Use of Methyl 2-(Bromomethyl)acrylate as a Chain-Transfer Agent To Yield Functionalized Macromonomers via Conventional and Living Radical Polymerizations

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ABSTRACT: The chain-transfer constants of methyl (2-bromomethyl)acrylate (MBrMA) in bulk polymerizations of methyl methacrylate (MMA) and styrene were determined at 70 °C using both the Mayo method ($1/DP_n$ as well as $2/DP_w$) and the chain-length-distribution procedure (Λ). The C_{MBrMA} values using $2/DP_w$ and Λ were consistent, i.e., 1.28 and 1.20 for MMA and 11.44 and 10.92 for styrene, respectively. MBrMA was used as a chain-transfer agent in the emulsion polymerization of MMA to yield an α-bromo-functionalized macromonomeric latex ($\langle M_n \rangle = 9.6 \times 10^3$ g mol^{-1}; PDI = 1.80), which was subsequently copolymerized with styrene to yield the corresponding poly(styrene-*graft*-MMA) copolymer. MBrMA was used as an addition−fragmentation agent in the living radical polymerization of MMA mediated by copper(I) bromide/*N*-(*n*-octyl)-2-pyridylmethanimine. In situ addition of a 5-fold equivalent of MBrMA and Cu(0) to this polymerization quenched the reaction and transformed the ω-bromide into the methacrylate-based macromonomer quantitatively.

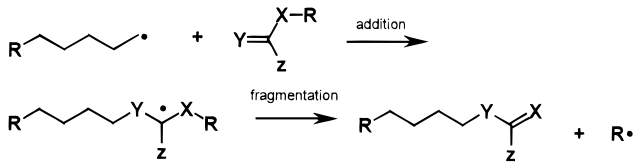
Introduction

In the past decade, addition−fragmentation reactions have received close attention in the field of radical polymerization.[1−3] The structure of the compound that undergoes addition and subsequent fragmentation determines the functionality introduced at the polymer chain ends (Scheme 1). Examples include vinyl ethers, allyl halides, allyl sulfides, allyl peroxides, etc. [4] A living radical polymerization[5] technique has recently been developed using reversible addition−fragmentation agents based on dithiocarboxylic esters, RAFT (Scheme 1, where X = Y = S).[6−9]

Kharasch et al. proposed an addition−fragmentation mechanism with allyl bromide (Scheme 1, with X = Y = C, Z = H, and R = Br) to explain results in photochemical studies on the addition of trichloromethyl radicals to olefins[10] and in studies on the thermal decomposition of diacetyl peroxide in refluxing allyl bromide.[11] This suggested that allyl bromide and similar compounds could be used as chain-transfer agents in radical polymerizations. Meijs[1,12] and Yamada[13−18] indeed showed that allyl bromide, methyl (2-bromomethyl)acrylate, and ethyl (2-bromomethyl)acrylate could be used to synthesize α-bromo- and ω-vinyl-functionalized polystyrene and poly(methyl methacrylate).

The overall rate coefficient for fragmentation of these types of chain-transfer agents is generally fast relative to propagation. Therefore, the radical species formed directly after the addition step is unlikely to propagate, and hence, the overall rate coefficient for chain transfer equals the rate coefficient of addition. Estimated values for the chain-transfer constants ($C_s = k_{tr}/k_p$) can be obtained from the reactivity ratios of the copolymerization of the monomer used in the polymerization and the nonhalogenated analogue of the addition−fragmentation, or chain-transfer, agent. For example, the chain-transfer constant of methyl (2-bromo methyl)acrylate

Scheme 1



will be close to one in the polymerization of methyl methacrylate (MMA). This produces a constant average molar mass throughout the entire polymerization process under batch conditions. The approximate number-average molar mass can be calculated from $[M]M_0/C_s[S]$ (in which C_s is the chain-transfer constant, M_0 is the molar mass of the monomer, and [M] and [S] are the concentration of monomer and chain-transfer agent, respectively), assuming that the production of dead polymer chains (permanent chain stoppage) is dominated by the chain-transfer process.

This paper investigates the chain-transfer constants for methyl (2-bromomethyl)acrylate (MBrMA) in the radical polymerization of methyl methacrylate (MMA) and styrene and its ability to act as an addition−fragmentation agent in the controlled synthesis of PMMA macromonomers in emulsion polymerization. The resulting macromonomeric latex was subsequently used as a seed in an emulsion copolymerization with styrene to produce a high molecular weight graft copolymer.

