Versatile Chain Transfer Agents for Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization to Synthesize Functional Polymeric Architectures

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ABSTRACT: We report the syntheses and uses of versatile chain transfer agents (CTAs) that produce well-controlled macromolecular architectures with specific chain-end functionalities, via reversible addition fragmentation chain transfer (RAFT) polymerization). Examples of architectures are given, including amphiphilic copolymers and block copolymers incorporating a biodegradable block. These CTAs are also used for the grafting of poly(styrene), poly(methyl methacrylate) and poly(methyl acrylate) from cotton.

Introduction

In recent years, polymer chemistry has moved away from the bulk synthesis of high molecular weight chemicals and is now targeting the synthesis of specialty compounds via the introduction of specific functionalities on polymer backbones or chain ends. Among the various polymerization processes that have been reported to achieve such products, living radical polymerization appears to be one of the most promising for high scale applications. The synthesis of functional polymers with predictable molecular weight and narrow molecular weight distribution can easily be achieved, under conditions similar to those of free radical polymerization.[1] To date, the most important processes are nitroxide mediated polymerization (NMP), transition metal mediated living radical polymerization, reversible addition fragmentation chain transfer (RAFT) polymerization, and macromolecular architecture design by interchange of xanthates (MADIX). NMP is based on the use of a stable nitroxide radical and, to date, is limited to few monomers (styrene derivatives, acrylates, *N*,*N*-dimethylacrylamide, acrylonitrile, dienes, and methacrylates as comonomers).[2] Transition metal mediated living radical polymerization[3,4] has been proven to efficiently polymerize a wider range of monomers, including styrene derivatives, (meth)acrylates, acrylonitrile, 4-vinylpyridine, and (meth)acrylamide, among other more specific monomers, in a variety of polymerization conditions.[5] An additional feature of this technique is the possibility to design polymeric chains with chain-end functionalities. Indeed, Haddleton et al. first reported the use of molecules bearing a hydroxyl group that can be transformed into initiators for copper mediated living radical polymerization.[6,7] This leads to the easy synthesis of block copolymers including blocks that cannot be formed through free radical polymerization, polymers showing specific functionalities at their chain-ends, star polymers, etc. The system is however limited by the use of a catalyst: pollution of the final product by the metal and/or ligand present in the catalyst system is often a major drawback for large-scale processes.

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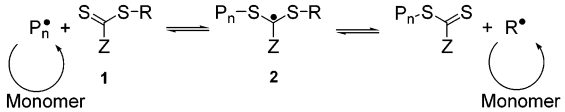
Scheme 1. Generally Accepted Reaction Scheme for Reversible Addition Fragmentation Chain Transfer (RAFT) and Macromolecular Architecture Design via Interchange of Xanthate (MADIX) Polymerizations



RAFT[8,9] and MADIX[10,11] seem so far the two most promising of the living radical polymerization systems. A wide range of monomers already successfully polymerized, ease of scaleup of the reaction and high tolerance to functional groups makes them the most suitable techniques to obtain well-defined polymeric architectures. RAFT and MADIX are based on a similar process which consist in the simple introduction of a small amount of dithioester of the generic formula **1**, Scheme 1, (chain transfer agent, CTA) in a classic free radical system (monomer + initiator). The transfer of the CTA between growing radical chains (Scheme 1), present at very low concentration, and dormant polymer chains, present at higher concentration (3 or 4 orders of magnitude), will regulate the growth of the molecular weight, and limit the termination reactions.

One of the key steps of the process is the design of the initial CTA, as the choice of R and Z groups depends on the monomer to be polymerized. Indeed, as the Z group influences strongly the stability of the dithioester radical intermediate, strong stabilizing groups will favor the formation of the radical intermediate, and therefore enhance the reactivity of the S=C bond toward radical addition. However, the stability of the intermediate needs to be finely tuned, to favor its fragmentation which will free the reinitiating group (R).[12−17] The R group must be chosen as a good leaving group by comparison to the growing polymeric chain and a good reinitiating species toward the monomer used. To a lesser extent than the Z group, R will also participate in the stabilization of the radical intermediate. Parameters such as the stability of the generated radical, steric bulk, and polarity need to be considered for the choice of the R group. Previous studies have shown the importance of this group when polymerizing monomers with a high rate of propagation.[18−20] To date, cumyl and cyanoisopropyl groups seem to be the most efficient for the reinitiation step.[21] Another important effect of the

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R group is its use to either introduce chain-end functionalities into polymers or design various polymeric architectures. This was initially achieved by the CSIRO group, through the use of a RAFT agent derived from the free radical initiator 4,4′-azobis(4-cyanopentanoic acid). This CTA shows a carboxylic acid function that can easily be reacted with OH groups to form macro-CTAs, or functional chain transfer agents. Applications include the use of poly(ethylene glycol)[22] or Kraton.[23] The drawback of such CTAs is their very demanding synthetic process which often requires three or four reaction steps.

In this work, we report the utilization of CTAs with improved structures (R group with better leaving and reinitiation ability) to control the living radical polymerization of the key monomers that are styrene, methyl methacrylate, methyl acrylate, and dimethyl acrylamide. The synthesis of the CTA is simplified to a one-step reaction and offers the opportunity to introduce any molecules bearing a hydroxyl group at the end of the polymeric chain, as has been previously demonstrated by transition metal mediated living radical polymerization. The technique reported here, however, offers supplementary advantages over transition metal mediated LRP: (a) there is no potential pollution of the end product by residual catalyst, (b) a wider range of monomers is available, and (c) the process has great potential for scaling up reactions. Examples of syntheses of block copolymers and cotton graft polymers are given.

Experimental Section

General Data. Materials. All solvents, monomers, and other reagents were purchased from Aldrich at the highest purity available and used as received unless otherwise stated. Methyl acrylate (MA, 99%), Styrene (99+%), methyl methacrylate (MMA, 99%), and dimethyl acrylamide (DMA, 99%) were filtered before utilization through a basic alumina (Brockmann I) column, to remove the radical inhibitor. Tetrahydrofuran (THF, Riedel-deHaën, HPLC grade), triethylamine (Lancaster, 99%) and *N*,*N*-dimethylformamide (99.9+%, HPLC grade) (DMF) were dried over molecular sieves 4 Å. 2,2-Azobis(isobutyronitrile) (AIBN, 99%) was recrystallized twice from ethanol. Bromobenzene (99.9%), carbon disulfide (99.9+%, HPLC grade), methyl-α-bromophenylacetate (97%), sodium methanethiolate (25 wt % in methanol), 2-chloro-2-phenylacetyl chloride (CPAC, 90%), L-lactic acid (85+% in water), phenylmagnesium chloride (2 M solution in THF), and poly(ethylene glycol) methyl ester (MeOPEG) ($M_n = 5000$ g mol^{-1}) were used as received. Diethyl ether, ethyl acetate and *n*-hexane were purchased from Riedel-deHaën (AR grade) Air- and moisture-sensitive compounds were manipulated using standard Schlenk techniques under a nitrogen atmosphere. Magnesium turning (AnalaR) was purchased from BDH. All cotton fabrics (scoured and bleached, fluorescent brightener-free) were supplied from Whaleys Bradford Ltds. (WBL) and dried overnight in a vacuum oven at 45 °C before use.

