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Synthesis of Well-Defined Macromonomers by Sequential ATRP−Catalytic Chain Transfer and Copolymerization with Ethyl Acrylate

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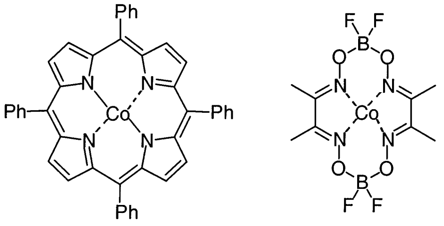
ABSTRACT: Polymer chains with unsaturated end groups can be produced by the addition of catalytic chain transfer agents near the end of an atom-transfer polymerization. The polymers were analyzed by MALDI−TOF, NMR, and TGA experiments to determine the degree of unsaturation with good agreement. These polymers can subsequently be used as macromonomers in copolymerizations with monomers such as ethyl acrylate.

Introduction

It has been shown that addition of certain catalytic chain transfer (CCT) agents (such as various cobalt porphyrins or cobalt oximes) to free-radical polymerizations of methyl methacrylate (MMA) leads to the formation of poly(methyl methacrylate) (PMMA) containing unsaturated end groups[1−7] (Scheme 1). These polymers have polymerizable end groups, so they can then be used as macromonomers in further copolymerizations.[8−16]

However, while the use of CCT agents has been shown to yield polymers with controlled molecular weights and end groups,[6] the polymerizations are not “living”; i.e., molecular weights do not increase linearly with conversion, and no sequential growth of further monomers is possible. Observed polydispersities are also typically in the region of 1.8−2.3.[6] It has been possible to use functional intitiators to produce low-polydispersity macromonomers by ATRP, but these require post-polymerization modification or the synthesis of unusual initiators.[17−23] In this paper we will investigate the use of atom-transfer radical polymerization (ATRP) to synthesize well-defined homopolymers or block copolymers, to which a CCT reagent will subsequently be added, thus producing polymers with unsaturated end groups, low polydispersity, and controlled molecular weights. The CCT reagents used were 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II) [Co(tpp), **1**] and bis{*μ*-[(2,3-butanedione dioximato) (2−) O:O′]} tetrafluorodiborato (2−) *N,N′,N″,N‴*cobalt(II), [CoBF, **2**], (Figure 1).

ATRP is a “living” free-radical polymerization process based on the reversible coordination of a transition metal catalyst to a halogen atom which is primarily attached to the growing end of a polymer chain. Early work on ATRP was carried out independently in 1995 by Matyjaszewski et al. using copper-based catalyst systems[24,25] and by Sawamoto et al. using ruthenium-based catalyst systems[26] (in conjunction with an aluminum alkoxide cocatalyst). Matyjaszewski et al. primarily use copper(I) halide catalysts complexed by substituted dipyridyl or linear amine ligands in conjunction with alkyl halide initiators,[24,27−30] although separate work has also been carried out in this field by Haddleton et al., using Schiff bases as ligands for a copper halide catalyst.[31,32] ATRP also works successfully with a range of other transition metal complexes and initiators. In addition to Sawamoto's use of $Ru^{II}Cl_2(PPh_3)_3$ as catalyst,[26,33,34] Percec et al. have used sulfonyl halides as initiators,[35−38] and Ni(II),[39,40] Fe(II),[41] Pd(II),[42] and Rh(III)[43] based ATRP systems also work under suitable conditions. However, for the purposes of the material discussed in this paper, the ATRP system employed is that developed by Matyjaszewski, using a Cu(I)Cl catalyst complexed by 2,2′-dipyridyl ligands with an alkyl halide initiator (see Scheme 2). We have used this system to exert good control over the weights and polydispersities (M_n up to 50 000 Da, $M_w/M_n = 1.2−1.4$) of homopolymers and block copolymers of (meth)-acrylates.

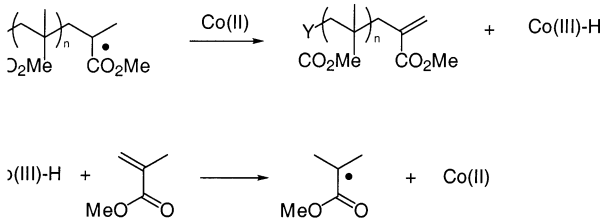


Co(tpp)
1

CoBF
2

Figure 1. CCT reagents.

Scheme 1. CCT Mechanism Producing an Unsaturated End Group on a Methacrylate Chain



The catalyst establishes an equilibrium between active and dormant chain ends, where the dormant species is halogen end-capped and the active species is a propagating radical. This propagating radical should

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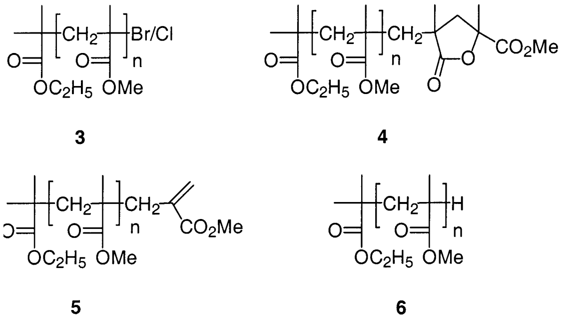
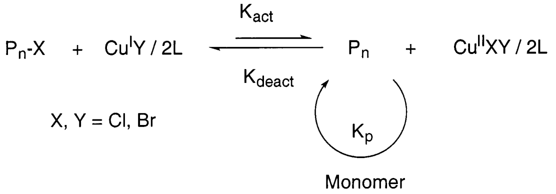


Figure 2. Mixed-halide ATRP generated PMMA **3**, lactone end group **4**, unsaturated **5**, and saturated **6** PMMA structures.