Furthermore, methyl (2-bromomethyl)acrylate (MBrMA) was used in transition-metal-mediated living radical polymerizations to replace the ω-halogen end group via addition−fragmentation to yield a methacrylate-based macromonomer. A more extended survey on the modification of the ω-terminus of polymers produced via metal-mediated living radical polymerization, while maintaining the polymerization conditions, has been reported elsewhere.[19]

Results and Discussion

Determination of C_s Values of Methyl (2-Bromomethyl)acrylate in Bulk Methyl Methacrylate

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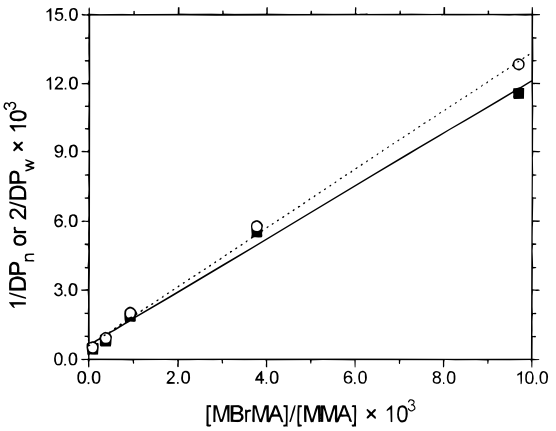

Figure 1. Mayo plot using $1/DP_n$ (■, —) and $2/DP_w$ (○, ···) for a bulk polymerization of methyl methacrylate (MMA) with methyl (2-bromomethyl)acrylate (MBrMA) at 70 °C.

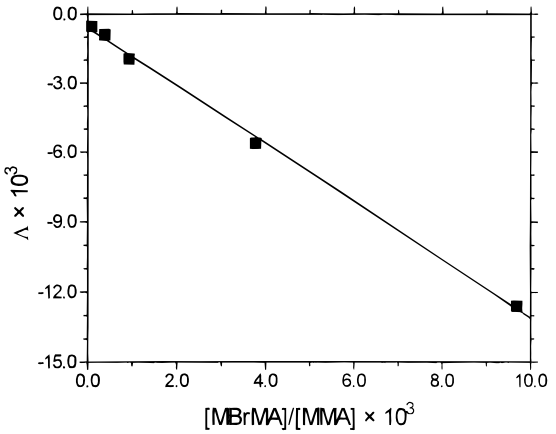

Figure 2. CLD plot for a bulk polymerization of methyl methacrylate (MMA) with methyl (2-bromomethyl)acrylate (MBrMA) at 70 °C.

Table 1. Chain-Transfer Constants of Methyl (2-Bromomethyl)acrylate (MBrMA) in Bulk Polymerizations of Methyl Methacrylate (MMA) and Styrene (Sty) at 70 °C

	Mayo		
	$1/DP_n$	$2/DP_w$	CLD
C_{MBrMA}(MMA)	1.15	1.28	1.20
C_{MBrMA}(Sty)	8.52	11.44	10.92

and Styrene Polymerizations. The chain-transfer constants, C_s, of methyl (2-bromomethyl)acrylate (MBrMA) were determined in bulk methyl methacrylate (MMA) and styrene (Sty) polymerization experiments at 70 °C. All polymerizations were stopped at conversions <1% in order to minimize feed composition drift. The C_{MBrMA} values were calculated from the molar mass data obtained with SEC analysis using the Mayo method[20,21] (using both the number-average degree, DP_n, and weight-average degree of polymerization, DP_w) and the chain-length-distribution (CLD) procedure[20,22−25] (using the slope determined from the high molar mass region with considerable signal intensity of ln(n(DP)), i.e. Λ,[26] see Supporting Information). Figures 1 and 2 present the results of the chain-transfer experiments in MMA in the form of $1/DP_n$, $2/DP_w$, and Λ vs [MBrMA]/[MMA]. The calculated C_{MBrMA}(MMA) values are given in Table 1. The results for the chain-transfer constants obtained from the styrene experiments, i.e., C_{MBrMA}(Sty), are also summarized in Table 1.

The C_{MBrMA} values calculated for MMA from the $1/DP_n$, $2/DP_w$, and the Λ data are relatively consistent, whereas for styrene the value obtained from the $1/DP_n$ data is approximately 20% less than from the $2/DP_w$ and the Λ data. This is as might be expected as DP_n values are more prone to baseline selection errors in determination by SEC.[20,26,27] Thus, $2/DP_w$ is preferred over $1/DP_n$ for determination of C_s by the Mayo method.