Size Exclusion Chromatography. 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) with a differential refractive index detector (Shodex, RI-101). Unless otherwise stated, tetrahydrofuran was used as an eluent at a flow rate of 1 mL min^{-1}, and toluene was used as a flow rate marker. Both poly(styrene) in the range 7 500 000−580 and poly(methyl methacrylate) in the range of 1 944 000−1020 were used for calibrations.

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

Gas Chromatography—Mass Spectrometry (GC—MS). GC chromatograms were recorded by Varian Star 3400 CX. The injection temperature was set at 250 °C. The GC column is Varian CP−Sil 8 CB low bleed/MS (5% phenylpolysiloxane/95% methylpolysiloxane), 30 m × 0.25 mm with 0.25 μm diameter and the temperature was controlled by the program from 50 to 250 °C with a rate of 10 °C/min. MS patterns were recorded by Varian Saturn 3 system (ion trap, electron ionization mode). The MS detector temperature was set at 250 °C.

FTIR and Raman Spectroscopy. FTIR spectra were recorded using a Perkin-Elmer Spectrum One infrared Fourier transform spectrometer. The contact sampler is a horizontal internal reflectance accessory (ATR) for most of samples, unless otherwise stated, with a resolution of 4.00 cm^{-1}. Scan speed was set at 0.5 cm/s for one hundred scans for ATR. The scan speed of the KBr disk technique was set at 0.2 cm/s for 16 scans

Raman spectra were monitored using a Perkin-Elmer system 2000 NIR FT Raman. The laser source is Nd:YAG with diode pumping. The scan speed was 0.2 cm/s for 16 scans.

Syntheses of Reversible Addition Fragmentation Chain-Transfer Agents. Synthesis of *S*-Methoxycarbonylphenylmethyl Dithiobenzoate (MCPDB, See Scheme 3, CTA$_1$). Phenylmagnesium bromide was synthesized from bromobenzene (3.14 g, 20.0 mmol) and magnesium turning (0.50 g, 21.0 mmol) in dry THF. The solution was heated to 40 °C and carbon disulfide (1.53 g, 20.0 mmol) was added dropwise over approximately 15 min, to produce a dark brown solution. Methyl α-bromophenylacetate (5.00 g, 21.8 mmol) was then added into the solution. The reaction temperature was raised to 80 °C and maintained for 24 h. Ice water was then added to the solution, before extracting the organic products with diethyl ether three times. The combined organic extracts were rinsed with water and dried over anhydrous magnesium sulfate. After solvent removal, column chromatography was undertaken (diethyl ether:*n*-hexane (1:9)) to afford an orange-red oil (52.4%).

^{1}H NMR, δ (ppm from TMS): 3.70 (3H, s, O−C*H*$_3$, 5.65 (1H, s, −S(Ph)C*H*−CO$_2$Me), 7.20−7.48 (8H, m, Ar−*H*), 7.91 (2H, dd, $J = 7.26$, 1.31 Hz, −SC(Ar−*H*)S−).

^{13}C NMR, δ (ppm from TMS): 53.04 (*C*H) 58.70 (O−C*H*$_3$) 126.92, 127.40, 128.81, 128.92, 129.30, 132.81, 133.21, 143.84 (*C*H of Ar), 166.95 (*C*═O), 226.72 (*C*S$_2$).

FTIR (cm^{-1}): 1736 (C═O); 1605−1444 (aromatic skeleton area); 1225 (C═S); 1151 (C−O stretching); 577 (C−S stretching).

MS (EI): $m/z = 302$ (M$^+$), 269, 193, 149, 121, 77.

Anal. Calcd: C, 63.55;H, 4.67; S, 21.21. Found: C, 63.61; H, 4.76; S, 21.29.

Synthesis of *S*-Methoxycarbonylphenylmethyl Methyltrithiocarbonate (MCPMT, See Scheme 3, CTA$_2$). Carbon disulfide (5.51 g, 72.5 mmol) in diethyl ether was added dropwise to a suspension of sodium methanethiolate (4.20 mL, 65.9 mmol) in diethyl ether (200 mL) at ambient temperature over 30 min. After 2 h, the solvent was removed and the residue extracted three times with ethyl acetate to afford sodium methyl trithiocarbonate (81.0%). The crude product was used without purification.

Methyl α-bromophenylacetate (2.04 g, 8.90 mmol) was added to the freshly prepared trithiocarbonate salt (1.30 g, 8.90 mmol) in 20 mL of ethyl acetate at room temperature. The solution was stirred for 4 h and quenched with saturated sodium chloride (25 mL). The aqueous layer was extracted with ethyl acetate (3 × 50 mL) and the combined organic layer washed with 10% HCl (50 mL), dried over anhydrous magnesium sulfate and filtered. After solvent removal, the residue was separated by column chromatography using 0.1% ethyl acetate in toluene affording a yellow, oily product (70.6%).

^{1}H NMR, δ (ppm from TMS): 2.66 (3H, s, S−C*H*$_3$), 3.70 (3H, s, O−C*H*$_3$), 5.79 (1H, s, −S(Ph)C*H*−CO$_2$Me), 7.20−7.44 (5H, m, Ar−*H*).

^{13}C NMR, δ (ppm from TMS): 20.40 (S−*C*H$_3$), 53.04 (*C*H), 58.70 (O−C*H*$_3$), 96.10, 128.80, 129.10, 129.20, 132.90, (*C*H of Ar), 166.95 (*C*═O), 222.30 (*C*S$_2$).

FTIR (cm^{-1}): 1732 (C═O); 1607−1452 (aromatic skeleton area); 1208 (C═S); 1158 (C−O stretching); 562 (C−S stretching).

MS (EI): m/z = 272 (M^+), 240, 149, 121, 97, 77.

Anal. Calcd: C, 48.50; H, 4.44; S, 35.31. C, 48.62; H, 4.53; S. 35.46.

Functionalization on Cotton Surface. Determination of the Degree of Substitution (DS). The degree of substitution on cotton substrate was calculated gravimetrically via the equation below.[24]

$$DS = 3\{(OH)_{substituted}/(OH)_{initial}\}$$

where $(OH)_{substituted}$ is the number of moles of the substituted groups on the cotton fabric and $(OH)_{initial}$ is the number of moles of hydroxyl groups on the cotton fabric (determined by weighing the cotton substrate and considering the molecular weight of a repeating unit, bearing three hydroxyl groups[24]).

Acylation of Cotton with 2-Chloro-2-phenylacetyl Chloride (CPAC). Cotton fabric (4.26 g) was suspended and stirred in a THF solution with triethylamine (0.75 mL, 72.4 mmol) at 60 °C. CPAC (5.00 g, 53.0 mmol) was added dropwise for 30 min. The reaction was left stirring for another 4 h, then cooled to room temperature. The light yellow fabric was washed with THF (3 × 20 mL) and rinsed thoroughly with deionized water. The treated cotton was oven-dried under vacuum to give the chlorophenylacetic acid cotton ester (cotton−CPA).

Degree of substitution (DS) = 0.53 (18%).

Preparation of Cotton—MCPDB. Phenylmagnesium chloride (2.25 mL, 4.50 mmol) was transferred in a dried two-neck-round-bottom flask. Carbon disulfide (0.27 mL, 4.50 mmol) was added dropwise to the round-bottom flask over 15 min and the solution temperature was then raised to 40 °C, forming a dark brown solution. The solution was transferred to another flask containing cotton−CPA (1.92 g). The reaction temperature was then increased to 80 °C and left for 24 h. The resulting fabric, of a characteristic orange color, was washed with THF (3 × 20 mL) and then rinsed thoroughly with deionized water. The treated cotton (cotton−MCPDB) was oven-dried under vacuum.