Scheme 2. Mechanism of ATRP



behave identically to a radical species generated by an azo-initiator. In principle, addition of a CCT agent toward the end of an (ethyl 2-bromoisobutyrate initiated) ATRP polymerization of MMA should therefore lead to formation of an ω-unsaturated PMMA macromonomer (Figure 2, **5**) with low polydispersity and controlled molecular weight (assuming no unfavorable side reactions such as interactions between the halogen end group and cobalt catalysts or new oligomer formation due to conventional chain-transfer events from the CCT catalyst). This process should be equally applicable to block polymers, where an initial well-defined polymer is produced by ATRP, isolated, and then used as a macroinitiator in the sequential polymerization of a different monomer by ATRP. CCT agent may then be added toward the end of the polymerization of this second block to control the end group and synthesize well-defined diblock macromonomers. It should be emphasized that the CCT agent is only acting as a chain terminater in this process and that chain transfer leading to initiation of new chains is actually undesired.

Experimental Section

Materials. MMA (Acros, 99%) and n-BMA (Lancaster, 99%) were passed over a column of neutral alumina and stored under N_2 at 6 °C. Ethyl acrylate was stirred over CaH_2 and distilled immediately prior to use. CuCl was prepared from $CuCl_2$ according to the literature procedure[44] and stored at 6 °C in a tinted glass vial. 2,2′-Dipyridyl (Aldrich, 99+%) and ethyl 2-bromoisobutyrate (Lancaster, 98%) were used as received. Ethyl acetate (Aldrich, 99.8% anhydrous), xylene (Aldrich, 97% anhydrous), and benzene (Aldrich, 99.8% anhydrous) were used as received and stored under N_2. AIBN (BDH, 97%) was recrystallized from warm methanol and stored at 6 °C. 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine cobalt(II) [Co(tpp), **1**] (Aldrich, synthetic) and bis{μ-[(2,3-butanedione dioximato) (2−) O:O′]} tetrafluorodiborato (2−) *N*,*N*′,*N*″,*N*‴cobalt(II), [CoBF, **2**] (ICI) were used as received (see Figure 2 for structures). All other solvents were lab grade and used as received.

Polymerizations. *PMMA Macromonomer Synthesis.* The polymerizations were carried out on a scale of 5 mL of MMA in a round-bottomed flask fitted with a magnetic stirrer bar and condenser. Copper chloride and 2,2′-dipyridyl were added to the flask, which was purged of air via three vacuum−nitrogen cycles. MMA, ethyl 2-bromoisobutyrate, and solvent, ethyl acetate (50 vol %), were transferred by syringe under nitrogen. Three freeze−thaw cycles were performed to remove molecular oxygen from the polymerization mixture, after which the reaction flask was immersed in an oil bath thermostated to 90 °C, with stirring. Co(tpp), **1**, or CoBF, **2**, was transferred by syringe, as solutions in 1 mL of THF. PMMA samples were recovered pre- and post-chain-transfer agent addition by dissolving 0.5 mL aliquots of reaction solution in THF, filtering over a column of neutral alumina in order to remove catalyst, and then precipitating in hexane. Polymers were dried in a vacuum oven at room temperature overnight.

Diblock Macromonomer Synthesis. The macroinitiating block (PMMA or PBMA) was prepared as above (except that no chain-transfer agent was added) and isolated by similar precipitation in hexane and drying. Macroinitiator, copper halide, ligand, solvent, and second monomer were added to a round-bottomed flask as above, degassed, and polymerized at 90 °C. A chain-transfer agent was added, and the final polymer was isolated as previously.

Copolymerizations. Copolymerizations of PMMA macromonomer with ethyl acrylate were carried out in Schlenk flasks. Ethyl acrylate was transferred by syringe into a Schlenk containing PMMA macromonomer (purified by precipitation into methanol and drying) and AIBN. Xylene or benzene was added as solvent. Three freeze−thaw cycles were performed to remove molecular oxygen from the polymerization mixture, after which the reaction flask was immersed in an oil bath thermostated to 60 °C, with stirring. Copolymers were recovered by precipitation in cold methanol (ca. −70 °C). Polymers were dried in a vacuum oven at 40 °C overnight.

Characterizations. ^{1}H NMR spectra were recorded on Bruker DPX-250 (250 MHz) and DRX-400 (400 MHz) instruments, using $CDCl_3$ for reference. Infrared spectra were recorded on a Nicolet 510 FT-IR spectrometer. Samples were analyzed by incorporation in KBr plates or as a film on NaCl plates. Molecular weights and molecular weight distributions were determined by SEC in chloroform at 30 °C using two Polymer Laboratories PLgel 5 μm mixed-C (300 × 7.5 mm) columns run in series. Calibration was carried out against linear PMMA standards (MW range: 1000−1 500 000). Analysis was by RI detection. Light-scattering measurements were carried out separately using a similar two-column system in chloroform, using a Wyatt Dawn multiangle light scattering detector and a Combined RI viscometer (Viscotek model 200). Thermogravimetric analysis (TGA) measurements were carried out under a nitrogen flow, with a heating rate of 10 °C/min. Elemental analysis was carried out in-house. Matrix-assisted laser desorption/ionization-time-of-flight (MALDI−TOF) mass spectrometry was carried out by the ICI Technology Science Support Group at Wilton on a TofSpec2E (Micromass UK Ltd., Manchester, UK) instrument, equipped with a nitrogen (N_2) laser, in the reflectron mode of operation. The sample was dissolved in chloroform (10 mg mL^{-1}) and mixed with the matrix (dithranol, also in chloroform at 10 mg mL^{-1}) in a 1:5 ratio. Lithium bromide (methanol, 30 mg mL^{-1}) was added to this mixture at a ratio of 1:120. Approximately 1 μL of this combination was deposited onto the sample stage and allowed to air-dry prior to analysis.