These chain-transfer constant values are significantly different to those reported by Yamada et al.,[15,16,18] who quoted C_{MBrMA}(MMA) = 0.93 and C_{MBrMA}(Sty) = 2.34, respectively. However, it is noted that they did not explicitly state that conversion was kept below 1%. We have indeed found that higher monomer conversions, especially in the case of styrene, markedly reduce the concentration of MBrMA and thus significantly lower the apparent values of the chain-transfer constant.

If the rate-determining step in the addition−fragmentation sequence is the actual addition of the polymeric radical to the C═C bond of MBrMA, then the cross-propagation values can be calculated (using k_p^{MMA} = 1.06 × 10^3 L mol^{-1} s^{-1},[28] k_p^{Sty} = 480 L mol^{-1} s^{-1},[29] and the CLD values of C_{MBrMA}) yielding $k_{MMA/MBrMA}$ = 1.27 × 10^3 L mol^{-1} s^{-1} and $k_{Sty/MBrMA}$ = 5.24 × 10^3 L mol^{-1} s^{-1}. The propagation kinetics of the copolymerization of styrene and MMA is described satisfactorily by the implicit penultimate model,[30] which implies that the cross-propagation coefficients can be calculated from the reactivity ratios (r values) obtained using the terminal model. A literature value of r_{Sty} = 0.49[31] leads to $k_{Sty/MMA}$ = 980 L mol^{-1} s^{-1}. Thus, MBrMA is 1.20 times more reactive than MMA toward a propagating PMMA radical and 5.35 times more reactive than MMA toward a propagating PSty radical. At face value this is inconsistent with the fact that the vinyl group has an increased nucleophilic character as a result of the presence of the electron-donating capability of the α-CH_2Br substituent. However, the α-CH_2Br group enhances radical stability (push−pull, or captodative effect[32]) which explains the higher rates of addition.

Addition−Fragmentation under Emulsion Polymerization Conditions. To determine the feasibility of using this type of addition−fragmentation agent in radical emulsion polymerizations so as to synthesize α-bromo-functionalized macromonomers, emulsion polymerizations of MMA were carried out in the absence and presence of methyl (2-bromomethyl)acrylate (MBrMA). Macromonomers with DP_n = 50 were targeted where MBrMA was used as chain-transfer agent. The MBrMA was added in one shot after a reaction time of ca. 5 min. This was carried out so as to form an in situ immature seed latex of high molar mass in order to shorten the nucleation period and to enhance the stability of the particles throughout the reaction. Experiments carried out in the presence of MBrMA yielded macromonomers with $\langle M_n \rangle$ = 9.6 × 10^3 and PDI = 1.80, approximately twice the targeted molar mass. This is ascribed to partitioning effects of the MBrMA between the aqueous and the organic phases (The partitioning coefficient of MBrMA was not determined.) Emulsion polymerization of MMA without addition of MBrMA yielded a stable latex with a molar mass of the order of 10^6 g mol^{-1}.

The olefinic protons from the unsaturated terminus of the macromonomeric latex were detected by ^{1}H NMR at 5.48 and 6.20 ppm (Figure 3). The methylene hydrogens next to the C═C bond are seen at 2.49 ppm.

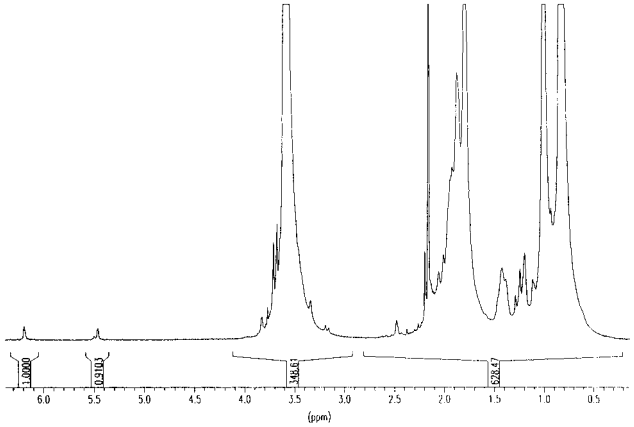

Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$) of the PMMA macromonomers prepared via emulsion polymerization.