DS = 0.45 (15%).

Macrochain transfer agents (MacroCTAs). Synthesis of Poly(L-lactic acid) (PLLA).[25] L-Lactic acid (30.00 g, 284.0 mmols) and *p*-toluenesulfonic acid (0.106 g, 0.600 mmols) were mixed in a round-bottom flask connected to a reflux condenser with vacuum system. The solution was first dehydrated at 150 °C at atmospheric pressure for 2 h, then brought to a reduced pressure of 100 Torr for 1 h. Tin(II) chloride dihydrate (0.062 g, 0.280 mmols) was added and the temperature was slowly increased to 180 °C. The pressure of the system was reduced gradually to reach 10 Torr. An increase of viscosity of the system was observed, confirming the polycondensation. The product was left to cool, then dissolved in chloroform, and subsequently reprecipitated into an excess of cold diethyl ether. The resulting product (9.40 g, 46%) was filtered and dried under vacuum.

^{1}H NMR, δ (ppm from TMS): 1.50 (d, CH_3 of PLLA), 1.61 (d, CH_3 of lactacte unit), 4.40 (q, C*H* of PLLA), 5.20 (q, C*H* of lactate unit).

^{13}C NMR, δ (ppm from TMS): 15.66 (*C*H_3), 17.04 (*C*H_3), 66.27 (*C*H), 69.40 (*C*H), 169.64 (*C*═O).

FTIR (KBr disk, cm^{-1}): 1759 (C═O); 1466 (CH_3); 1091 (C−O−C).

M_n = 8300; PDI = 1.41 (SEC, MMA calibration).

Synthesis of Chlorophenylacetic Acid PLLA Ester. Poly(l-lactic acid) (PLLA) (9.40 g, 1.13 mmol) was placed in a three-necked round-bottom flask under nitrogen atmosphere. Dry THF (100 mL) and dry triethylamine (1.00 mL, 7.20 mmol) were transferred to the round-bottom flask. CPAC (0.472 g, 2.500 mmol) was added to the PLLA solution dropwise. The reaction was refluxed and left for 10 h before the solution was taken up in dichloromethane (200 mL) and rinsed with saturated sodium hydrogen carbonate (10 mL). The resultant organic solution was dried over anhydrous magnesium sulfate and the solvent was evaporated in vacuo to give the chlorophenylacetic acid PLLA ester (PLLA−CPA) (85.0%).

^{1}H NMR, δ (ppm from TMS): 1.50 (d, CH_3 of PLLA), 1.61 (d, CH_3 of lactacte unit), 4.40 (q, C*H* of PLLA), 5.20 (q, C*H* of lactate unit), 5.40 (1H, s, C*H*Cl(Ar), 7.38 (5H, m, Ar−*H*).

^{13}C NMR, δ (ppm from TMS): 15.66 (*C*H_3), 17.04 (*C*H_3), 66.27 (*C*H), 69.40 (*C*H), 72.26 (*C*H), 125.92, 126.88, 127.15, 128.64, 129.18, 132.63, (*C*H of Ar), 169.64 (*C*═O), 169.86 (*C*═O).

M_n = 7200; PDI = 1.44 (SEC, MMA calibration).

Synthesis of PLLA—MCPDB. Phenylmagnesium chloride (2 mL, 4 mmol) was stirred in a three-necked round-bottom flask contained THF (10 mL). Carbon disulfide (1.00 mL, 16.6 mmol) was then added dropwise to give a dark brown solution. This solution was added to a solution of PLLA−CPA (8.00 g, 1.11 mmol) in THF (100 mL) ,and the reaction was refluxed overnight. The orange-red product was also reprecipitated in 100 mL of cold diethyl ether (72.0%).

^{1}H NMR, δ (ppm from TMS): 1.50 (d, CH_3 of PLLA), 1.61 (d, CH_3 of lactate unit), 4.4 (q, C*H* of PLLA), 5.20 (q, C*H* of lactate unit), 5.31 (1H, s, −S(Ph)C*H*−CO_2Me), 7.22−7.45 (8H, m, Ar−*H*), 7.89 (2H, d, −SC(Ar−*H*)S−).

^{13}C NMR, δ (ppm from TMS): 15.66 (*C*H_3), 17.04 (*C*H_3), 66.27 (*C*H), 69.40 (*C*H), 72.26 (*C*H), 125.92, 126.88, 127.15, 128.64, 129.18, 132.63, 133.01, 143.47 (*C*H of Ar), 169.64 (*C*═O), 169.86 (*C*═O), 225.45 (CS_2).

FTIR (KBr disk, cm^{-1}): 1759 (C═O); 1637 (C═C);1467 (CH_3); 1090 (C−O−C).

Anal. Calcd: C, 62.06; H, 10.15; S, 0.94. Found: C, 62.21; H, 10.21; S, 1.11.

M_n = 6600; PDI = 1.50 (SEC, MMA calibration).

Synthesis of Chlorophenylacetic Acid [Poly(ethylene glycol) methyl ester] Ester (MeOPEG—CPA). Poly(ethylene glycol) methyl ester (MeOPEG) (9.04 g, 1.80 mmol), triethylamine (0.50 mL, 3.60 mmol), and CPAC (0.416 g, 2.200 mmol) were mixed in a round-bottom flask using dry THF (150 mL) as a solvent, and the solution was refluxed for 2 days at atmospheric pressure. The solvent was then removed, and dichloromethane (150 mL) was added. The resulting solution was washed with saturated sodium hydrogen carbonate, and the yellow organic phase was dried over anhydrous magnesium sulfate. The solvent was then removed in vacuo to give an ester of chlorophenylacetic acid with poly(ethylene glycol) methyl ester (MeOPEG−CPA). The product (93.0%) was reprecipitated in cold diethyl ether.

^{1}H NMR ($CDCl_3$, 298 K, 400 MHz), δ (ppm from TMS): 3.36 (s, O−CH_3), 3.60 (s, CH_2−CH_2−O), 5.33 (1H, s, C*H*Cl), 7.36 (5H, m, Ar−*H*).

^{13}C NMR δ (ppm from TMS); 70.91 (O−*C*H_3), 72.30 (O−*C*H_2), 69.40 (*C*H), 127.30, 127.76, 128.80, 129.11, 129.42, 133.21 (*C*H of Ar), 169.14 (*C*═O).

M_n = 7300; PDI = 1.11 (SEC, MMA calibration).

Synthesis of MeOPEG—MCPDB. MeOPEG−CPA (4.00 g, 0.78 mmol) was placed in a round-bottom flask with dry THF (100 mL), equipped with a condenser. Phenylmagnesium chloride (1.50 mL, 3.00 mmol) was prepared as above, and carbon disulfide (1.00 mL, 16.6 mmol) was added dropwise for approximately 10 min, to lead to a dark brown solution. This solution was added to the MeOPEG−CPA solution and was allowed to reflux overnight. The orange-red product was reprecipitated in cold diethyl ether to give MeOPEG−MCPDB (98.0%).

^{1}H NMR, δ (ppm from TMS): 3.33 (s, O−CH_3), 3.63 (s, CH_2−CH_2−O), 5.65 (1H, s, −S(Ph)C*H*−CO_2Me), 7.20−7.50 (8H, m, Ar−*H*), 7.93 (2H, d, Ar−H).

