n*-butyl methacrylate)-*b*-poly(styrene), poly(methyl methacrylate)-*b*-poly(*n*-butyl methacrylate)-*b*-poly(methyl methacrylate), and poly(hydroxyl methyl methacrylate)-*b*-poly(methyl methacrylate)-*b*- poly(hydroxyl methyl methacrylate).[15] Donovan et al. reported the use of an acrylamido-based difunctional CTA to polymerize *N*,*N*-dimethylacrylamide, but unlike its monofunctional analogue, bimodal and trimodal molecular weight distributions were observed at high conversions.[19] Bussel et al. also used a similar approach, by mediating RAFT polymerization with a novel difunctional dithiocarbamate CTA, to produce poly(n-butyl acrylate) homopolymers in miniemulsion.[18] Double hydrophilic block copolymers consisting of poly(acrylamide)-*b*-poly(acrylic acid-*stat*-acrylamide)-*b*- poly(acrylamide) were synthesized by Taton et al. using a difunctional xanthate based CTA.[28] At the time of writing this paper, Goh et al. published their work on the use of a difunctional CTA to tailor the molecular weight distribution of polystyrene, and their findings provide nice complementary information to the results presented in this paper.[20]

We report here the synthesis and use of a novel difunctional CTA that can produce a variety of multiblock copolymers containing, methacrylate and acrylate type monomers and

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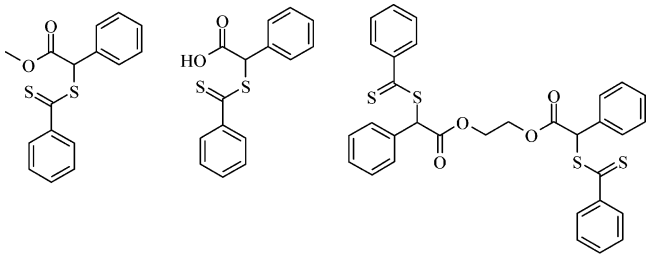


CTA_1 CTA_2 CTA_3

Figure 1. Difunctional CTA_3 and its monofunctional analogues.

discuss the experimental and kinetic factors which influence the synthesis of such block copolymers.

Experimental Section

Materials. All chemicals were used as received unless otherwise stated. *n*-butyl acrylate (BA) (99%, Aldrich), *n*-butyl methacrylate (BMA) (99%, Aldrich) and methyl methacrylate (MMA) (99%, Aldrich), were purified by passing through aluminum oxide; activated basic Brockmann I (Aldrich). Azobis(isobutyronitrile) (AIBN) was recrystallized from cold methanol and dried in vacuo overnight. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise stated. All air and moisture sensitive compounds were manipulated using standard Schlenk techniques under a dry nitrogen atmosphere.

Instrumentation. Both ^{1}H (400 MHz) and ^{13}C (100 MHz) Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker 400 UltraShield spectrometer at 25 °C and chloroform-*d* was used as a solvent, unless otherwise stated.

Molecular weight distributions were recorded using size exclusion chromatography (SEC) at ambient temperature using a system equipped with a Polymer Laboratories 5.0 μm-bead-size guard column (50 × 7.5 mm) and two Polymer Laboratories PLgel 5 μm MIXED-C columns (molecular weight range of 2,000,000 − 500 g mol^{-1}) with a differential refractive index detector (Shodex, RI-101). Tetrahydrofuran was used as an eluent at a flow rate of 1 mL min^{-1} and toluene was used as a flow rate marker. Poly(methyl methacrylate) standards in the range of 1 944 000 to 1020 g mol^{-1} were used as calibrants.

Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer Spectrum One FTIR spectrometer in the region between 4000 and 400 cm^{-1}, with 100 scans per sample.

Modulated differential scanning calorimetry (mDSC) was carried out on a Universal V2.5H TA instrument.

Synthesis of Carboxylic Acid Containing RAFT Agent, CTA_2 (See Figure 1). 1-Bromobenzene (8.6 g, 55 mmol) was introduced over 15 min to a round bottomed flask containing anhydrous tetrahydrofuran (150 mL), magnesium turnings (1.4 g, 57 mmol), and a crystal of iodine. The reaction mixture was heated to 80 °C and allowed to reflux for 2 h, after which time no magnesium metal could be observed. The reaction mixture was then cooled to 0 °C and carbon disulfide (8.3 g, 109 mmol) introduced dropwise, via a degassed syringe. A color change from clear to deep orange was observed, and the reaction mixture was allowed to reach room temperature. To this reaction mixture, α-bromophenyl acetic acid (11.83 g, 55 mmol) in anhydrous tetrahydrofuran (99.99%) was transferred by syringe. The temperature was raised to 100 °C and maintained for 24 h after which time the crude product was concentrated by removal of solvent in vacuo and then dissolved in ethyl acetate. The product was isolated by first extracting into the aqueous layer using a 2 molar solution of sodium hydroxide (200 mL) and then returned to a fresh layer of ethyl acetate using a 1 M solution of HCl (200 mL). The product (9.5 g, 33 mmol; yield 60%) was isolated as orange crystals by recrystallization in a solution of ethyl acetate and hexane (1:50).

^{1}H NMR ($CDCl_3$, 298K, 400 MHz): δ (ppm from TMS) 5.75 (1H, s, C−*H*), 7.36−7.56 (8H, m, Ar−*H*), 8.01 (2H, dd, J = 7.26, 1.31 Hz, SC(Ar−*H*)S).

^{13}C NMR ($CDCl_3$, 298 K, 100.59 MHz): δ (ppm from TMS) 58.84 (*C*H), 127.36, 128.83, 129.33, 129.55, 133.30, 144.13 (*C*H of Ar), 175.17 (*C*═O), 225.68 (CS_2).

Anal. Calcd for $C_{15}H_{12}O_2S_2$: C, 62.47; H, 4.19; S, 22.24; Found: C, 62.3; H, 3.95; S, 22.0.

FTIR (cm^{-1}): 3025−2567 (carboxylic acid skeleton area); 1698 (C═O); 1605−1444 (aromatic skeleton area); 1241 (C═S).

Melting point: 132 − 133 °C.