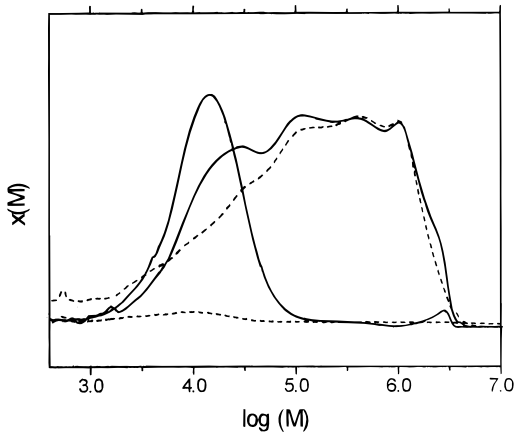

Figure 4. Differential log molecular weight distribution of both the PMMA macromonomeric latex and the PSty−PMMA graft copolymer (DRI detetction, —; UV detection at 254 nm, ···).

The calculated molar mass from NMR ($\langle M_n \rangle = 12 \times 10^3$) is in approximate agreement with the SEC results.

Copolymerization of Macromonomeric Seed Latex with Styrene. Copolymerization of these methacrylate macromonomers with methyl acrylate and styrene has been reported to lead to graft copolymers, whereas copolymerization with methacrylates results in reversible addition−fragmentation to yield block copolymers.[4] The first process is of interest so as to incorporate controlled amounts of hydrophilic monomers, such as 2-hydroxyethyl methacrylate and methacrylic acid, into the hydrophobic latex particles. We attempted to synthesize a graft copolymer, i.e., poly(styrene-*g*-MMA), via seeded emulsion polymerization by addition of a batch of styrene to the PMMA macromonomeric latex once conversion reached >90% (4 h). The resulting latex was stable with no marked coagulation. A graft copolymer between the macromonomers and styrene is formed (the high molar mass cutoff of this GPC system was ca. $10^{6.3}$ g mol^{-1}), with the final SEC plots of the PSty−PMMA graft copolymer together with the PMMA macromonomeric latex shown in Figure 4.

Use of Addition−Fragmentation in Transition-Metal-Mediated Living Radical Polymerization. Transition-metal-mediated living radical polymerizations generally produce polymer chains with a halogen ω-terminus. Addition−fragmentation agents may be used to transform these groups into a different, more useful, functionality. For example, Sawamoto et al.[33] has used a silyl enol ether as the addition−fragmentation agent to prepare ω-keto functionalized polymers. We thus investigated the use of methyl (2-bromomethyl)-acrylate as an addition−fragmentation agent to synthesize methacrylate-based macromonomers, when added under living radical polymerization conditions to polymers produced by Cu(I)Br/*N*-(alkyl)pyridylmethanimine-mediated polymerization.[34,35] Two identical polymerizations were carried out using MMA as monomer and α-bromoisobutyric acid phenyl ester as the halogen initiator. After 45 min one of the polymerizations had an aliquot of methyl (2-bromomethyl)acrylate introduced ($[MBrMA]/[MMA]_{t=0} = 0.02$ and $[MBrMA]/[I] = 2$). Both polymerizations were stopped after 4 h to yield a PMMA of $\langle M_n \rangle = 3125$ and PDI = 1.11 for the experiment to which the addition−fragmentation agent was added and a polymer having $\langle M_n \rangle = 6970$ and PDI = 1.09 for the conventional living radical polymerization experiment.

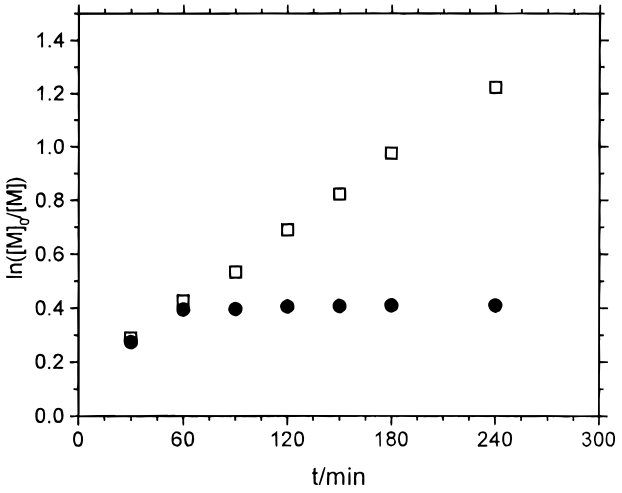

Figure 5. Ln($[M]_0/[M]$) vs time of the atom transfer polymerization of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[*n*-oct]/[I] = 100:1:2:1, with (●) and without (□) addition of 2 equiv of methyl (2-bromomethyl)acrylate (MBrMA) after 45 min.