^{13}C NMR, δ (ppm from TMS): 70.91 (O−*C*H_3), 72.30 (O−*C*H_2), 72.26 (*C*H), 127.30, 127.76, 128.80, 129.11, 129.42, 133.21, 133.51, 144.22 (*C*H of Ar), 169.14 (*C*═O), 227.07 (CS_2).

FTIR (KBr disk, cm^{-1}): 2889 (CH_2 stretching); 1739 (C═O); 1640 (C═C); 1113 (C−O−C).

Anal. Calcd: C, 55.05; H, 8.90; S, 1.21. Found: C, 55.19; H, 9.03; S, 1.23.

M_n = 7460; PDI = 1.12 (SEC, MMA calibration).

Polymerizations. Homopolymerization in Bulk. Styrene (12.70 g, 121.8 mmol), MCPDB (0.074 g, 0.244 mmol), and α,α′-azoisobutyronitrile (AIBN; 0.004 g, 0.024 mmol) were prepared, and 1 mL of the solution was transferred in different ampules. Nitrogen gas was then flowed through the solutions for 5 min. The ampules were placed in a water bath preheated to 60 °C. Each ampule was taken out at various times (see Figure 2, ■) and placed into an ice bath to quench the reaction. The percentage conversions were measured by ^{1}H NMR and molecular weights and PDI were analyzed by SEC (see Figures 2 and 4, ■).

Polymerization Using PLLA—MCPDB as MacroCTA. Methyl methacrylate (90.50 mmol), PLLA−MCPDB (1.441 g, 0.181 mmol), and α,α′-azobis(isobutyronitrile) (AIBN) (0.003 g, 0.020 mmol) were transferred to an ampule with toluene (6 mL). The ampule was deoxygenated by flushing out with nitrogen for approximately 10 min. The ampule was placed in a preheated oil bath at 60 °C. The reaction was stopped after 60 h by cooling of the reaction tube in an ice bath and then terminated by air. Poly(L-lactic acid)-*block*-poly(methyl methacrylate) were reprecipitated in cold diethyl ether. (Conversion = 52.4%, M_n = 31 000, and PDI = 1.33.)

Polymerization Using MeOPEG—MCPDB as MacroCTAs. Methyl methacrylate (9.061 g, 90.5 mmol), MeOPEG−MCPDB (1.350 g, 0.180 mmol), and α,α′-azobis(isobutyronitrile) (AIBN) (0.003 g, 0.020 mmol) were added into an ampule. Toluene (6 mL) was added to the ampule. The ampule was deoxygenated with nitrogen for approximately 10 min and then placed in a preheated oil bath at 60 °C. The reaction was stopped after 60 h by cooling the reaction tube in an ice bath and exposed to air. Poly(ethylene glycol) methyl ester-*block*-poly(methyl methacrylate) was precipitated in cold diethyl ether. (Conversion = 24.3%, M_n = 17,150, and PDI = 1.28.)

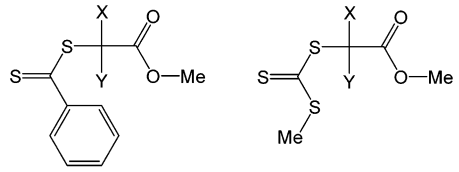
Polymerization Using Cotton MacroCTAs. Styrene (9.350 g, 90.00 mmol), cotton−MCPDB (0.018 g, 0.090 mmol), and α,α′-azobis(isobutyronitrile) (AIBN) (0.002 g, 0.010 mmol) were added in ampules in ratios of 10000:10:1. The ampules were deoxygenated with nitrogen for approximately 10 min and then placed in a preheated oil bath at 60 °C. After reaction (99% conversion), the grafted cotton substrate was washed three times with toluene, and twice with THF (while stirring overnight) to remove nongrafted polymeric chains, mainly due to the free radical initiator (<10%). The cotton substrate was then submitted to acid hydrolysis in THF, using 35% hydrochloric acid, to isolate the grafted polymeric chains. The solvents were removed in vacuo and water was added to the product to precipitate the polymeric chains and remove the mono and disaccharide residues from cotton hydrolysis. After drying, the sample was submitted to SEC analysis (M_n = 106 900, PDI = 1.35).

Results and Discussion

Choice and Synthesis of the CTAs. In most cases, CTAs for RAFT or MADIX polymerizations are not yet commercially available and their synthesis is an important step in the process of polymer design. Unfortunately, most of the CTAs that have so far been reported to efficiently control the living radical polymerization of a wide range of vinyl monomers require multistep and often complex reactions. Typical examples can be found in the synthesis of cumyl dithiobenzoate or 2-(2-cyanopropyl) dithiobenzoate.[8] On the other hand, the preparation of CTA through the use of α-haloesters is remarkable as it often requires only a one-step reaction, under less stringent conditions, and is more quantitative. Unfortunately, such CTAs usually lead to a poor control of the living radical polymerization of most monomers.[8,26]

For a CTA to efficiently control polymerization, its R group needs to form a radical that not only is stable enough to be formed but also is reactive enough to add onto the double bond of the monomer. This has been thoroughly discussed in many publications,[18,19,21,26,27] but the specific case of ester leaving group has raised very little interest.[18,21,26,27] The substituents variation on the C in α of the carbonyl group leads to generated radicals of various stability (see Scheme 2): When X = Y = CH_3, the R group is stable enough to form a radical, but not reactive enough to add on monomer. Therefore, a reasonably good controlled polymerization can be obtained with styrene and acrylate derivatives, but poor control is observed with methacrylates because of the bulkiness of the generated radical.[21] If X = CH_3 and Y = H, the control of the polymerization of styrene and acrylates is still achievable, but again a poor efficiency toward methacrylate derivatives is observed.[18,26] Finally, in the case of X = Y = H, the generated radical is not very stable, and a poor control over the polymerization of styrene and acrylates is obtained, while no control at all is observed for the polymerization of methacrylates.[26] It was therefore interesting to test the capacity in controlling radical polymerization of a leaving group with X = Ph and Y = H. The presence of a phenyl group is anticipated to increase the stability of the generated radical, while the H reduces its bulkiness. In a recent publication, the CSIRO group reported the use of a similar R group to synthesize a multiarm CTA.[28] In another comunication by Lebreton et al., the same α-bromophenyl acetic acid group is used for the synthesis of a fluorinated CTA. In the latter case, promising results were obtained in the polymerization of styrene (S), methyl methacrylate (MMA), ethyl acrylate (EA), and 1,3-butadiene.[27] These types of radicals have also been very efficient to control the polymerization of styrene, acrylate, and methacrylate derivatives by atom transfer radical polymerization.[29−31] To confirm data already published by others, we undertook the copper mediated living radical polymerization of MMA in toluene (50% v/v) using a classic initiator for this system (ethyl-2-bromoisobutyrate) and methyl α-bromophenylacetate. The results of these polymerizations are summarized on Figure 1, which shows the evolution of M_n and PDI with monomer conversion. Both initiators control the living polymerization of MMA, but methyl α-bromophenylacetate leads to lower PDI and a M_n closer to that predicted.