Synthesis of Difunctional RAFT Agent, CTA_3 (See Figure 1). To a stirred solution of ethylene glycol (1 g, 16 mmol) and anhydrous triethylamine (3.3 g, 32 mmol) in anhydrous tetrahydrofuran (150 mL) at 0 °C was added 2-chloro-2-phenylacetyl chloride (6.1 g, 32 mmol) dropwise (ca. 15 min). The reaction was allowed to reach room temperature and stirred for 3 h, after which time a white precipitate of NaCl was filtered off, and diethyl ether (200 mL) was added to the resulting pale yellow solution. This was washed with saturated sodium hydrogen carbonate (3 × 100 mL), followed by deionized water (3 × 100 mL). The organic layer was then collected and dried over sodium sulfate, before filtration and removal of solvent under reduced pressure. The compound obtained (**1**) was a pale yellow oil, (11.4 g, 31 mmol, yield: 96.2%) and was used without further purification. 1-bromobenzene (8.6 g, 55 mmol) was introduced over 15 min to a round bottomed flask containing anhydrous tetrahydrofuran (150 mL), magnesium turnings (1.4 g, 57 mmol) and a crystal of iodine. The reaction mixture was heated to 80 °C and allowed to reflux for 2 h, after which time no magnesium metal could be observed. The reaction mixture was then cooled to 0 °C and carbon disulfide (8.3 g, 109 mmol) introduced dropwise, via a degassed syringe. A color change from clear to deep orange was observed and the reaction mixture was allowed to reach room temperature. After 30 min, a solution of **1** (10 g, 27 mmol) in anhydrous tetrahydrofuran (15 mL) was introduced and the reaction allowed to reflux at 80 °C for 24 h. After this time, the reaction vessel was cooled in an ice−water bath. To the reaction flask, hydrochloric acid (10 M, 15 mL) was introduced. The resulting precipitate was filtered off, and deionized water was added. The product was extracted into ethyl acetate (2 × 200 mL), and the organic layers were reunited. These were washed with saturated sodium hydrogen carbonate (2 × 100 mL) and finally with deionized water (2 × 100 mL). The organic layer was dried over sodium sulfate, and after removal of solvent, CTA_3 was obtained by flash chromatography on silica using ethyl acetate and hexane (1:4) as eluent. The product (4 g, 7 mmol, yield: 24%) was isolated in two distinct solid forms (variation was in physical appearance and color) by crystallization. Recrystallization was carried out using the column conditions. Crystal type 1 forming after 24 h at −18 °C and crystal type 2 forming after 3 days at −18 °C. Both crystal types were fully characterized by ^{1}H NMR, ^{13}C NMR, microanalysis, and FT−IR, and both were confirmed as being the desired compound (CTA_3). However, a small variation between shifts of C*H*(Ph) proton was observed in the ^{1}H NMR, which leads us to believe that two stereoisomeric forms of CTA_3 have been isolated. However, crystals obtained from the synthesis of CTA_3 were not of sufficient size for further analysis by X-ray crystallography. CTA_{3a} was used in all experiments unless stated.

CTA_{3a}. ^{1}H NMR ($CDCl_3$, 298K, 400 MHz): δ (ppm from TMS) 4.4−4.3 (4H, m, O−CH_2CH_2), 5.67 (2H, s, C−*H*), 7.20−7.48 (16H, m, Ar−*H*), 7.91 (4H, dd, J = 7.26, 1.31 Hz, SC(Ar−*H*)S).

^{13}C NMR ($CDCl_3$, 298 K, 100.59 MHz): δ (ppm from TMS) 58.66 (*C*H), 63.41 (O-*C*H_2), 126.98, 128.42, 128.86, 128.96, 129.09, 132.82, 132.96, 143.84 (*C*H of Ar), 168.63 (*C*═O), 225.65 (CS_2).

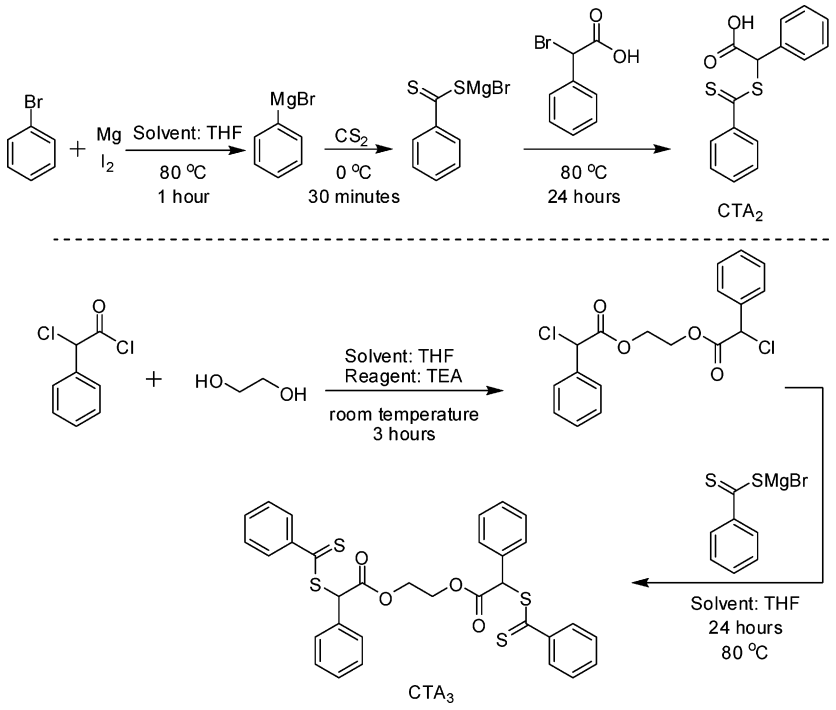
Anal. Calcd for $C_{32}H_{26}O_4S_4$: C, 63.76; H, 4.35; S, 21.28. Found: C: 63.56; H, 4.21; S, 21.43.

FTIR (cm^{-1}): 1733 (C═O); 1605−1444 (aromatic skeleton area); 1230 (C═S); 1143 (C−O stretching).

Melting point: 90−91 °C.

CTA_{3b}. ^{1}H NMR ($CDCl_3$, 298K, 400 MHz): δ (ppm from TMS); 4.4−4.3 (4H, m, O−CH_2CH_2), 5.69 (2H, s, C−*H*), 7.20−7.48 (16H, m, Ar−*H*), 7.91 (4H, dd, J = 7.26, 1.31 Hz, SC(Ar−*H*)S).

Scheme 1. Synthesis of CTA_1 and CTA_3 (THF, Tetrahydrofuran; TEA, Triethylamine)



^{13}C NMR ($CDCl_3$, 298 K, 100.59 MHz,): δ (ppm from TMS); 58.70 (*C*H), 63.41 (O-*C*H_2), 126.99, 128.39, 128.42, 128.97, 129.01, 132.82, 132.87, 143.84 (*C*H of Ar), 168.60 (*C*═O), 225.70 (*C*S_2).

Anal. Calcd for $C_{32}H_{26}O_4S_4$: C, 63.76; H, 4.35; S, 21.28. Found: C, 63.51; H, 4.52; S, 21.35.

FTIR (cm^{-1}): 1733 (C═O); 1605−1444 (aromatic skeleton area); 1221 (C═S); 1139 (C−O stretching); 574 (C−S stretching).

Melting point: 69−70 °C.

Typical Polymerization Procedures: Homopolymerizations. A stock solution of MMA (9.4 mol L^{-1}) as monomer, AIBN (7.52×10^{-3} mol L^{-1}) as initiator, CTA_{3a} (1.88×10^{-2} mol L^{-1}) as RAFT agent, and toluene (1.88 mol L^{-1}) as solvent was divided equally into five degassed test tubes sealed with rubber septas (suba seal). The solutions were deoxygenated by nitrogen for 5 min and subsequently transferred to an oil bath heated at 60 °C. The test tubes were removed at predetermined intervals and polymerizations stopped by placing test tubes in liquid nitrogen. Conversion was calculated gravimetrically, and purification was by precipitation into cold hexane followed by drying under vacuum to constant weight.