Experiments A−C, PMMA. ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.08 (qt, OCH_2, initiator), 3.76 (s, ω-OMe), 3.59 (s, backbone-OMe), 1.88−1.81 (CH_2 ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1736.6, 1458.7, 1244.5, 1194.4, 1150.0.

Experiments A−C, PMMA Macromonomer. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.20 (s, C═C−H_1), 5.48 (s, C═C−H_2), 4.08 (qt, OCH_2, initiator), 3.75 (s, ω-OMe), 3.59 (s, backbone-OMe), 2.49 (allylic CH_2), 1.88−1.81 (CH_2 ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1726.9 (br), 1483.8, 1449.1, 1389.3, 1273.5, 1242.6, 1194.4, 1150.0.

Experiment F, P(MMA-*b*-BMA). ^{1}H NMR (250 MHz, $CDCl_3$): δ 4.10 (m, ω-OCH_2 *PBMA* + OCH_2 *initiator*), 3.94 (s, backbone-OCH_2, *PBMA*), 3.60 (s, backbone-OMe, *PMMA*), 1.90−1.81 (CH_2 ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1732.7, 1489.6, 1456.8, 1389.3, 1275.4, 1244.5.

Experiment F, P(MMA-*b*-BMA) Macromonomer. ^{1}H NMR (250 MHz, CDCl$_3$): δ 6.20 (s, C=C$-H_1$, small peak), 5.46 (s, C=C$-H_2$, small peak), 4.10 (m, ω-OCH$_2$ *PBMA* + OCH$_2$ *initiator*), 3.94 (s, backbone-OCH$_2$, *PBMA*), 3.60 (s, backbone-OMe, *PMMA*), 2.50 (allylic CH$_2$), 1.90−1.81 (CH$_2$ ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1732.7, 1449.1, 1389.3, 1242.6, 1148.1.

Experiment G, P(BMA-*b*-MMA). ^{1}H NMR (250 MHz, CDCl$_3$): δ 3.94 (s, backbone-OCH$_2$, *PBMA*), 3.75 (m, ω-OMe, *PMMA*), 3.60 (s, backbone-OMe, *PMMA*), 1.90−1.81 (CH$_2$ ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1732.7, 1489.6, 1456.8, 1389.3, 1275.4, 1244.5.

Experiment G, P(BMA-*b*-MMA) Macromonomer. ^{1}H NMR (250 MHz, CDCl$_3$): δ 6.20 (s, C=C$-H_1$, small peak), 5.48 (s, C=C$-H_2$, small peak), 3.94 (s, OCH$_2$, *PBMA*), 3.75 (m, ω-OMe, *PMMA*), 3.60 (s, backbone-OMe, *PMMA*), 2.50 (allylic CH$_2$), 1.90−1.81 (CH$_2$ ethylene backbone), 1.59−0.81 (α-Me backbone). IR ν(KBr)/cm^{-1}: 1732.7, 1449.1, 1389.3, 1146.1.

Experiments H and J, P(MMA-*co*-EA). ^{1}H NMR (250 MHz, CDCl$_3$): δ 4.10 (br s, OCH$_2$, *EA*), 3.60 (s, OMe, *PMMA*), 2.27 (br s, α-H, *PEA*), 1.90−0.85 (CH$_2$ ethylene backbone + α-Me backbone). IR ν(NaCl, film)/cm^{-1}: 1732.7, 1686.4, 1655.5, 1458.7.

Results and Discussion

End Group and Thermal Stability of PMMA. The structure of polymers formed in the CCT polymerizations of MMA can be studied by a variety of methods, especially NMR, MALDI−TOF, and TGA analysis. The presence of unsaturated end groups in the final polymer (Figure 2, **5**) is seen in the ^{1}H NMR spectrum by the appearance of two singlet peaks at 6.20 and 5.47 ppm (olefinic CH$_2$) and a peak at 2.50 ppm (allylic CH$_2$).[14] Thermal analysis of PMMA shows that the stability of the polymer depends on the type of end groups. Conventional free-radical-produced PMMA homopolymers are known to begin degrading at approximately 175 °C (due to scission of head-to-head linkages in the polymer),[41] and the unsaturated end groups formed by oxidation during disproportionation begin to degrade at approximately 225 °C.[45] The other possible end group is the saturated product of disproportionation, and this has been shown to be thermally stable in a nitrogen atmosphere to 300 °C.[45] However, the quoted temperatures at which these degradations occur do vary between publications (Rizzardo et al. quote 190 and 255 °C for head-to-head and unsaturated degradation, respectively)[46] and are dependent to a certain extent on the definition of the exact point at which the onset of degradation occurs.

Shown below (Figure 3) are TGA spectra recorded by us (using 10 °C/min heating rates, under nitrogen) of PMMA produced via four separate polymerization techniques: (a) by conventional free-radical polymerization (FRP) using AIBN initiator (M_w = 146 400, M_n = 60 600); (b) by ATRP, using the system detailed in the Experimental Section (M_w = 5700, M_n = 4100); (c) by screened anionic polymerization (SAP) to yield saturated PMMA with hydrogen end groups (M_w = 16 500, M_n = 14 300) and by catalytic chain transfer (CCT) polymerization using cobolt(II) tetraphenylporphyrin (M_w = 8100, M_n = 3900).