Scheme 2. General Structures of the Chain Transfer Agents (CTAs) Reported in This Study



To test the influence of the Z group on the polymerizations, CTAs with Z = phenyl (CTA_1, Scheme 3) and Z = methanethiol (CTA_2, Scheme 3) were synthesized. It was anticipated that CTA_1 would lead to a more efficient chain transfer agent, as the intermediate radical would be more stabilized,[16,17] while CTA_2 would benefit from a more straightforward synthesis.

The synthesis of *S*-methoxycarbonylphenylmethyl dithiobenzoate (Scheme 3, CTA_1; MCPDB) was achieved by a Grignard reaction, through the addition of methyl-α-bromophenylacetate to a solution of phenylmagnesium bromide and carbon disulfide in THF. *S*-Methoxycarbonylphenylmethyl methyltrithiocarbonate (Scheme

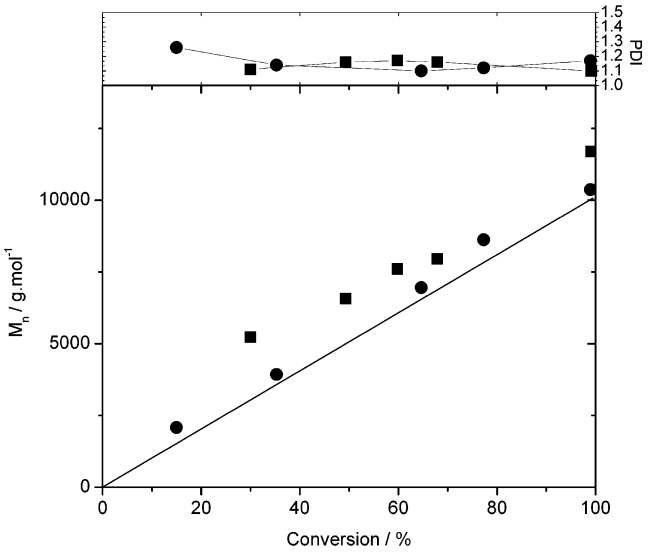


Figure 1. Molecular weight and PDI evolution with monomer conversion for the polymerization of methyl methacrylate in toluene (50% v/v) at 90 °C using a ratio monomer/initiator/copper(I)/ligand = 100/1/1/2 with initiator = ethyl 2-bromoisobutyrate (■) and methyl α-bromophenylacetate (●).

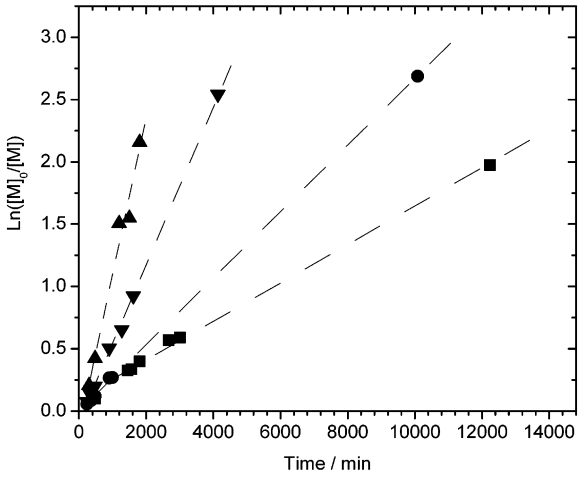


Figure 2. Pseudo-first-order rate plot for the bulk polymerization of styrene (■), methyl acrylate (●), dimethyl acrylamide (▼), and methyl methacrylate (▲) mediated by *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) at 60 °C.

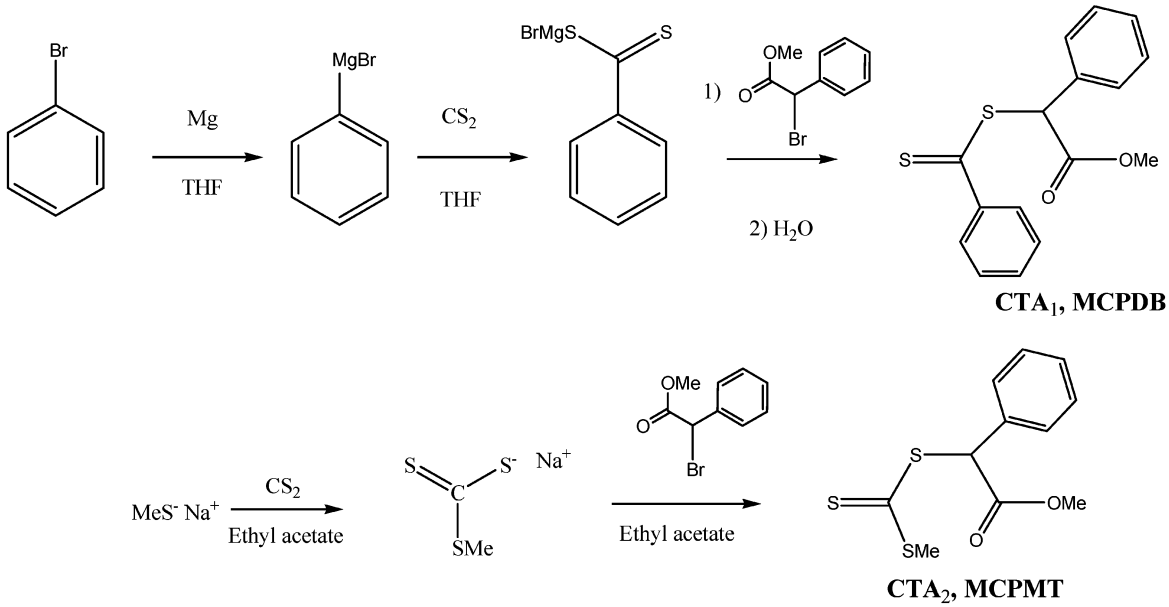
3, CTA_2; MCPMT) was prepared following the addition of methyl-α-bromophenylacetate to a solution of sodium methyl trithiocarbonate, prepared from carbon disulfide and methanethiolate, in ethyl acetate at room temperature. An additional feature of this reaction is that using sodium methoxide instead of sodium methanethiolate would lead to the preparation of the equivalent MADIX agent (Scheme 3).

Polymerizations. Both CTAs were tested in the polymerization of styrene, methyl acrylate, methyl methacrylate and dimethyl acrylamide. A common feature of all polymerizations is the faster kinetics of reaction when using MCPMT by comparison to MCPDB. Indeed, MCPMT generates an intermediate radical **2** (Scheme 1) less stable than that formed from MCPDB (The phenyl Z group of MCPDB is a better stabilizing group than the methanethiol of MCPMT). It leads to a higher rate of fragmentation of **2**; therefore faster polymerization rates are obtained (especially in the case of MA and DMA), while keeping good control of the molecular weight (PDIs are generally below 1.2 when using MCPMT).

Styrene Polymerization. Styrene is the most studied monomer in RAFT and MADIX polymerizations. MCPDB and MCPMT show a similar control over its polymerization, up to high conversion. Styrene polymerization is the slowest of all monomers (9.5% conversion in 8 (MCPDB) or 7 h (MCPMT); Figures 2 and 3). In both case the molecular weight increases linearly with conversion, as expected for a living system. In the case of MCPDB mediated polymerization, the values at higher conversion are lower than theoretical predictions (Figure 4). A reviewer has suggested that this could be due to a low transfer constant of the CTA to styrene. However, in each case, the polydispersity values average 1.1 (Note: For a better clarity of Figure 3, the point corresponding to 86.7% after 166 h, M_n = 30 700, PDI = 1.08, has not been plotted.)