The first-order kinetic plots of these reactions (Figure 5) show that the addition−fragmentation reaction completely quenches the polymerization. This efficient quenching of the reaction may be caused by either (1) quantitative addition and subsequent fragmentation of MBrMA and/or (2) elimination of bromine radicals as a direct result of the addition−fragmentation process and subsequent production of copper(II) species. The first possibility consumes the ω-bromo species that initiates living radical polymerization, whereas the second process shifts the equilibrium of reversible chain-activation toward the dormant side. This decreases the probability of addition, of both methyl (2-bromomethyl)acrylate and MMA, and thus would lead to a partial end-capping of the polymer chains. The first possibility cannot fully explain the quenching of the reaction, since the rates of addition of MMA and MBrMA to an active polymer chain should be similar (note: $C_s = 1.20$ at 70 °C). Hence, no instantaneous quenching of MMA consumption is likely to occur. Formation of precipitate with an associated color change, from dark brown to green, indicates that Cu(II) species are being formed upon addition of MBrMA. ^{1}H NMR confirms that the production of Cu(II) species are the reason for this observed quenching. The intensities of the vinylic resonances at 6.18 and 5.45 ppm are only minor peaks with the ultimate unit of the PMMA polymer chain, i.e., (H_3C)-

$CBrCO_2Me$, still being clearly visible, 3.77 ppm. The relative intensities correspond to less than 10% transformation into the corresponding macromonomer structure.

To compensate for the shift in the equilibrium toward the dormant R−Br species, as a result of Cu(II) formation, reactions were repeated, with 2 equiv of MBrMA *and* Cu(0) (with respect to the initial amount of CuBr) added. Matyjaszewski[36] and Percec[37] have shown that Cu(0) reduces $Cu(II)Br_2$ to 2Cu(I)Br, independent of the activation−deactivation equilibrium, thereby shifting the equilibrium back toward active polymer chains.

This ultimately increased the amount of MBrMA addition. The final polymer showed an $\langle M_n \rangle$ of 6340 with a PDI of 1.28. Both values are higher in comparison with those from the polymer obtained in absence of Cu(0). This is accounted for by competitive rates for addition of MMA, which will lead to further growth of the polymer chains, and addition of MBrMA, producing the permanent terminated macromonomer. Figure 6a ($\ln([M]_0/[M]$ vs time) and Figure 6b ($\langle M_n \rangle$ and PDI vs conversion) indeed show that the polymerization is not quenched instantaneously.

We have tentatively assigned the ^{1}H NMR resonances at 5.45 and 6.18 ppm to the vinylic protons of the macromonomer. Integration of both the vinylic resonances and the terminal methoxy signal at 3.71 ppm showed a ratio of $^1/_3$, as expected for quantitative conversion (see Figure 7).

The polymerization was repeated using 3, 4, and 5 equiv of both MBrMA and Cu(0) in order to favor the addition of MBrMA over the addition of MMA and hence give better control of $\langle M_n \rangle$ and polydispersity of the macromonomeric product, by inducing rapid quenching. Figure 6a,b shows that the rate of quenching of the living radical polymerization increases with increasing the amounts of both MBrMA and Cu(0). ^{1}H NMR and SEC analysis of the final polymer product using 5 equiv of both MBrMA and Cu(0) confirms that the ω-bromide is quantitatively transformed into the macromonomeric structure ($\langle M_n \rangle$ = 3540 and PDI = 1.25).

Conclusions

Methyl (2-bromomethyl)acrylate (MBrMA) is an efficient chain-transfer agent operating via an addition−fragmentation sequence. α-Bromo-functionalized PMMA macromonomers were prepared via emulsion polymerization and were used to synthesize a graft polymer, i.e., poly(styrene-*g*-MMA), by emulsion copolymerization under seeded conditions. Finally, the ω-bromo end group of polymers prepared via living radical polymerization were transformed quantitatively in situ into methacrylate-based macromonomers in the presence of excess amounts of Cu(0) and MBrMA.

Experimental Section

General Data. All reactions were carried out using standard Schlenk techniques under an inert atmosphere of oxygen-free nitrogen, unless otherwise stated. Molar mass distributions were measured using size exclusion chromatography (SEC), on a system equipped with two PL gel 5 μm mixed C-columns (300 × 7.5 mm) and one PL gel 5 μm guard column (50 × 7.5 mm) (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran at 1.0 mL min^{-1} as the eluent. Poly(MMA) standards (1 × 10^6−200 g mol^{-1}) and polystyrene standards ((3.1 × 10^6−560 g mol^{-1}) were used to calibrate the SEC. The analyzed samples contained (0.2% vol) toluene as an internal standard, and flow marker. Monomer conversions were determined gravimetrically. ^{1}H and ^{13}C spectra were recorded on Bruker DPX 300 or ACF-400 spectrometers in chloroform-*d* at ambient temperature, using $SiMe_4$ as an external standard.