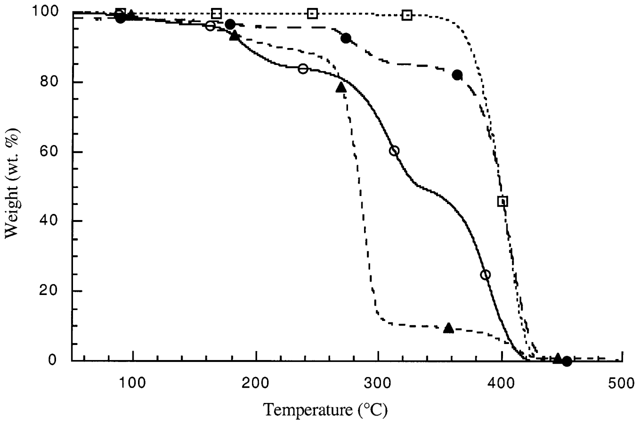


Figure 3. TGA spectra of PMMA prepared by different polymerization techniques: free radical polymerization (FRP) (○), catalytical chain transfer (CCT) polymerization (▲), ATRP (●), and screened anionic polymerization (□).

As may be seen from Figure 3, PMMA produced by FRP displays the degradation characteristics described earlier, head-to-head linkages begin degrading at approximately 170 °C, and unsaturated end groups begin to degrade at approximately 250 °C, whereas the final degradation step (presumably degradation of saturated chains) occurs in excess of 330 °C. Our degradation values for FRP-produced PMMA are therefore somewhere in between those quoted by Smith and Rizzardo.[45,46] PMMA produced by ATRP shows degradations at similar temperatures; however, these are far less pronounced (only ca. 15% weight loss at 300 °C, cf. ca. 50% weight loss at 300 °C in FRP-produced PMMA). This is presumably due to the lower radical concentration in ATRP, which minimizes the number of head-to-head linkages and disproportionation reactions. There are fewer papers on the thermal stability of ATRP-produced PMMA. Moineau et al. prepare PMMA (M_n = 39 000, PD = 1.26) using a NiBr$_2$(PPh$_3$)$_2$/ethyl 2-bromoisobutyrate ATRP system which shows a ca. 5% weight loss at 300 °C,[47] and Irvine et al. report that ATRP-produced polymers also show a small weight loss (1−2%) corresponding to loss of methyl halide at ca.150 °C.[48] CCT-polymerized PMMA shows a major degradation at 260−300 °C attributed to the unsaturated end groups. Note finally that PMMA produced by SAP (Figure 3) has 100% abundance of saturated end groups and shows negligible weight loss until just in excess of 350 °C, which implies that head-to-head linkages and disproportionation reactions have been totally eliminated.

MALDI−TOF analysis allows more detailed study of polymer end groups, with intense peaks corresponding to more common repeat units in the polymer. Figure 2 shows the polymer structure, **3**, one would expect for ATRP-produced PMMA, using ethyl 2-bromoisobutyrate initiator and copper chloride catalyst. Matyjaszewski et al.[49] showed that, in ATRP with a mixed halide initiator/catalyst system, the bulk of the polymer chain ends are terminated by chlorine if $[\mathrm{CuCl}]_0 \geq [\mathrm{RBr}]_0$, where $[\ ]_0$ denotes initial concentration. However, in this case $[\mathrm{CuCl}]_0 < [\mathrm{RBr}]_0$, so there are probably significant quantities of both chlorine and bromine end-capped polymers. Nevertheless, the identity of the halogen end group may not be important for the purposes of this paper, since it has been shown that the lability of the carbon−halogen bond leads to fragmentation in the MALDI source, such that oligomers with a lactone end group, **4**, are formed.[48] Figure 2 also shows the structure of such a lactone, along with saturated, **6**, and unsaturated, **5**, oligomer end group structures. **5** is the expected end group of the generated macromonomers, but both **5** and **6** have been shown to be present at low concentrations in PMMA produced by ATRP.[48]

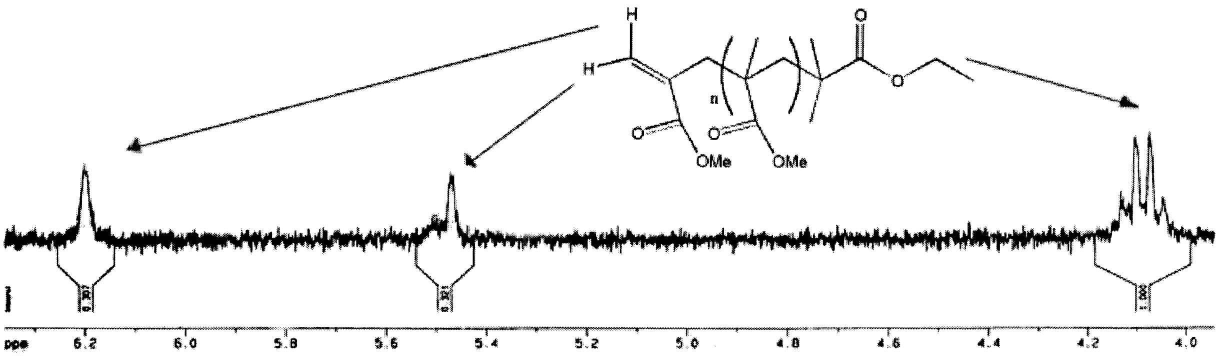


Figure 4. Partial ^{1}H NMR spectrum of unsaturated PMMA produced by ATRP (from experiment A(ii)).

Table 1. Addition of CCT Agents to PMMA Prepared by ATRP[a]

	ATRP (i)		CCT	ATRP + CCT (ii)		unsatd	unsatd
expt	$M_{n,i}$[b]	PD$_i$[c]	(mol %)[d]	$M_{n,f}$[e]	PD$_f$[c]	%, NMR[f]	%, TGA[g]
A	4100	1.39	0.019[h]	4100	1.38	76.0	78
B	3800	1.44	0.019[h]	4200	1.42	86.6	85
C	3600	1.33	0.035[i]	3400	1.39	6.6	8

[a] All reactions carried out using CuCl/Bipy/ethyl 2-bromoisobutyrate [0.33/1/3.30 mol % relative to MMA] in 50% ethyl acetate solution (v/v) at 90 °C. Experiment A + C: polymerized for 90 min by ATRP before addition of CCT reagent (then heated for a further 90 min). Experiment B: polymerized for 120 min by ATRP before addition of CCT reagent (then heated for further 1350 min). [b] M_n of initial polymer (before CCT agent added) by ^{1}H NMR. [c] Polydispersity by SEC. [d] Molar percent relative to MMA, added as solution in THF. [e] M_n of final polymer (after CCT agent added) by ^{1}H NMR. [f] Percentage unsaturated end groups calculated by ^{1}H NMR. [g] Percentage unsaturated end groups, calculated by % weight loss at 225−275 °C, by TGA. [h] Co(tpp) used. [i] CoBF used.