Methyl Acrylate Polymerization. The polymerization mediated by MCPDB shows a good control, and

Scheme 3. Synthetic Schemes for *S*-Methoxycarbonylphenylmethyl Dithiobenzoate (MCPDB) and *S*-Methoxycarbonylphenylmethyl Methyltrithiocarbonate (MCPMT)



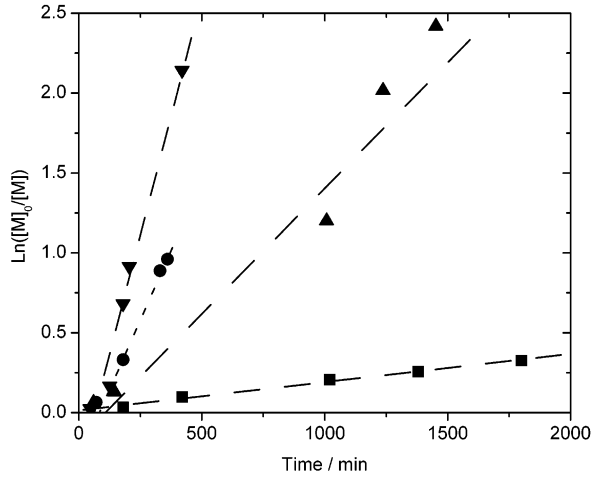


Figure 3. Pseudo-first-order rate plot for the bulk polymerization of styrene (■), methyl acrylate (●), dimethyl acrylamide (▼), and methyl methacrylate (▲) mediated by *S*-methoxycarbonylphenylmethyl methyltrithiocarbonate (MCPMT) at 60 and 50 °C (methyl acrylate).

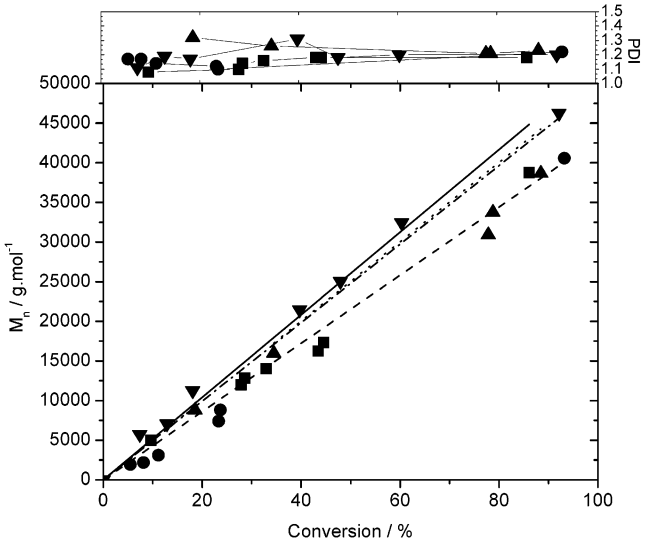


Figure 4. Molecular weight and PDI evolution with monomer conversion for the bulk polymerization of styrene (■), methyl acrylate (●), dimethyl acrylamide (▼), and methyl methacrylate (▲) mediated by *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) at 60 °C. The lines show the theoretical evolution of M_n with conversion[34] for poly(styrene) (−), poly(methyl acrylate) (- -), poly(methyl methacrylate) (···), and poly(dimethyl acrylamide) (-.-).

leads to polymers with molecular weight close to that expected and low PDI (Figures 4). Figure 2 shows that MA polymerization is far slower than MMA polymerization. This order is somewhat surprising when compared to traditional kinetic data for classic free radical polymerization of the two monomers. The fact that MMA polymerization is faster than MA polymerization can be explained by the better stability of the generated radical in the case of MMA ($P_m^\bullet$, Scheme 1), which will favor its formation and therefore enhance the overall rate of polymerization. If we modify the Z group from a phenyl to a methanethiol (MCPMT), the intermediate radical **2** is less stable and therefore more prompt to fragmentation. This leads to faster generation of propagating radicals and therefore increases the overall speed of reaction. Indeed, the polymerization of methyl acrylate mediated by MCPMT was initially attempted at 60 °C. A significant exothermal was observed with the

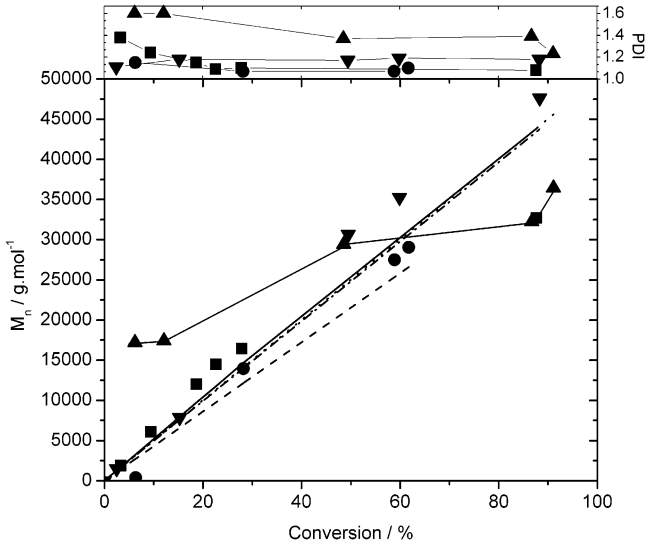


Figure 5. Molecular weight and PDI evolution with monomer conversion[34] for the bulk polymerization of styrene (■), methyl acrylate (●), dimethyl acrylamide (▼) and methyl methacrylate (▲) mediated by *S*-methoxycarbonylphenylmethyl methyltrithiocarbonate (MCPMT) at 60 °C and 50 °C (methyl acrylate). The lines show the theoretical evolution of M_n with conversion[34] for poly(styrene) (−), poly(methyl acrylate) (- -), poly(methyl methacrylate) (···), and poly(dimethyl acrylamide) (-.-).

resultant auto-accelerated reaction causing the monomer to boil and the septum to break at the very start of the reaction. To improve the efficiency of MCPMT as chain transfer agent, the temperature was then lowered to 50 °C. In these conditions, the reaction was faster than that mediated by MCPDB at 60 °C: 6 h led to a conversion of 8.1% when using MCPDB and 61.8% when using MCPMT. The molecular weight increased linearly with the monomer conversion, following very closely the theoretical predictions (Figure 5). As in the case of styrene, the PDI decreases with conversion to reach values around 1.1.

Dimethyl Acrylamide Polymerization. Both CTAs show a good control over the polymerization of DMA. As in the case of MA, using MCPMT leads to an increase in the speed of polymerization (18% in 8 h when using MCPDB and 88% in 7 h with MCPMT, Figures 2 and 3). While in the case of MCPDB, the molecular weight stays very close to that expected during the polymerization, the polymerization mediated by MCPMT leads to a molecular weight slightly higher than anticipated, possibly due to the fact that not all the CTA is consumed and/or radical coupling inherent to LRP processes. This observation should however be moderated by the fact that the experimental molecular weights reported are calculated using PMMA standards. In both cases, the polydispersities remain under 1.2 (Figures 4 and 5).