Block Extension Polymerizations. A stock solution of BMA (8.95 mol L^{-1}) as monomer, AIBN (7.16×10^{-3} mol L^{-1}) as initiator, a macroCTA comprised of a 21 600 g mol^{-1} poly(methyl methacrylate) (PMMA) synthesized using CTA_{3a} following standard conditions (1.79×10^{-2} mol L^{-1}) and toluene (1.79 mol L^{-1}) as solvent was divided equally into five degassed test tubes sealed with rubber septas. The solutions were deoxygenated by nitrogen for 5 min and subsequently transferred to an oil bath, heated at 60 °C. The test tubes were removed at predetermined intervals and polymerizations were stopped by placing test tubes in liquid nitrogen. Conversion and BMA block length was calculated by ^1H NMR.

Results and Discussions

Choice and Synthesis of Difunctional Chain Transfer Agents (CTAs). CTAs have the generic structure S═C(Z)S−R, with Z and R groups depending upon the monomer class to be polymerized. The Z group influences the stability of the thiocarbonyl thio radical intermediate and must be finely tuned to not only activate the addition to the S═C, but also allow rapid fragmentation of R from the intermediate radical formed. The R group must form a radical stable enough to favor rapid fragmentation from the dithioester radical intermediate, but also efficiently initiate polymerization. In previous work by our group, the synthesis of CTA_1 was detailed.[29] Due to the superior leaving and reinitiating ability of the methoxycarbonylphenyl R group by comparison to most R groups reported to date, CTA_1 was shown to effectively mediate the polymerization of methyl methacrylate, methyl acrylate, styrene and dimethyl acrylamide. The advantage of CTA_1 over CTAs of similar versatility such as cyanopropyldithiobenzoate is the ease of synthesis and potential for incorporation onto materials bearing hydroxyl functionality. Two analogues of CTA_1 (CTA_2 and CTA_3, see Figure 1) were synthesized for this study and the synthetic pathways are detailed in Scheme 1. The synthesis of CTA_2 has been previously reported by Gotthardt et al.,[30] although not to be used as a RAFT chain transfer agent; however, our modified method offers an improvement on the yield, and all starting materials are readily commercially available.

Synthetic routes to difunctional CTAs include nucleophilic substitution of bis(halo) compounds by di- or trithioester salts,[28] dithioester interchange reactions using suitable bis(thiol) compounds,[31,32] Markownikov addition across an electron dense diolefin precursor,[15] and the conversion of bis(carboxylic acid) precursors to bis(dithiobenzyl), using tetraphosphorus decasulfide and benzyl mercaptan.[16] Initially we attempted an alternative

Table 1. Glass Transition Temperature of the ABA Triblock Copolymers Investigated in This Study

sample[a]	PDI[b]	T_{g1} (°C)	T_{g2} (°C)
PMMA[c]	1.26	107	
PBA_{63}-*b*-$PMMA_{217}$-*b*-PBA_{63}	1.20	−48	105
PBA_{206}-*b*-$PMMA_{217}$-*b*-PBA_{206}	1.44	−48	105
$PBMA_{125}$-*b*-$PMMA_{217}$-*b*-$PBMA_{125}$	1.30	37	
$PBMA_{176}$-*b*-$PMMA_{217}$-*b*-$PBAM_{176}$	1.27	37	110

[a] PBA-*b*-PMMA-*b*-PBA: poly(butyl acrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl acrylate). PBMA-*b*-PMMA-*b*-PBMA: poly(butyl methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl methacrylate). PBA_x denotes a poly(butyl acrylate) block of *x* units of butyl acrylate. [b] Determined by size exclusion chromatography. [c] Synthesized via RAFT using CTA_{3a}, $M_n = 21\,700$ g mol^{-1}.

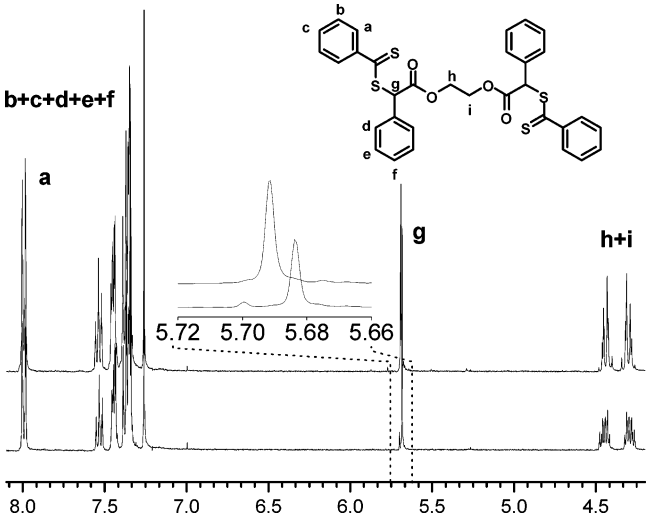


Figure 2. ^{1}H NMR spectra in $CDCl_3$ of CTA_{3a} and CTA_{3b} isolated after recrystallization.

approach—coupling 2 equiv of carboxylic acid functional CTA_2, to an ethylene glycol molecule. Various reactants, including thionyl chloride, oxalyl chloride, butyllithium, and *p*-toluenesulfonic acid, were unable to esterify CTA_2 due to the acidic nature of the tertiary hydrogen, which resulted in undesired reaction pathways. Note that such an approach has been successfully used for the production of multifunctional CTAs, when using a trithiocarbonate CTA with benzyl and carboxylic acid functionality.[33] To overcome this synthetic issues, a two-step synthesis to the production of CTA_3 was considered. In a first step, ethylene glycol was esterified with 2-chloro-2-phenylacetyl chloride in presence of triethylamine in anhydrous tetrahydrofuran. The diester obtained was further reacted with preformed dithiobenzoic acid, at 80 °C in THF for 24 h, to yield CTA_3. CTA_3 was purified by crystallization, and two compounds were isolated (CTA_{3a} and CTA_{3b}). NMR spectroscopy analyses revealed that both compounds had similar structure, and they only differed by the shift of the tertiary hydrogens (Figure 2). Furthermore, CTA_{3a} and CTA_{3b} were found to exhibit different melting points. These analyses suggest that both compound are isomers, but we could not further prove the structure by X-ray crystallography, due to the size of the molecule Nevertheless, it is remarkable that CTA_3 is obtained as a crystalline solid, as few examples of solid difunctional CTAs exist, despite their noticeable purity and stability. Indeed, recent reports have demonstrated that impurities not effectively removed by column chromatography and breakdown products formed over time may have a detrimental effect on polymerization.[34,35]

Polymerizations Using CTA_{3a} and CTA_{3b}. Kinetic studies were undertaken to test whether CTA_{3a} and CTA_{3b} possessed different reactivities in the polymerization of butyl acrylate. Linear first-order kinetics were observed throughout both polymerizations, indicating living behavior, with final conversions above 89% in both cases (Figure 3), and the rates of polymerization were identical for CTA_{3a} and CTA_{3b}. Molecular weights increased linearly with conversion for both CTAs and were close to theory (Figure 4). Multimodal molecular weight distributions were observed for conversions above 15% in polymerizations mediated by both CTAs, with PDI increasing with conversion, and these results are discussed below. As similar results were obtained for both CTAs, CTA_{3a} was used for the rest of this study.