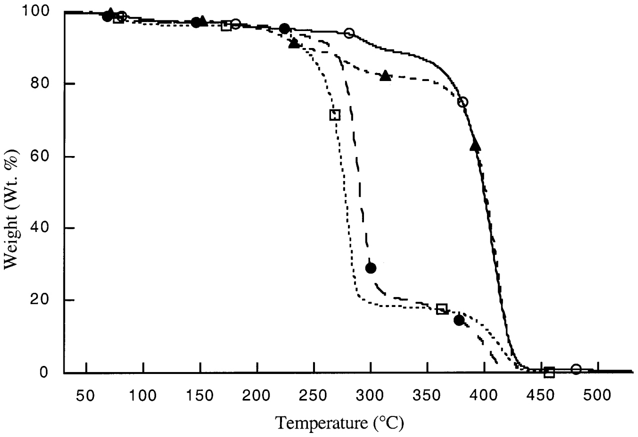


Figure 5. TGA spectra of polymers A(ii) (□), B(ii) (●), C(ii) (▲), and PMMA produced by ATRP (○).

Addition of CCT Reagents to PMMA Prepared by ATRP. As it was important to maximize the living nature of the chain ends at the time of CCT catalyst addition, the molecular weight of the initial MMA polymerization was aimed at a moderate level of 3000 by using a 30/1 molar ratio of monomer to initiator. The polymerization was continued until approximately 80% monomer conversion (by IR, 120 min polymerization time) whereupon an aliquot of the reaction mixture was taken for analysis in order to yield an ATRP "control" polymer. CCT catalyst was then added to the remaining reaction mixture as a concentrated solution in THF. Unfortunately, the CCT catalysts proved insufficiently soluble in the ATRP solvent, ethyl acetate, at the concentrations used, so THF was used instead. THF is not an ideal solvent in radical reactions due to its higher hydrogen transfer potential, but it was the solvent in which the CCT reagents were most soluble. The reaction mixture was subsequently maintained at 90 °C for another 90 min. During this time analysis by NMR and SEC of aliquots of reaction mixture revealed no significant change in the molecular weights or polydispersities of the polymer observed, indicating that chain growth had effectively stopped. Longer periods of time (in excess of 20 h) led to the appearance of a small separate peak (at lower molecular weight than the main polymer peak) in the SEC trace of nonprecipitated polymer. Precipitation of a concentrated solution of this polymer into hexane led to fractionation of the lower molecular weight material into the hexane layer, as evidenced by the disappearance of the smaller peak in the SEC trace of the collected precipitate. Analysis of the hexane layer by SEC revealed the presence of an oligomeric species ($M_n = 390$, PD = 1.20), and subsequent analysis of this oligomer by ^{1}H NMR revealed it to be PMMA containing unsaturated end groups. However, no evidence of a peak at 4.08 ppm corresponding to the ATRP initiator was seen, which suggests that the oligomer was not formed by the usual ATRP process. The oligomer may therefore have been produced by conventional chain transfer of residual unreacted MMA monomer by the CCT catalyst or by a combination of CCT and ATRP operating to control a propagating radical. Either way, the concentration of oligomer formed in these reactions is small, and it may be easily removed from the bulk well-defined polymer by precipitation into hexane.

Three representative results for the addition of CCT reagent to "live" ATRP mixtures can be seen in Table 1, using both Co(tpp) and CoBF as chain transfer agents. Molecular weights of PMMA by ^{1}H NMR were determined by the ratio of integrals of the peaks at 3.59−3.76 ppm (backbone and terminal CO*OMe* resonances)[32] to the peak at 4.08 ppm (CO*OCH*$_2$, initiating species),[32] assuming one initiating species per polymer chain. Good agreement was observed between this value and that obtained by size-exclusion chromatography (SEC). Figures for percentage of unsaturated end groups per polymer chain by ^{1}H NMR were obtained by comparison of integrals of peaks at 6.20 and 5.47 ppm to the peak at 4.08 ppm (Figure 4).

Figures for percentage of unsaturated end groups per polymer chain by TGA were obtained by comparison of the percentage of weight lost in the temperature range 225−275 °C (due to degradation of unsaturated end groups) in the TGA traces for both initial (ATRP) and final (ATRP + CCT) polymers prepared in experiments A−C (Figure 5). It must be stressed, however, that

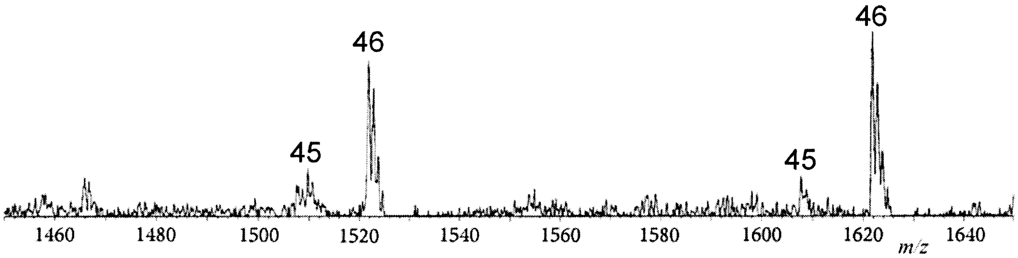


Figure 6. Partial MALDI−TOF spectra of PMMA produced in experiment A(ii).

thermogravimmetric analysis does not provide an absolute value for the percentage of unsaturated end groups per polymer chain, since end groups may be altered during the course of heating the sample. We will therefore use TGA results to corroborate figures obtained by ^{1}H NMR, but the values quoted should be taken as approximations rather than absolutes.