Methyl Methacrylate Polymerization. MCPDB gives also good results in the polymerization of MMA. As explained above, the polymerization is relatively slow (Figure 2), but the molecular weight evolution is close to theory within a reasonable error, and the PDI obtained remains under 1.3 (Figure 4). To the best of our knowledge, this is the first time the control of MMA polymerization via RAFT is achieved with a leaving group (R) showing a secondary carbon radical.

The MCPMT mediated polymerization of MMA shows, however, no control. At 60 °C, the molecular weight evolution is different from that predicted by theory, with

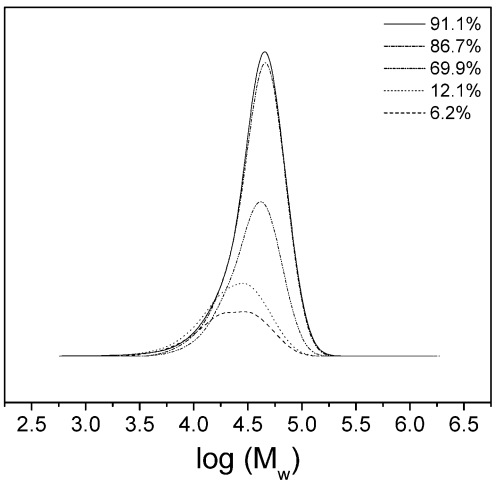


Figure 6. Molecular weight distribution evolution during polymerization of methyl methacrylate in bulk mediated by *S*-methoxycarbonylphenylmethyl methyltrithiocarbonate (MCPMT) at 60 °C.

very high values at low conversion. The difference in kinetics for each CTA is less obvious than that observed for other monomers: 77.8% are reached in 20 h in the case of MCPDB while it takes 20 h and 40 min to reach 86.7% when using MCPMT. When looking at the evolution of the molecular weight distribution during the reaction (Figure 6), one can distinctly observe a bimodal curve at low conversion. When the reaction proceeds to high conversion, the two molecular weight distributions level up and the PDI decreases (Figure 5). Similar observations have already been made by Barner-Kowollik et al.[16] in the case of MMA polymerization mediated by RAFT agents with a Z group that lowers the stability of the intermediate radical **2** (Scheme 1). On a similar model, we expect the methanethiol Z group of MCPMT to induce slower reaction of the initial CTA with the growing polymer chains by comparison to what is observed with MCPDB. Furthermore, the fact that MCPMT has a lower chain transfer constant with MMA than with S, MA, and DMA, leads to the presence of two different chain transfer agents at the start of the reaction: the initial CTA which has not yet reacted and a macroCTA generated by the addition of a polymeric chain on the initial chain transfer agent.[16] Both CTAs have very different chain transfer constants, therefore two parallel mechanisms occur, which generate two different types of molecular weight distributions. Eventually, when the initial CTA is fully consumed, the polymerization is only mediated by the macroCTA. Steric hindrance effects facilitate the rapid growth of the smallest chains, allowing homogenization of the molecular weight distribution, as illustrated by a monomodal molecular weight distribution at high conversion (Figure 6). The final product shows a reasonably low PDI with a molecular weight lower than that expected. To achieve a better control over the polymerization, we tried to slow the growth of the polymer chains by decreasing the temperature to 25 °C. However, similar observations to that at higher temperature were made. In conclusion, MCPMT is not as good CTA as MCPDB for the polymerization of MMA. Nevertheless, polymers with PDI < 1.4 and molecular weight slightly under that expected can be obtained.

In conclusion, MCPDB and MCPMT offer good control over the living polymerization of styrene, MA, and DMA by comparison to more classic RAFT agents such as

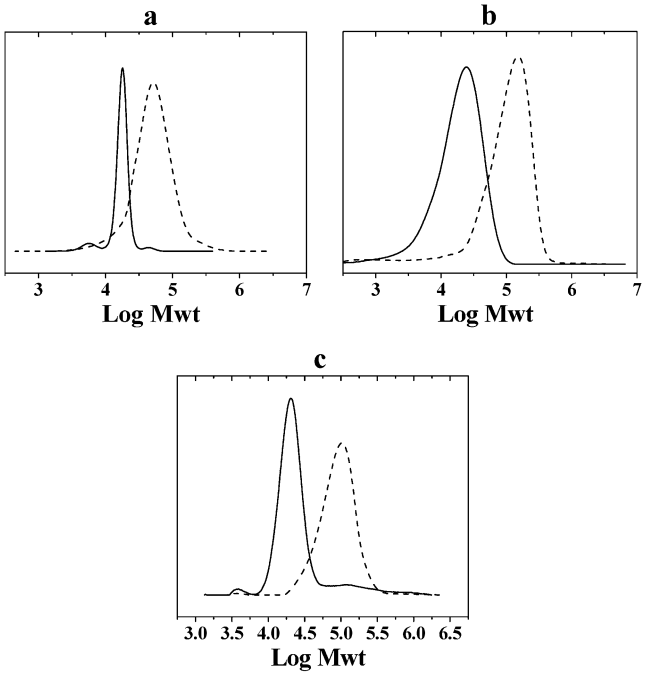


Figure 7. Molecular weight distribution of (a) poly(ethylene glycol) (—) and [poly(ethylene glycol)-*b*-poly(methyl methacrylate)] (- -), (b) poly(L-lactic acid) (—) and [poly(L-lactic acid)-*b*-poly(methyl methacrylate)] (- -), and (c) poly(methyl methacrylate) (—) and [poly(methyl methacrylate)-*b*-poly(styrene)] (- -).

cumyl dithiobenzoate and cyanoisopropyl dithiobenzoate.[8] MMA polymerization, however, is well controlled when mediated by MCPDB but lead to broader molecular weight distributions in the presence of MCPMT.

End Chain Functionalities and Polymeric Architectures. One of the main characteristic of living radical polymerization is the use of various types of functional molecules, or macromolecules, to initiate polymerization. This has been well documented for transition metal mediated living radical polymerization in the particular case of α-haloesters initiators. The appropriate acid halide can easily be reacted with various functional groups through a straightforward esterification reaction to form the corresponding initiator.[6,7,32] We used a similar approach to produce functional CTAs for RAFT and MADIX from inexpensive reagents and through a straightforward synthesis. A molecule bearing a hydroxyl group is reacted with 2-chloro-2-phenylacetyl chloride to form the corresponding 1-alkoxycarbonyl-1-phenyl methyl. The product is then further reacted following the procedure highlighted for MCPDB and MCPMT to form the corresponding dithiobenzoate or trithioester, respectively (see Scheme 2).