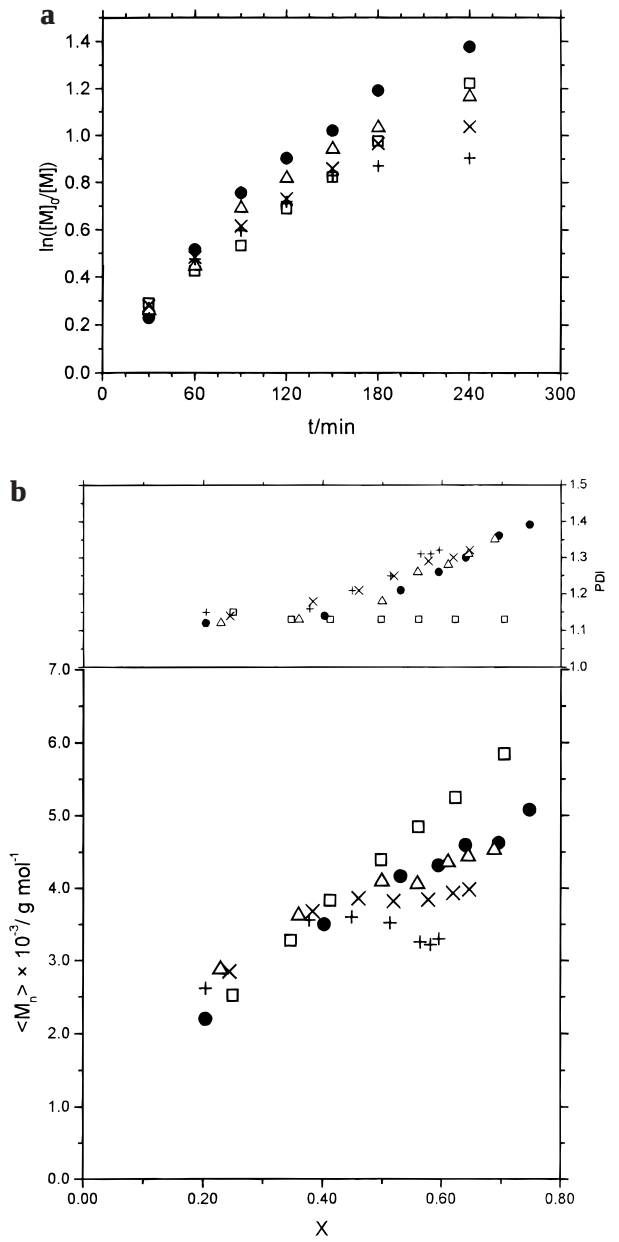

Figure 6. (a) $\ln([M]_0/[M])$ vs time of the atom transfer polymerization of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[*n*-oct]/[I] = 100:1:2:1, with addition of 0 (□), 2 (●), 3 (△), 4 (×), and 5 equiv (+) of methyl (2-bromomethyl)acrylate (MBrMA) and Cu(0) after 45 min. (b) $\langle M_n \rangle$ and PDI vs MMA conversion (X) of the atom transfer polymerization of MMA in xylene at 90 °C, [MMA]/[Cu(I)Br]/[*n*-oct]/[I] = 100:1:2:1, with addition of 0 (□), 2 (●), 3 (△), 4 (×), and (+) 5 equiv of methyl (2-bromomethyl)acrylate (MBrMA) and Cu(0) after 45 min.

Chemicals. Methyl (2-hydroxymethyl)acrylate was prepared using a variation of the reported procedure for ethyl (2-hydroxymethyl)acrylate by Hoffmann et al.[38] Methyl (2-bromomethyl)acrylate was prepared by slight variation of the procedure reported by Villieras et al.[39] Methyl acrylate was dried over 3 Å molecular sieves prior to use. Methyl methacrylate (Aldrich, 99%) was passed over a short column of activated basic alumina (Aldrich, Brockmann I, standard grade) to remove its inhibitor prior to use. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff.[40] *N*-(*n*-Octyl)-2-pyridylmethanimine was prepared as reported previously.[34] α-Bromoisobutyric acid phenyl ester