As discussed earlier, it is possible to focus on representative polymer repeat units and end groups of PMMA by detailed analysis of MALDI−TOF spectra. Recent literature results on PMMA produced by ATRP, using ethyl 2-bromoisobutyrate initiator, CuBr or CuCl catalyst, and similar reaction conditions, show no evidence of a halogenated end group species **3** by MALDI−TOF.[48,49] However, a prominent peak is seen at *m*/*z* values which correspond to loss of methyl halide and the subsequent formation of lactonized species **4**. Low-level termination reactions in the polymerization are evidenced by the presence of smaller peaks corresponding to oligomers analogous to **5** and **6**.

Figure 6 shows the partial MALDI−TOF spectrum (using a [^{7}Li]$^+$ counterion) of PMMA (produced by ATRP) to which chain-transfer agent has been added (experiment A(ii) from Table 1). The sample is largely comprised of unsaturated species analogous to **5** [1521 (+1621) *m*/*z*], with lactonized species **4** [1507 (+1607) *m*/*z*] also present, but in significantly lower concentration. (The multiplicity of the peaks is due to the ^{13}C isotope pattern distribution.) These MALDI results therefore complement results obtained by NMR and TGA, indicating formation of predominantly unsaturated end group PMMA upon addition of Co(tpp).

It was hoped that the addition of a large amount of CCT agent would stop the polymerization and convert all polymer end groups from terminal halogens to the unsaturated type of polymer **5**. Molecular weights of final and initial polymers compare well, indicating that addition of CCT agent is effective, and ^{1}H NMR results show that there has been large-scale (about 85%) conversion to an unsaturated end group species. Elemental analysis results also show lower levels of chlorine in the PMMA macromonomer (experiment A(ii): Cl = 0.14%) than in PMMA produced by ATRP (experiment A(i): Cl = 0.96%, theoretical value assuming an M_n of 4100 is Cl = 0.87%). This predominance of unsaturated end groups is supported by the TGA and MALDI results. However, despite many efforts to increase this percentage, 85% conversion seems to be the upper limit for this method. MALDI results also indicate the presence of residual halide-capped chains (lactonized species **4** in Figure 6), and it may be that at this level of conversion the reaction equilibrium favors coordination of the cobalt species to smaller growing oligomeric chains (growing by means of conventional chain transfer) over coordination to the longer halide-capped chains. Alternatively, this may be due to CuCl coordinating to new radicals which have not yet been converted to unsaturated end group species by the CCT reagent. It should be emphasized that CoBF showed a markedly lower ability to convert the polymer chain ends in this instance (experiment C, Table 1), which may be due to its much lower solubility in the reaction mixture or may imply inactivation of the catalyst by halide coordination.

Table 2. Effect of Copper Catalyst on CCT Conversion Process under ATRP Conditions[a]

	ATRP (i)		Co(tpp)	ATRP + CCT (ii)		unsatd	unsatd
expt	$M_{n,i}$[b]	PD$_i$[c]	(mol %)[d]	$M_{n,f}$[e]	PD$_f$[c]	%, NMR[f]	%, TGA[g]
D	3000[h]	1.42	0.065	3800	1.42	0	0
E	3000[i]	1.42	0.060	3700	1.45	33.7	52
F	4650[k]	1.46	0.044	4150	1.45	74.4	71

[a] Initial polymer prepared by ATRP using CuCl/Bipy/ethyl 2-bromoisobutyrate [0.33/1/3.30 mol % relative to monomer] in 50% ethyl acetate solution (v/v) at 90 °C for 120 min. Filtered to remove catalyst, precipitated in hexane and dried. [b] M_n of initial polymer (before CCT agent added) by ^{1}H NMR. [c] Polydispersity by SEC. [d] Molar percent relative to MMA, added as solution in THF. [e] M_n of final polymer (after CCT agent added) by ^{1}H NMR. [f] Percentage unsaturated end groups calculated by ^{1}H NMR. [g] Percentage unsaturated end groups calculated by % weight loss at 225−275 °C, by TGA. [h] Polymer dissolved in 66% ethyl acetate solution at 90 °C. [i] Polymer dissolved in 66% ethyl acetate solution at 90 °C with CuCl/Bipy [1/3 mol % relative to repeat units of PMMA]. [j] 0.5 g polymer dissolved in 1 mL of ethyl acetate solution and 0.5 mL of MMA, at 90 °C with CuCl/Bipy [0.5/1.5 mol % relative to added MMA monomer].

To determine whether the presence of copper catalyst is necessary for conversion of PMMA−Cl/Br to the unsaturated end group species by CCT, a living PMMA polymer (which was shown to reinitiate qualitative addition of a second methacrylate block by ATRP) was isolated from a standard ATRP polymerization under similar conditions as described earlier. Copper was removed by filtration over alumina. A solution of this polymer in ethyl acetate was then added to either experiment D, just Co(tpp); experiment E, a mixture of CuCl, 2,2′-dipyridyl, and Co(tpp); or experiment F, a mixture of CuCl, 2,2′-dipyridyl, Co(tpp), and further MMA monomer (see Table 2).