By this process, block copolymers with polymers formed by other (nonradical) mechanisms can easily be synthesized. We chose MMA as the model monomer. According to the previous kinetic studies, the polymerization of MMA is the most difficult to control with MCPDB. Therefore, achieving well-controlled architectures with MMA should prove that good control could also be achieved with the other monomers investigated in this study. An amphiphilic AB block copolymer with reasonably low PDI was formed by transforming a poly(ethylene glycol) methyl ether (MeOPEG) chain into CTA, following the process described above, and its use to polymerize MMA (see Table 1, entry 1). On the same

Scheme 4. Scheme Showing the Transformation of Molecules Bearing a Hydroxyl Group into Initiator for Transition Metal Mediated Living Radical Polymerization and/or Chain Transfer Agent for Reversible Addition Fragmentation Chain Transfer (RAFT) and Macromolecular Architecture Design via Interchange of Xanthate (MADIX) Polymerization

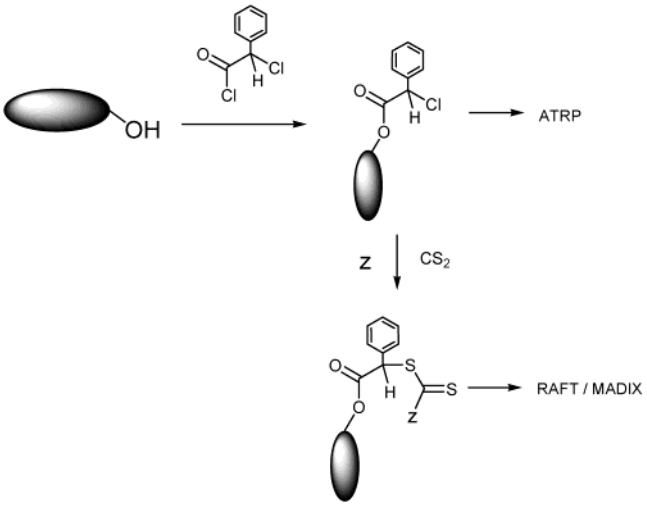


Table 1. Molecular Weight Data for AB Diblock Copolymers

	monomer A	M_n[a]	PDI[b]	monomer B	M_n[b,c]	$PDI_{copolymer}$[b]
1	ethylene oxide	5000	1.12	MMA	17 150	1.28
2	L-lactic acid	1800	1.50	MMA	31 000	1.33
3	MMA	13 400[b]	1.18	styrene	63 600	1.27
4	cellulose			styrene	106 900[d]	1.35
5	cellulose			MA	84 850	1.38
6	cellulose			MMA	60 500	2.22

[a] Determined by ^{1}H NMR using $CDCl_3$ as solvent. [b] Determined by SEC using THF as eluent and PMMA standards. [c] M_n of the copolymer. [d] PS as SEC standards.

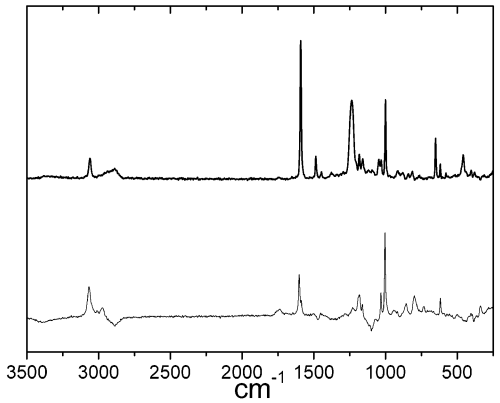


Figure 8. Subtraction of Raman spectra showing cotton ester − cotton (bottom) and cotton chain transfer agent − cotton ester (top).

model, an AB block copolymer incorporating a biodegradable block, poly(L-lactic acid) (PLLA), and a PMMA block was also produced (see Table 1, entry 2). The GPC traces (Figure 8) show the clean conversion of the initial polymer into a AB block copolymer after addition of MMA. These results can be compared to entry 3 (Table 1), which shows the molecular weight and PDI of a PMMA-*b*-PS block copolymer synthesized by further reacting a PMMA macroCTA (synthesized with MCPDB) with styrene.

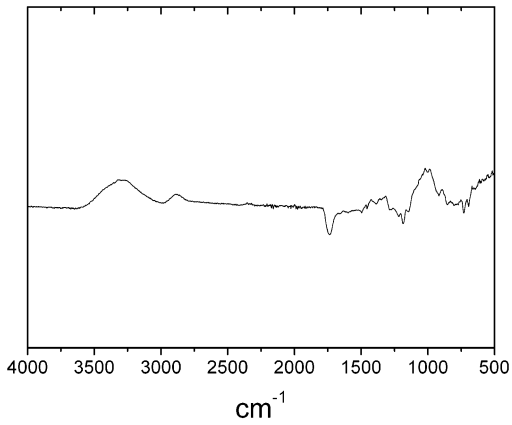


Figure 9. Subtraction of FTIR spectra showing cotton ester − cotton.

To demonstrate the versatility of the process, solid suported polymerization was also undertaken. A recent communication by Carlmark et al. has shown the possibility to grow polymeric chains in a controll manner from cotton substrate via transition metal mediated living radical polymerization.[34] However, the authors had difficulty in characterizing the molecular weight of the grafted chains. We decided to follow a similar route using the principle highlighted above. The hydroxyl groups of a cotton fabric were treated with 2-chloro-2-phenylacetyl chloride and further transformed into dithioesters to be used as supported CTA for polymerization. Each reaction step was followed by Raman and FTIR spectroscopy (Figures 8 and 9). Raman spectroscopy (Figure 8, bottom spectrum) illustrates the successful reaction of 2-chloro-2-phenylacetyl chloride with the cotton hydroxyl groups by incorporation of the monosubstituted phenyl (1602, 1583, and 1004 cm^{-1}) and the C−Cl bond (peak at 617 cm^{-1}) of the acid chloride. Further confirmation was also obtained from FTIR spectroscopy, Figure 9, with stretches at 1736 and 1187 cm^{-1}, characteristic of C═O and C−O, respectively.

The transformation into dithioester is also illustrated by Figure 9, where the strong Raman bands at 1236 and 651 cm^{-1} (top spectrum) are attributed to the C═S and C−S bonds, respectively. The characteristic peaks of aromatic structure are still observed at 1602 and 1001 cm^{-1}, demonstrating the incorporation of an extra phenyl ring. The degree of substitution of the hydroxyl groups of the cotton fabric was estimated to be 14% by gravimetry. The reactions were therefore prepared aiming for a degree of polymerization DP = [M]/[CTA], with [CTA] obtained from the degree of substitution.

The cotton supported polymerizations of MMA, MA, and styrene were undertaken in bulk, up to full conversion. After polymerization, a sample of cotton was hydrolyzed in acidic conditions to collect the grafted PMMA, PS, and PMA chains, which were then analyzed by SEC. Table 1 illustrates the remarkable control obtained during polymerization of styrene and methyl acrylate. PS and PMA (entries 3 and 4) show a molecular weight very close to that expected ($M_{n,theor}$ = 104 200 and 99 100, respectively) with polydispersities as low as 1.35. In the case of PMMA (entry 6), a lower molecular weight than anticipated was obtained ($M_{n,theor}$ = 100 100), with higher PDI. Nevertheless, an easy process for supported polymerization was demonstrated, which leads to a remarkable control of the polymeric chains molecular weight. Furthermore, this

technique brings a new scope into the grafting and functionalization of natural textiles. Further studies to improve the current technique are currently being undertaken in our laboratories.

Conclusion

In conclusion, we have described the facile synthesis of versatile CTAs that can produce an extensive range of polymers with predictable M_n and low PDI from styrene, methyl acrylate, methyl methacrylate, and dimethyl acrylamide. Furthermore, these CTAs allow the easy incorporation of any molecules bearing a hydroxyl group at the end of a polymeric chain. We believe this technique will provide new opportunities in the synthesis of functional polymers, so far dominated by atom transfer radical polymerization. Indeed, not only will the use of RAFT/MADIX avoid the potential pollution of the final product by a catalyst but also the process is easier to undertake, with a wider range of monomers.

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

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(34) Calculated using the following formula: $M_{n,theor} = [monomer]/[CPDB] \times M \times c$, where M is the monomer molecular mass and c the fractional conversion.

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