Homopolymerizations of Acrylates and Methacrylates Mediated by CTA_{3a}. The syntheses of acrylate and methacrylate homopolymers in the presence of CTA_{3a} were followed kinetically. Figure 5 shows linear first-order kinetic plots for the polymerization of butyl acrylate, butyl methacrylate, and methyl methacrylate, as expected from previous results for the polymerization mediated by a monofunctional analogue of CTA_{3a}, CTA_1 (Figure 1).[29] Both methacrylate monomers polymerize at a similar rate, and Figure 6 shows that high conversions (>87%) are reached while keeping low molecular weight distributions (<1.25). Close inspection of the narrow molecular weight distributions of methyl methacrylate and butyl methacrylate (Figures 7 and 8, respectively) reveals a slight shoulder at low molecular weights. Such phenomena has been observed in other difunctional systems.[19] We attribute this to a small degree of termination of one and/or both active RAFT moieties during polymerization. Figure 6 demonstrates that lower than expected molecular weights are obtained, which could be due to competitive chain transfer reactions or termination.

GPC curves for both methacrylate monomers show a degree of low molecular weight tailing which is consistent with disproportionation reactions observed in the free radical polymerizations of the methyl acrylate class of monomers. Figure 5 shows that polymerization rates are significantly slower for

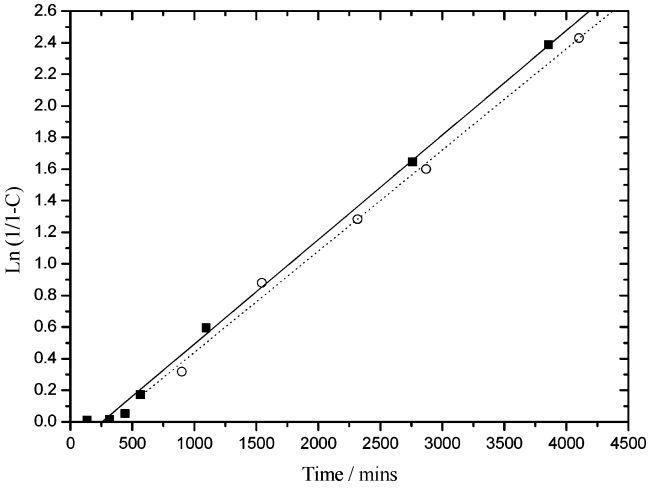


Figure 3. Pseudo-first-order rate plot for the solution polymerization of butyl acrylate using CTA_{3a}, (○) and CTA_{3b} (■) at 60 °C, with ratio of initiator to CTA = 0.4:1. (CTA; chain transfer agent).

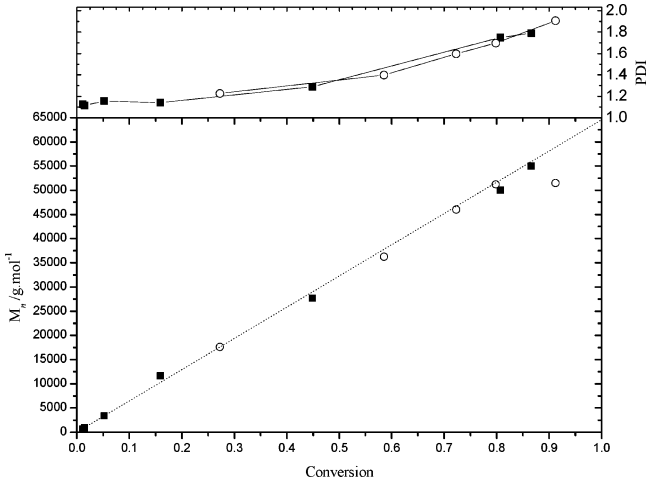


Figure 4. Molecular weight and PDI evolution with monomer conversion for the solution polymerization of butyl methacrylate using CTA_{3a} (○) and butyl acrylate using CTA_{3b} (■) at 60 °C, with ratio of initiator/CTA/monomer = 0.4:1:500. Key: (···) theorectical molecular weight. (CTA, chain transfer agent; PDI, polydispersity index).

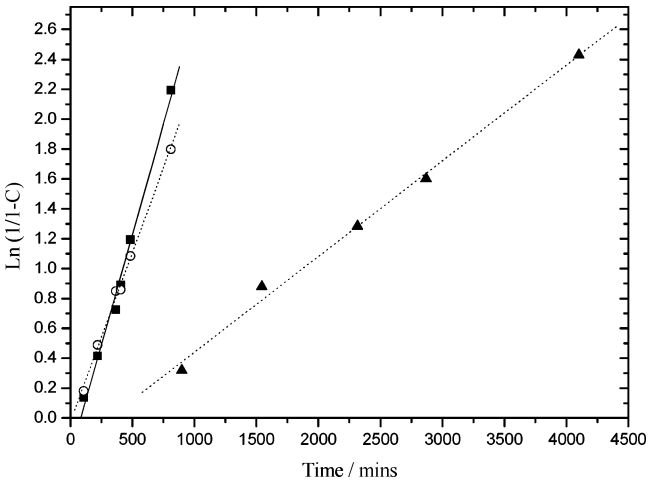


Figure 5. Pseudo-first-order rate plot for the solution polymerization of butyl methacrylate (■), methyl methacrylate (○) and butyl acrylate (▲), mediated by CTA_{3a} at 60 °C, with ratio of initiator/CTA/monomer = 0.4:1:500 (CTA, chain transfer agent).

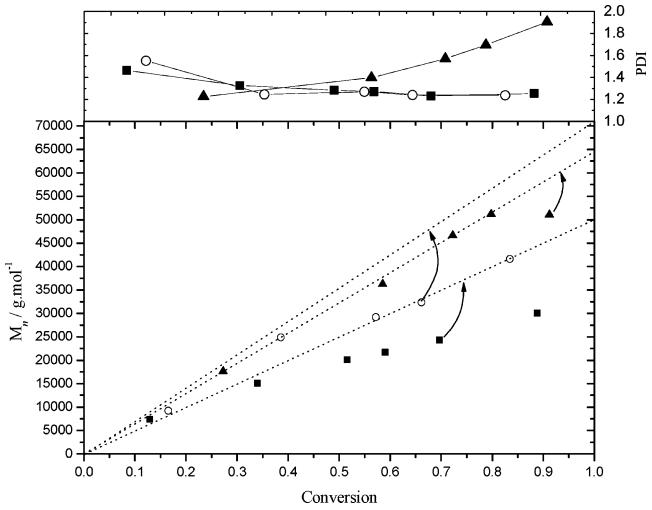


Figure 6. Molecular weight and PDI evolution with monomer conversion for the solution polymerization of butyl methacrylate (○), methyl methacrylate (■), and butyl acrylate (▲) with CTA_{3a} at 60 °C, with ratio of initiator/CTA/monomer = 0.4:1:500. Key: (•••) theoretical molecular weight (CTA, chain transfer agent; PDI, polydispersity index).