In the absence of copper transition metal catalyst to coordinate to the halide at the end of the polymer chain and liberate a free radical species, experiment D, no conversion to the unsaturated end group species occurs. When catalyst is present (experiments E and F), conversion to unsaturated species occurs; however, the degree of conversion is dependent on the presence of MMA monomer to regenerate the active Co(III) catalyst by hydrogen transfer. For example, in experiment E, where no further monomer is added, the degree of conversion to unsaturated species is lower than seen earlier (experiments A and B, Table 1), whereas in experiment F, where MMA is added, the active Co(III) catalyst seems to be regenerated more effectively to

Table 3. Addition of Co(tpp) to Block Copolymers Prepared by ATR[a]

	ATRP (i)			ATRP + CCT (ii)	
expt	$M_{n,i}$[b]	PD_i[c]	Co(tpp) (mol %)[d]	$M_{n,f}$[e]	PD_f[c]
G	8580	1.34	0.78	8050	1.38
H	8520	1.44	0.21	9080	1.31

[a] Experiment G: P(MMA-*b*-BMA) prepared [65.1:34.9 mol % by ^{1}H NMR] by addition of BMA to PMMA macroinitiator (M_n = 4300, PD = 1.42, by SEC) in the presence of CuCl/Bipy [1/3 mol % relative to BMA], in ethyl acetate (50% v/v) at 90 °C. Co(tpp) reagent added after 120 min polymerization time of BMA monomer and stirred at 90 °C for further 120 min. Experiment H: P(BMA-*b*-MMA) prepared [56.4:44.6 mol % by ^{1}H NMR] by addition of MMA to PBMA macroinitiator (M_n = 5460, PD = 1.50, by SEC) in the presence of CuCl/Bipy [1/3 mol % relative to MMA], in ethyl acetate (50% v/v) at 90 °C. Co(tpp) reagent added after 120 min polymerization time of MMA monomer and stirred at 90 °C for further 180 min. [b] M_n of block copolymer (before CCT agent added) by SEC. [c] Polydispersity by SEC. [d] Molar percent of Co(tpp) relative to second monomer, added as solution in THF. [e] M_n of final polymer (after CCT agent added) by SEC.

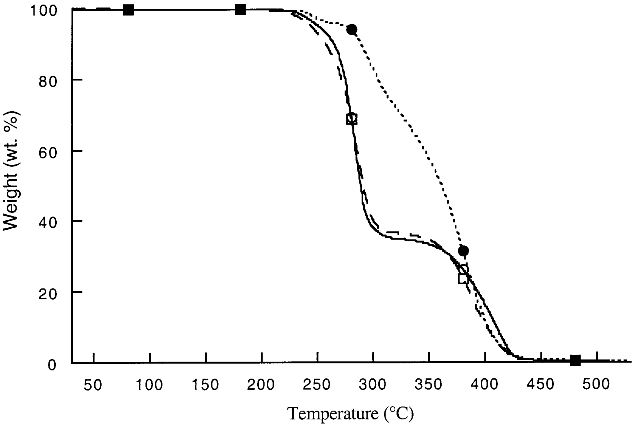


Figure 7. TGA's of polymers G(ii) (□), H(ii) (●), and P(BMA-*b*-MMA) (○) produced by ATRP.

Table 4. Copolymerization of PMMA Macromonomer with Ethyl Acrylate

expt	macro[a]	yield (%)[b]	$M_{n,f}$[c]	MMA_{th}[d] (%)	MMA_{NMR}[e] (%)	macro units[f]
J	A(ii)	100	28 800[g]	9.4	9.4	0.66
K	B(ii)	100	52 300[h]	22.8	23.4	2.91
M		98.0	204 100[i]	0	0	0

[a] Macromonomer according to Table 1 (A(ii): M_n = 4100, B(ii): M_n = 4200, by NMR). [b] Weight of final polymer as a percentage of the total macromonomer plus monomer in feed. [c] By SEC. [d] Theoretical weight percentage MMA in product (according to feed). [e] Observed weight percentage MMA in product (by ^{1}H NMR). [f] Macromonomer units per chain, as shown by NMR and SEC results. [g] Polymerization conditions: 0.48 mol % AIBN (relative to ethyl acrylate) in 60% xylene solution (v/v), at 60 °C for 72 h. [h] Polymerization conditions: 0.45 mol % AIBN (relative to ethyl acrylate) in 60% benzene solution (v/v), at 60 °C for 27 h. [i] Polymerization conditions: 0.41 mol % AIBN (relative to ethyl acrylate) in 65% benzene solution (v/v), at 60 °C for 60 h.

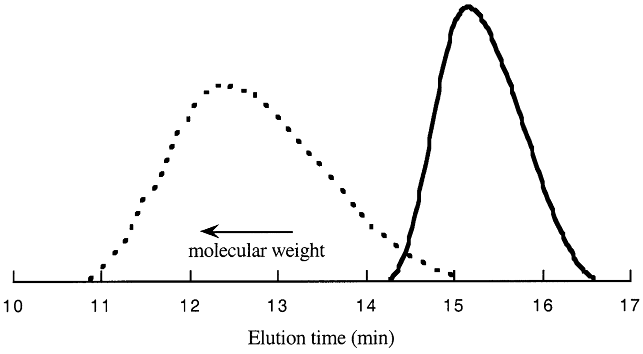


Figure 8. SEC trace of macromonomer A(ii) (—) and copolymer (- - -) with ethyl acrylate (experiment J).

increase the degree of conversion. Nevertheless, the degree of conversion in experiment F is still slightly lower than when Co(tpp) is added to a "live" polymerizing ATRP mixture, so the addition of further MMA monomer may be necessary to increase this value.

Addition of CCT Reagent to Methyl- and *n*-Butyl Methacrylate Diblock Copolymers. Two diblock copolymers, P(MMA-*b*-BMA) and P(BMA-*b*-MMA), were also converted into macromonomeric species. The macroinitiating block was prepared by ATRP under the conditions described above, filtered to remove catalyst, precipitated, and dried under vacuum. This polymer was subsequently used for the further polymerization of MMA or BMA by ATRP. The initiation of the second block appeared to go cleanly, and low polydispersity and monomodal GPC traces were found as would be expected. ^{1}H NMR studies of the final unsaturated block polymer require the terminal olefinic CH_2 signals to be visible above the noise region of the spectrum, so attempts were made to restrict each block to a weight of 5000 Da. The CCT catalyst was once again added as a concentrated THF solution after approximately 80% conversion of the second monomer (120 min).