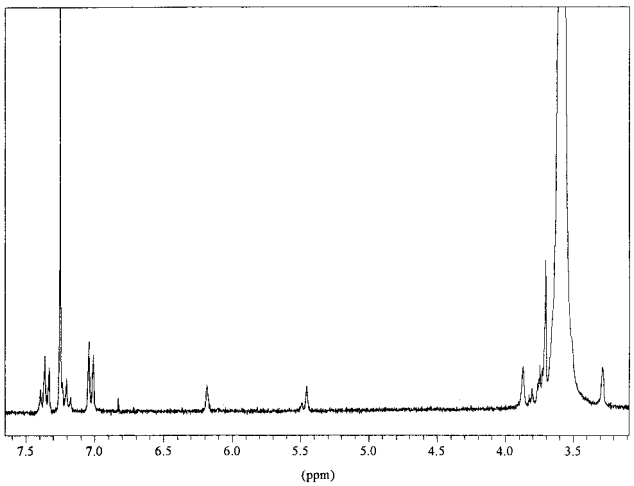

Figure 7. ^{1}H NMR (300 MHz, $CDCl_3$) of PMMA macromonomer terminated with 2 equiv of methyl (2-bromomethyl)-acrylate (MBrMA) and 2 equiv of Cu(0).

was prepared as reported previously.[41] All other standard chemicals were purchased in analytical grade from ACROS or Aldrich and were used without further purification.

Methyl (2-Hydroxymethyl)acrylate. This reaction required dry conditions and an inert atmosphere. A mixture of methyl acrylate (500 mL, 5.55 mol), anhydrous dimethyl sulfoxide (50 mL), paraformaldehyde (83.52 g), and 1,4-diazabicyclo[2,2,2]-octane (31.07 g, 0.28 mol) was stirred (1 L round-bottom flask) at 55 °C for 12 h. Next, the reaction mixture was cooled to room temperature, diethyl ether (300 mL) was added, and the mixture was washed with 1% aqueous HCl (3 × 100 mL). The aqueous layers were combined and extracted with diethyl ether (200 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the crude product was obtained by filtering off the $MgSO_4$ and removing diethyl ether and unreacted methyl acrylate by rotary evaporation. Distillation under reduced pressure (0.1 Torr, 43 °C) yielded 156.3 g (24.3%) of methyl α-hydroxy methacrylate as a transparent liquid.

^{1}H NMR ($CDCl_3$): δ 2.87 (br s, 1H, O*H*), 3.73 (s, 3H, OCH_3), 4.27 (m, 2H, CH_2OH), 5.81 and 6.21(each dd, 1H, H*H*C=). ^{13}C NMR ($CDCl_3$): δ 51.7, 61.6, 125.3, 139.3, 166.6 (C=O). IR (liquid ATR Cell): 3422 (br) (O−H) 2954, 1713 (C=O), 1635, 1438, 1392, 1306, 1271, 1196, 1152, 1051, 948, 817, 687. Anal. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94. Found: C, 51.58; H, 6.94.

Methyl (2-Bromomethyl)acrylate (MBrMA). This reaction required dry conditions and an inert atmosphere. To a cooled, −4 °C, solution of methyl (2-hydroxymethyl)acrylate (58.05 g, 0.50 mol) and anhydrous diethyl ether (250 mL) (500 mL round-bottom flask, using an ice/NaCl bath), phosphorus tribromide (23.5 mL, 0.25 mol) was added dropwise (30 min). A white precipitate formed, and the reaction was stirred for 3 h and allowed to warm to room temperature. The solution was then cooled again to −4 °C, and water (50 mL) was cautiously added dropwise. This resulted in evolution of HBr. After adding water (100 mL), the resulting solution was extracted into hexane (3 × 200 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. The $MgSO_4$ was filtered off, and the crude product was obtained by removing the solvent by rotary evaporation. Methyl (2-bromomethyl)acrylate was purified by distillation under reduced pressure (43 °C, 1.0 Torr) as a slightly yellowish liquid. Yield = 65.4 g (73%).

^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H), 4.15 (m, 2H), 5.93 (m, 1H), 6.31(m, 1H). ^{13}C NMR ($CDCl_3$): δ 29.0, 51.8, 128.8, 137.0, 164.7 (C=O). IR (liquid, ATR Cell): 2952, 1721 (C=O), 1631, 1439, 1397, 1334, 1313, 1222, 1196, 1171, 1117, 993, 957, 832, 811, 719. Mass Spectroscopy (+EI) (*m*/*z*): 180, 178, 149, 123, 121, 99, 69, 59. Anal. Calcd for $C_5H_7O_2Br$: C, 33.55; H, 3.94. Found: C, 33.55; H, 3.89.