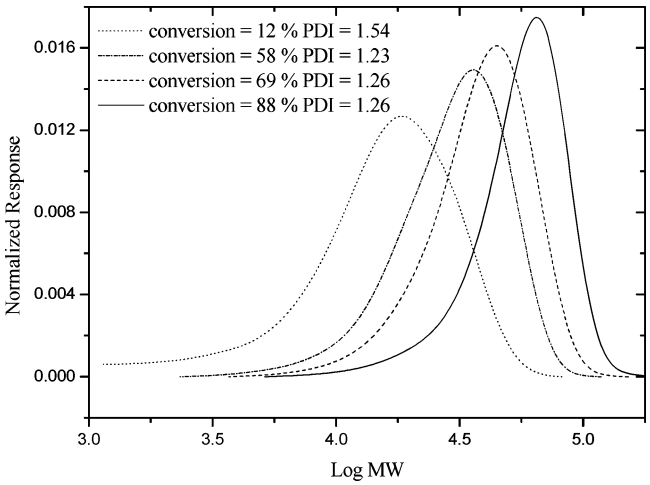


Figure 7. Gel permeation chromatography chromatograms showing the evolution of molecule weight with conversion for the solution polymerization of methyl methacrylate in toluene at 60 °C using CTA_{3a}, with ratio of initiator/CTA/monomer = 0.4:1:500 (CTA, chain transfer agent).

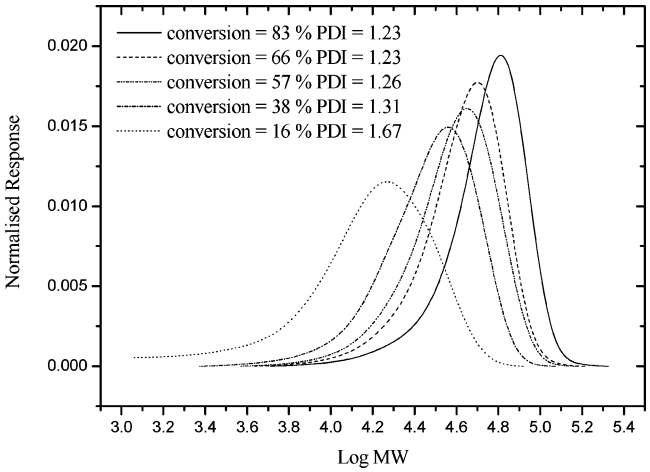


Figure 8. Gel permeation chromatography chromatograms showing the evolution of molecule weight with conversion for the solution polymerization of butyl methacrylate in toluene at 60 °C using CTA_{3a}, with ratio of initiator/CTA/monomer = 0.4:1:500 (CTA, chain transfer agent).

butyl acrylate when compared to butyl methacrylate and methyl methacrylate. Traditional free radical polymerization of acrylates is typically faster than methacrylates, due to the faster propagation rates of the secondary acrylate radical, compared to the bulkier tertiary methacrylate radical. However, the situation is reversed in RAFT mediated polymerization due to slower fragmentation of the acrylate radical, when the thiocarbonylthio radical intermediate is stabilized by a strongly electron donating Z group such as a phenyl; although the rate of propagation of acrylate radicals remains unchanged, the overall rate of polymerization is retarded.[8,9] An inhibition period of $\sim$ 400 min is seen in the polymerization of butyl acrylate, as observed previously in acrylate polymerizations mediated by RAFT.[36] As observed in the initial kinetic study comparing CTA_{3a} and CTA_{3b}, complex molecular weight distributions are observed for the polymerization of butyl acrylate (Figure 9). These results are unexpected given the unimodal molecular weight distributions achieved when polymerizing acrylate with CTA_1[29]

Upon inspection of the molecular weight distributions illustrated in Figure 9, we notice three distinctive peaks. The occurrence of a shoulder at high molecular weights, increasing with conversion, is caused by chain branching during the RAFT polymerization of acrylate monomers and has been discussed in details by a recent publication by Postma et al.[37] Previous work by Ahmad et al. also identified chain branching during conventional free radical polymerization of butyl acrylate.[38] There are multiple pathways for chain branching in acrylate polymerizations, and branches are classed as either long or short. Short chain branches are thought to originate from intramolecular chain backbiting, followed by continued propagation from the newly formed radical. Long chain branches are considered to be a consequence of intermolecular radical transfer, and also by β-scission following intramolecular backbiting, which introduces a macromonomer into the system. Chain branching clearly has interesting consequences for a system with multiple RAFT functionality and a large variety of macromolecular species clearly exist, as shown by the broad molecular weight distributions observed at high conversion (Figure 9). The two peaks present at lower molecular weight can be attributed to the difunctional (XPX, where P is the polymeric chains and X the thiocarbonyl thio end group) and monofunctional polymeric chains (PX, formed via termination

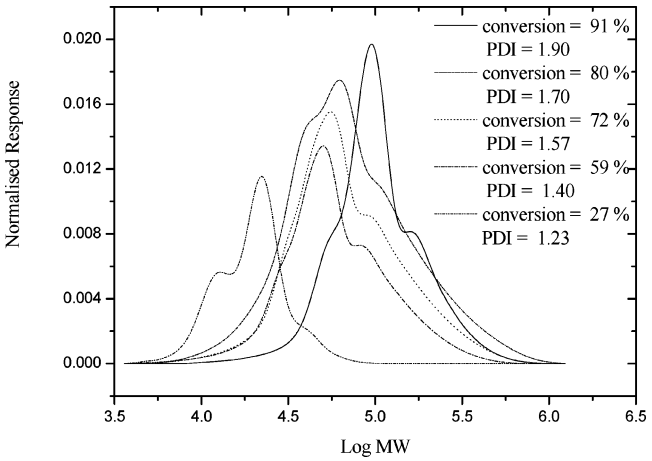


Figure 9. Gel permeation chromatography chromatograms showing the evolution of molecular weight with conversion for the solution polymerization of butyl acrylate in toluene at 60 °C using CTA_{3a}, with ratio of initiator/CTA/monomer = 0.4:1:500 (CTA, chain transfer agent).