Representative results can be seen in Table 3. Unfortunately, no quantitative value for percentage of unsaturated end groups per polymer chain was calculable by ^{1}H NMR, due to overlap of signals at 3.94 ppm (CO*OCH*$_2$, PBMA) and 4.08 ppm (CO*OCH*$_2$, initiating species). However, the terminal olefinic CH_2 signals at 6.20 and 5.47 ppm are visible, indicating the presence of unsaturated end groups. Conversion to an unsaturated end group species is also indicated by TGA results (Figure 7), although quantification is difficult.

Copolymerization of Macromonomers. Although the macromonomers were contaminated by a relatively small number of chains without unsaturated end groups, some copolymerizations were attempted. The isolated and purified macromonomers A(ii) and B(ii) (from Table 1) were then copolymerized with ethyl acrylate under standard free-radical polymerization conditions to give quantitative yields of graft copolymers and approximately correct molar (= weight in this case) ratios of MMA (δ 3.59, OCH_3) to EA (δ 4.10, OCH_2) by ^{1}H NMR as compared to the feed weight ratios (see Table 4). Poly(ethyl acrylate) homopolymer was also prepared under the same conditions as a control.

Note that values for numbers of macromonomer units per chain were calculated simply from the observed weight percentage of PMMA in the final polymer; e.g., for experiment J, 9.4 wt % of 28 800 Da is 2707 Da. The weight of the PMMA macromonomer is 4100 Da; hence, 2707/4100 = 0.66 macromonomer units per chain. Note also that all copolymers were collected by precipitation in cold methanol (ca. −70 °C), so that any unreacted macromonomer may be fractionated into the methanol layer.

SEC analysis shows no unreacted macromonomer in the copolymerization of macromonomer A(ii) (Figure 8), although a low level of unreacted macromonomer B(ii) is present in the second copolymerization (Figure 9), possibly due to the higher initial concentration of macromonomer (and corresponding, nonpolymerizable chains).

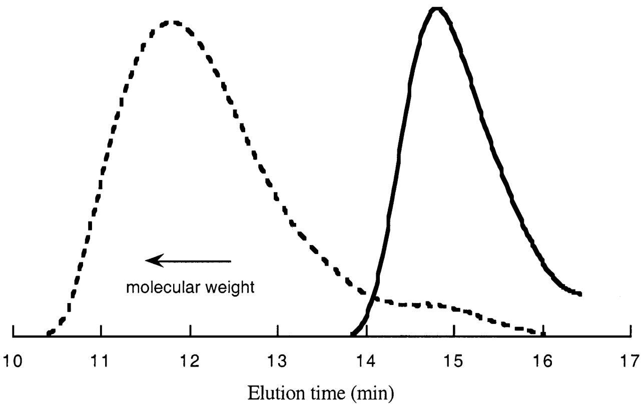


Figure 9. SEC traces of macromonomer B(ii) (—) and copolymer (- - -) with ethyl acrylate (experiment K) CCT mechanism producing an unsaturated end group on a methacrylate chain.

Observed molecular weights of the final copolymers by SEC (see Table 4) suggest that, at 10% weight incorporation of macromonomer, less than one macromonomer is present on average in each copolymer chain, while at higher levels of incorporation (30 wt %), up to three macromonomers may be present. However, it should be noted that any molecular weights obtained for these copolymers by SEC may be underestimations due to the probable smaller hydrodynamic volume of these polymers as compared to linear standards of the same molecular weight. For this reason we analyzed polymers prepared in experiments J−M by SEC with on-line light-scattering detection (SEC-LS) in order to obtain a more accurate estimate of weight-average molecular weight, M_w. Note that we assumed 100% recovery of injected mass when calculating M_w by SEC-LS, since dn/dc of the copolymers is unknown.

As we might expect, M_w values obtained by SEC and SEC-LS are in good agreement for linear PEA homopolymer prepared in experiment M (SEC: $M_w = 606\,200$; SEC-LS: $M_w = 626\,500$); however, the values are also in reasonable agreement for copolymer prepared in experiment J (SEC: $M_w = 102\,000$; SEC-LS: $M_w = 143\,700$), which seems to confirm our hypothesis that few macromonomers are incorporated per final polymer chain in this experiment. The difference in M_w obtained by the two analysis methods is more pronounced for copolymer prepared in experiment K, however (SEC: $M_w = 143\,000$; SEC-LS: $M_w = 358\,000$), which suggests that SEC underestimates this polymer's molecular weight, probably due to the incorporation of more macromonomer units per chain during the copolymerization with EA.

Nevertheless, the molecular weights of copolymers prepared in experiments J and K are considerably lower than that of the "control" polymer obtained upon the conventional free-radical homopolymerization of ethyl acrylate (experiment M), and these findings suggest that the macromonomer may be acting as fragmentation-transfer agents as well as conventional monomers under the present conditions.

Conclusion

Low molecular weight, narrow polydispersity PMMA polymers prepared by ATRP have been converted in high yield (85%) to the ω-unsaturated PMMA species by the addition of Co(tpp), in-situ to an ATRP reaction mixture. These species have been copolymerized successfully with ethyl acrylate using an azo-initiator with little or no sign of the original macromonomer. Narrow polydispersity diblock copolymers (of MMA and BMA) prepared by ATRP have also been converted to the corresponding unsaturated end group species by the addition of Co(tpp) in solution to a "live" reaction mixture.

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