Determination of Chain-Transfer Constants. The polymerizations were carried out using standard Schlenk techniques with three freeze−pump−thaw cycles. AIBN was used as free radical initiator at 1.2×10^{-3} mol L^{-1}. Polymerizations were carried out at 70 °C for less than 10 min to keep the conversion <1%. Small reaction volumes and proper mixing by shaking restricted the warm-up period to less than 30 s. The chain-transfer constants were determined from the SEC data, using both the number- and weight-average degree of polymerization and applying the classical Mayo method: [20,21]

$$\frac{2}{\mathrm{DP_w}} \text{ or } \frac{1}{\mathrm{DP_n}} = \frac{1}{\mathrm{DP_0}} + C_s \frac{[\mathrm{S}]}{[\mathrm{M}]}$$

Alternatively, the chain-length-dependent (CLD) method was used.[20,22−25]

$$\Lambda = \Lambda_0 - C_s \frac{[\mathrm{S}]}{[\mathrm{M}]}$$

in which Λ is the slope of linear fit on the high molar mass part of ln[*n*(DP)] (natural logarithm of the number molar mass distribution as a function of the degree of polymerization) with significant signal intensity.[26] See Supporting Information.

All fitting procedures were carried out with an $ax + b$ relationship using a NLLS method.

Emulsion Polymerizations. Reactions were carried out under a nitrogen atmosphere. MMA and styrene were deoxygenated by purging with nitrogen for at least 2 h prior to use. Methyl (2-bromomethyl)acrylate (MBrMA) was deoxygenated via three freeze−pump−thaw cycles. Distilled and deionized water, stored under and continuously purged with nitrogen, was used.

A typical recipe for the macromonomer synthesis has MMA/water 0.11 g/g, MBrMA/MMA 3.57×10^{-2} g/g, sodium dodecyl sulfate 5.14 mmol L^{-1}, $NaHCO_3$ 4.41 mmol L^{-1}, and $((NH_4)_2SO_4)_2$ 3.25 mmol L^{-1}. Reactions were carried out on a 0.5 L scale in a 1 L flange flask glass reactor at 60 °C using turbine impeller at 150 rpm under a nitrogen atmosphere. Ab initio conditions were applied, except for the addition−fragmentation agent, MBrMA, which was added as a single shot after 5 min of reaction time. Total reaction time was 4 h.

The graft copolymerizations in emulsion were carried in a semicontinuous way. First, the marcomonomeric PMMA seed latex was prepared, as reported above. Next, after a reaction period of 4 h, a single shot of styrene (Sty/solids content: 0.20 g/g) was added, and the reaction was allowed to proceed overnight (at 60 °C).

No marked coagulation was observed, and the resulting latexes were stable upon storage.

Living Radical Polymerizations. Polymerization reactions were carried out at 90 °C using *N*-(*n*-octyl)-2-pyridylmethanimine as bidentate ligand for copper complexation. A typical polymerization recipe is based on 30 vol % monomer in xylene. The ratio of initiator:CuBr:ligand is 1:1:2 on a molar basis. The specific amounts of initiator (9.34×10^{-4} mol), monomer (10 mL), xylene (20 mL), and ligand (1.86×10^{-3} mol) were charged into a Schlenk and placed under an inert nitrogen atmosphere via three freeze−pump−thaw cycles (pressure $<10^{-2}$ mbar). Next this mixture was transferred into a Schlenk containing CuBr (9.34×10^{-4} mol) under a nitrogen atmosphere. The reaction mixture was placed in an oil bath at 90 °C and left for an overall reaction time of 4 h. The specific amounts of methyl (2-bromomethyl)acrylate (MBrMA) and Cu-(0) were added after 45 min (Supporting Information). In the case of addition of MBrMA solely 30 min after the addition of MBrMA, the reaction medium had turned green in color, and a dark green precipitate had started to fall out of solution. Samples were quenched in liquid nitrogen and passed over a basic alumina column prior to analysis using tetrahydrofuran as eluent to remove the copper and ligands. Final polymer products were further purified by precipation from a THF solution in *n*-heptane. See also Supporting Information.

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Supporting Information Available: The molar mass distribution data relevant for the calculation of the chain-transfer constants, i.e., the number- and weight-average molar masses, [MBrMA]/[monomer], and the linear fits on the high molar mass part of ln[*n*(DP)] with significant signal intensity, as well as the conversion vs time and molar mass distribution details for the atom transfer polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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