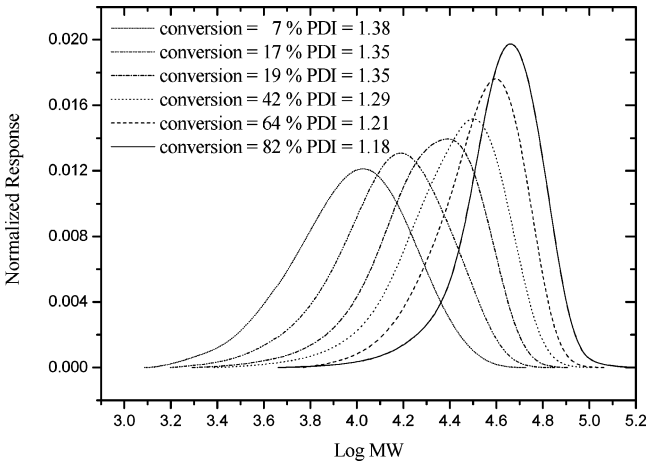


Figure 10. Gel permeation chromatography chromatograms showing the evolution of molecule weight with conversion for the solution polymerization of butyl methacrylate in toluene at 60 °C using CTA_{3a}, with ratio of initiator/CTA/monomer = 0.2:1:500 (CTA, chain transfer agent).

of one end of the XPX species). Both species remain living during polymerization (Figure 9 shows that the molecular weight distributions shift toward high molecular weights with increasing conversion), and the higher molecular weight of XPX by comparison to PX is explained by a higher chain transfer constant (twice that of PX), meaning that the monomers incorporate twice as fast to the difunctional than to the monofunctional polymeric chain. Similar observations were recently made by Goh et al. in their theoretical study of the RAFT polymerization of styrene mediated by a difunctional CTA.[20] Finally, slow initial fragmentation of oligomers from the stabilized intermediate may also explain the broader and multimodal molecular weight distributions seen in Figure 9 for butyl acrylate in the early stages of polymerization. Indeed, initial fragmentation of the R group may occur at different rates on each side due to one side overcoming the inhibition period significantly earlier that the other.

It is noteworthy that similar side reactions must occur during the polymerization of methacrylate monomers, but the resulting polymeric species are not easily observable by GPC, due to broader PDI and the masking of multimodal peaks by the low molecular weight tailing caused by the termination by disproportionation reactions.

Polymerizations Using CTA_{3a}. Variation of Initiator Concentration. In RAFT polymerization, lowering the concentration of initiator with respect to CTA decreases molecular weight distributions and increases reaction time. Indeed, a lower radical concentration decreases the probability of termination reactions, but also decreases the overall rate of polymerization, due to lowering of radical concentration. Therefore, effective block extension experiments of homopolymers, require products which still retain a high degree of functionality. In order to test the influence of the ratio initiator:CTA, experiments were performed on butyl methacrylate with ratios of 0.4:1 and 0.2:1. Little change was observed in the rate of polymerization, with both systems nearly identical as shown in Figure 11. For both polymerizations, molecular weights increased in a linear fashion with conversion and were close to theoretical (Figure 12). As mentioned previously, a shoulder was observed at low molecular weights for both initiator concentrations (Figures 8 and 10) at low conversion, but narrow molecular weight distributions were obtained when increasing conversion for both initiator concentrations, The only observable difference occurs, at low conversions (below 20%). Broader molecular weight distributions were

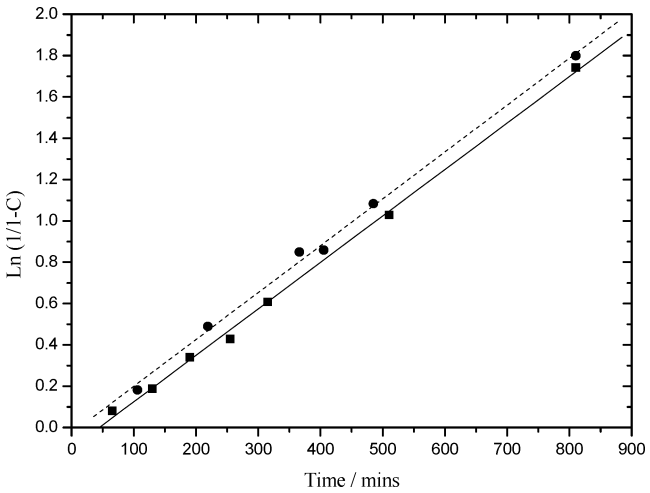


Figure 11. Pseudo-first-order rate plot for the solution polymerization of butyl methacrylate mediated by CTA_{3a} at 60 °C, with varying ratios of initiator/CTA/monomer: (■) 0.2:1:500; (●) 0.4:1:500 (CTA, chain transfer agent).

observed for an initiator:CTA ratio of 0.4:1 (PDI > 1.5 in Figure 8), whereas for initiator:CTA ratios of 0.2:1, narrower molecular weight distributions were obtained (Figure 10). Also, at final conversions, a lower AIBN concentration results in a PDI of 1.18, whereas for the higher concentration, a PDI of 1.23 is obtained. It is clear that in the present system the variation in initiator concentration is not sufficient to induce a significant change in the polymerization kinetics.

Block Extension Polymerizations. Block extension experiments in RAFT mediated polymerization occur when the first block from the macroCTA fragments in preference to all other possible leaving groups. For this to happen, the second monomer to be polymerized must be of similar or greater reactivity than the first. This pushes the equilibrium toward fragmentation of the first block, introducing homopolymers with radically active chain ends into the system.[12] For the block extension of PMMA, methacrylate and acrylate derivatives were considered suitable monomers. Interestingly, although a group generating a single unit methyl methacrylate radical does not make a good R group for a CTA because it is slow to fragment,[39] we found that PMMA seems to be an efficient leaving and reinitiating group. A macroCTA consisting of PMMA was thus synthesized from

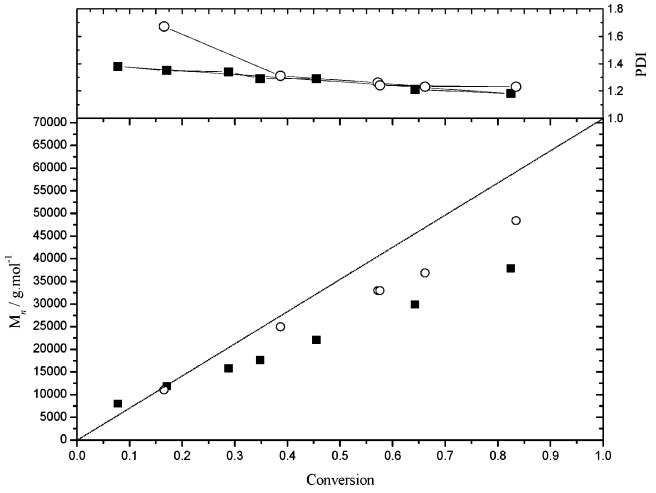


Figure 12. Molecular weight and PDI evolution with monomer conversion for the solution polymerization of butyl methacrylate mediated by CTA_{3a} at 60 °C, with varying ratios of initiator/CTA/monomer: (■) 0.2:1:500; (○) 0.4:1:500. Key: (···) theorectical molecular weight (CTA, chain transfer agent; PDI, polydispersity index).

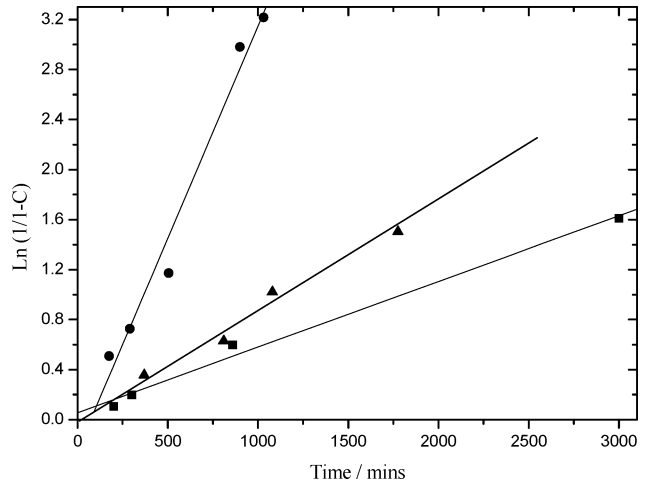


Figure 13. Pseudo-first-order rate plot for the block extension polymerizations using $PMMA_{217}$ macroCTA (synthesized from CTA_{3a} using initiator/CTA/monomer ratio = 0.4:1:500, conversion = 50%) with (●) butyl acrylate (initiator/CTA/monomer = (0.4:1:500), (▲) butyl methacrylate (initiator/CTA/monomer = 0.25:1:500), and (■) butyl acrylate (initiator/CTA/monomer = 0.25:1:500), at 60 °C in toluene (PMMA, poly(methyl methacrylate); CTA, chain transfer agent).

CTA_{3a} (M_n = 21 700 g mol^{-1}, PDI = 1.26) and further used to mediate the polymerization of butyl methacrylate and butyl acrylate.

Figures 13 and 14 show the linear first-order kinetics and the variation of molecular weight and polydispersity with conversion for the block extension polymerizations of butyl acrylate and butyl methacrylate, respectively, suggesting that both systems are leaving. The block extension with butyl methacrylate is well controlled, as demonstrated by the evolution of unimodal molecular weight distributions (Figure 15) and low polydispersities obtained at high conversion. As seen above, a consequence of multiple RAFT functionality is that termination on a single functionality during polymerization of the first block still produces a living polymer. Block extension of such species would lead to the formation of AB block copolymers and such compounds would be of lower molecular weight than the ABA block copolymers. However, AB blocks cannot be conclusively distinguished from the ABA blocks in the GPC traces (Figures 15−17), potentially masked by the tailing of the distribution

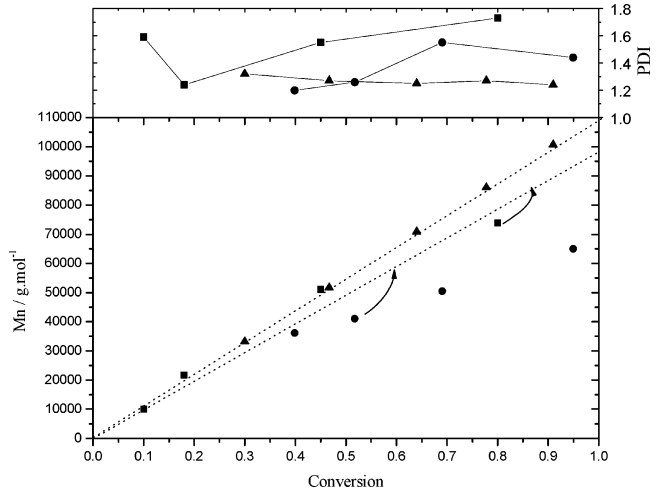


Figure 14. Molecular weight and PDI evolution with monomer conversion for block extension polymerizations using $PMMA_{217}$ macroCTA (synthesized from CTA_{3a} using initiator/CTA/monomer ratio = 0.4:1:500, conversion = 50%) with (●) butyl acrylate (initiator/CTA/monomer = (0.4:1:500), (▲) butyl methacrylate (initiator/CTA/monomer = 0.25:1:500), and (■) butyl acrylate (initiator/CTA/monomer = 0.25:1:500), at 60 °C in toluene. Key: (···) theorectical molecular weight (PMMA, poly(methyl methacrylate); CTA, chain transfer agent; PDI, polydisperisty index).

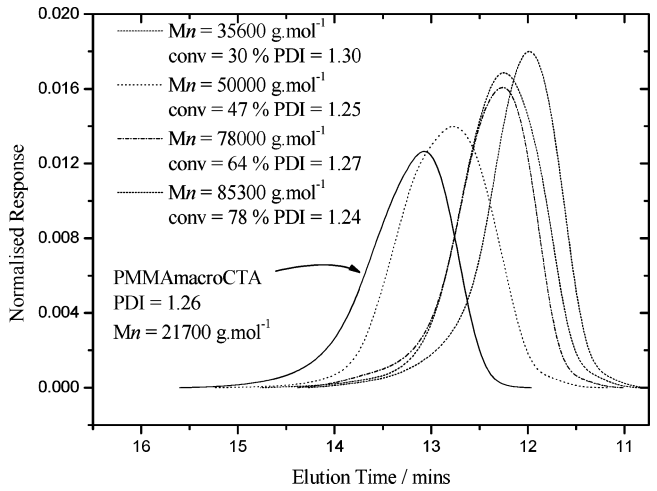


Figure 15. Gel permeation chromatography chromatograms showing the evolution of molecular weight with conversion for the block extension polymerization of butyl methacrylate using $PMMA_{217}$ macroCTA (synthesized from CTA_{3a} using initiator/CTA/monomer ratio = 0.4:1:500, conversion = 50%), with AIBN/CTA/monomer = 0.25:1:500 in toluene at 60 °C. Molecular weights for poly(butyl methacrylate) blocks calculated by ^{1}H NMR (PMMA, poly(methyl methacrylate); CTA, chain transfer agent; PDI, polydispersity index).

from termination by disproportionation when polymerizing methacrylate derivatives (Figures 15 and 16). However, the polymerization of butyl acrylate (Figure 17) also shows low molecular weight tailing, which is uncharacteristic for such monomers, and may indicate the presence of AB block copolymers.

As expected, the data showed that the block extension polymerization of butyl acrylate was slower than that of its methacrylate equivalent at the same ratio AIBN:macroCTA. First-order kinetics were also observed for the polymerization of butyl acrylate using different initiator:macroCTA ratios. Figures 16 shows the evolution of molecular weight distribution with initiator:macroCTA ratios of 0.4:1. As the homopolymerizations, bimodal molecular weight distributions were observed for conversions higher than 40%, leading to experimental

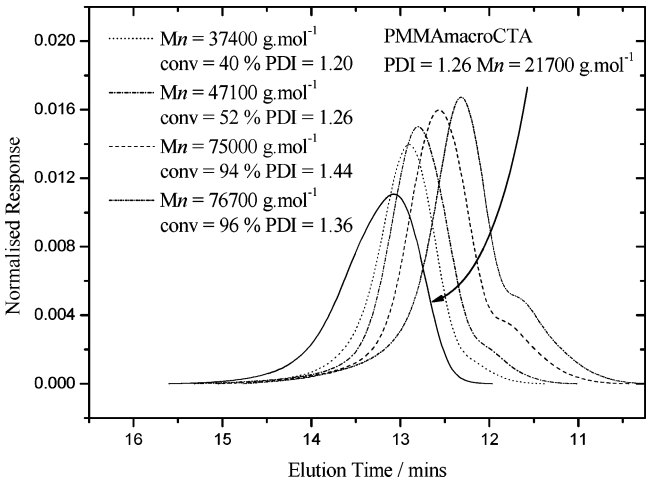


Figure 16. Gel permeation chromatography chromatograms showing the evolution of molecular weight with conversion for the block extension polymerization of butyl acrylate using $PMMA_{217}$ macroCTA (synthesized from CTA_{3a} using initiator/CTA/monomer ratio = 0.4:1:500, conversion = 50%), with AIBN/CTA/monomer = 0.4:1:500 in toluene at 60 °C. Molecular weights for poly(butyl acrylate) blocks calculated by ^{1}H NMR (PMMA, poly(methyl methacrylate); CTA, chain transfer agent; PDI, polydispersity index).

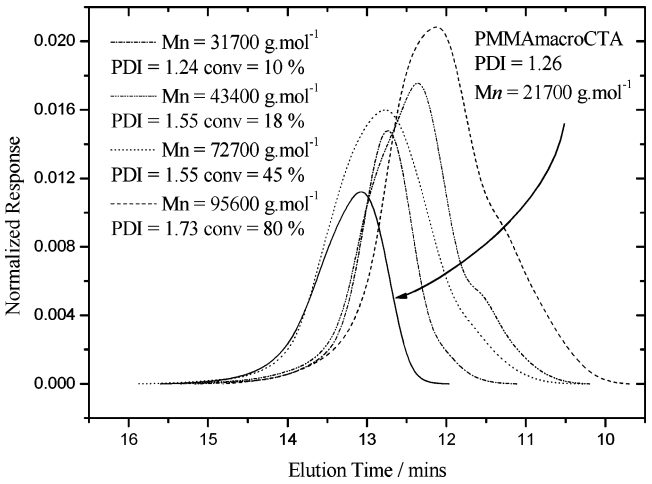


Figure 17. Gel permeation chromatography chromatograms showing the evolution of molecular weight with conversion for the block extension polymerization of butyl acrylate using $PMMA_{217}$ macroCTA (synthesized from CTA_{3a} using initiator/CTA/monomer ratio = 0.4:1:500, conversion = 50%), with AIBN/CTA/monomer = 0.25:1:500 in toluene at 60 °C. Molecular weights for poly(butyl acrylate) blocks calculated by ^{1}H NMR (PMMA, poly(methyl methacrylate); CTA, chain transfer agent; PDI, polydispersity index).

molecular weight deviating from theoretical molecular weight. Note that in this case, uneven initiation from both sides of the CTA is unlikely, as the PMMA block is more likely to fragment from the inetremdiate RAFT adduct radical.Indeed, no detectible inhibition period was observed in the block extension polymerizations of butyl acrylate. In order to minimize side reactions of chain branching and termination, a polymerization using a lower ratio of AIBN:macroCTA (0.25:1) was undertaken. The lower radical concentration led to significantly slower polymerization time, but bimodal molecular weight distributions were still observed at high conversions (Figure 17). Therefore, in order to minimize high molecular weight shoulders when chain extending with butyl acryate, it is necessary to quench reactions at moderate conversions. Figure 16 shows that a low polydispersity (1.26) with only a small fraction of high molecular weight shoulder present and an outer block size of 25 400 g mol^{-1} can be achieved if polymerization is allowed to reach 52% conversion. This is consistent with the observations made by Goh et al. in the polymerization of styrene.[20]

Thermal Analyses. The synthesized triblock copolymers were subjected to thermal analysis using modulated differential scanning calorimetry (mDSC).[40,41] mDSC differs from conventional DSC as the linear heating ramp is modulated sinusoidally, which produces thermal profiles of greater resolution, precision, and sensitivity. The direct measurement of heat capacity at the glass transition is also possible, which is independent of enthalpic effects due to relaxation events, and multiple glass transitions due to different phases can be resolved when occurring over similar temperature ranges. The thermal profiles of a low and high molecular weight poly(butyl acrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl acrylate) (PBA-*b*-PMMA-*b*-PBA) triblock copolymer, with PBA of varying molecular weights were compared. Multiple thermal transitions can be seen for both samples, however a well-defined endothermic transition with a corresponding change in the heat capacity of the material at −48 °C is seen for the high molecular weight material. This is in the range of reported glass transition temperatures for poly(butyl acrylate).[42] The identification in both samples of a glass transition temperature for PMMA at 105 °C, which is consistent with reported values for atactic PMMA,[42] indicates the immiscibility of the two blocks. Some samples also showed small thermal events between −48 and +105 °C, indicating phases of mixed composition coexisting with the phase separated material.

Poly(butyl methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(butyl methacrylate) (PBMA-*b*-PMMA-*b*-PBMA) samples with PBMA of varying molecular weight were also subjected to DSC analyses. For samples with PBMA of lower molecular weight, an endothermic shift in the heat flow was observed at 37 °C corresponding to the expected glass transition temperature of PBMA. Subzero endotherms were also evident in some materials, believed to be a result of side-chain relaxations. Interestingly, there was no sign of a transition above 100 °C, potentially because of the size of the blocks, as chain length is known to influence polymer chain miscibility in block copolymers[43] and in blends.[44] As the molecular weight of the PBMA increases, a small transition appears at approximately 110 °C, suggesting that phase separation does occur and is indeed influenced by the molecular weight of the PBMA.

Conclusions

We have synthesized a new chain transfer agent for RAFT polymerization (CTA_3) and demonstrated its usefulness to control the synthesis of telechelic homopolymers and ABA triblock copolymers from acrylate and methacrylate derivatives. We have shown that the use of a difunctional chain transfer agents allows us to keep a high concentration of living chains, as chains remain active at at least one end, despite termination reactions. This is however at the expense of the molecular weight distribution, which broadens with increasing conversion. In the case of polymerization of acrylate monomers, chain branching events also contribute to the broadening of the molecular weight distribution. Nevertheless, good control over molecular weight and PDI below 1.2 for conversions up to 90% can be achieved for the polymerization of methyl methacrylate and butyl methacrylate, and similar results were obtained for butyl acrylate, although at lower conversions. Block extension experiments were undertaken using a telechelic PMMA as macro-RAFT agent mediating the RAFT polymerization of butyl methacrylate and butyl acrylate. Well-defined triblock copolymers were obtained from the methacrylate derivative, while

chain branching and termination events led to less well-defined block copolymers in the case of the acrylate derivative. Thermal analysis showed that phase separation occurs between blocks of triblock copolymers with the outer block consisting of butyl acrylate. The same phenomenon was only observed in the case of block copolymers where the outer blocks consist of butyl methacrylate of higher molecular weights.

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Supporting Information Available: Tables summarizing the data for all the polymerization reactions reported in this study and figures showing DSC graphs. This material is available free of charge via the Internet at http://pubs.acs.org.

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