Modification of the ω-Bromo End Group of Poly(methacrylate)s Prepared by Copper(I)-Mediated Living Radical Polymerization

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ABSTRACT: Four different approaches to introduce a specific functional group at the ω terminus of poly(methacrylate)s (PMMAs) prepared via copper(I)bromide/pyridinalimine-mediated atom transfer polymerization, under polymerization conditions, are reported. Method 1 involves the homolysis of the ω-C—Br bond with a subsequent reaction, via coupling or disproportionation, with an external radical species. The reaction with 2,2,6,6-tetramethylpiperidin-*N*-oxyl shows a high conversion (>78%) of the ω-bromo PMMA chains into their corresponding macromonomer analogues. Method 2 utilizes monomers that are able to undergo radical addition followed by subsequent fragmentation. Reactions with trimethyl[1-(trimethylsiloxy)phenylethenyloxy]silane and allyl bromide show quantitative and 57% transformation, respectively. Method 3 is the reaction of a monomer that yields a relatively more stable secondary, or primary, carbon–halogen bond. Reactions with divinylbenzene, *n*-butylacrylate, and ethylene showed quantitative, 62%, and quantitative additions, respectively. Method 4 is the addition of nonhomopropagating monomers, that is, maleic anhydride. This reaction proceeds quantitatively. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2678–2686, 2000

Keywords: living radical polymerization; copper(I); end-group modification; poly(methacrylate)s

INTRODUCTION

The design and development of living radical polymerization techniques is one of the most important contributions of the last decade to the field of chain-growth polymerization. These novel polymerization techniques, such as nitroxide-mediated living radical polymerization,[1–5] metal-mediated atom transfer polymerization,[6–14] and reversible addition fragmentation,[15,16] all show control over the molecular weight distribution (MWD) to produce polymers with a low polydispersity index (PDI). Facile synthesis of functional halogen initiators for atom transfer polymerization has been shown to be extremely useful in designing molecules of complex composition and topology.[17–21] This leads to polymers with α-terminal functionality derived from the initiator. However, the quantitative formation of ω functionality by chemical transformation of the halide, which is typically present in this type of process, has not met with as much success.

Little work has been carried out on the modification of the carbon–halogen at the ω terminus of polymers produced by atom transfer polymerization under conditions similar to those for the polymerization reactions. This would allow these

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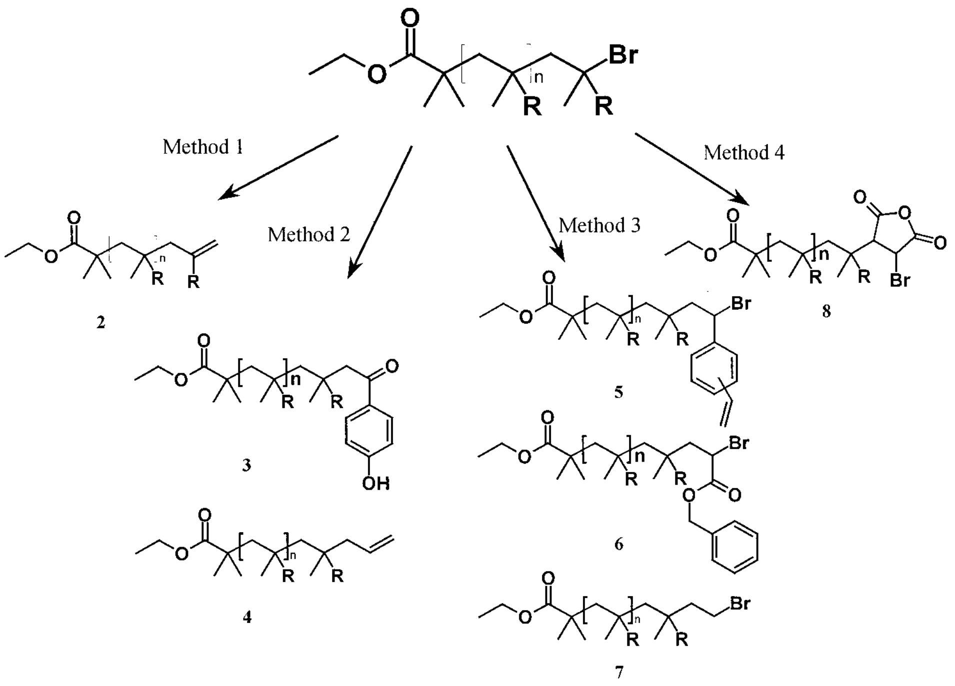


Scheme 1

transformations to be performed *in situ*, thus facilitating the process. Perhaps the most successful report to date has been by Sawamoto et al.,[22] who made use of silyl enol ethers, α-(trimethylsiloxy)styrene and *p*-methoxy-α-(trimethylsiloxy)-styrene, as efficient terminators, yielding ω-ketone end-functional polymers. During the period of this study, Kallitsis et al.[23] showed the terminal functionalization of polystyrene, prepared via metal-mediated living radical polymerization, with maleic anhydride. Matyjaszewski reported ω dehalogenation with tributyltin hydride,[24] the introduction of an allyl group with allyltri-*n*-butylstannane, and the use of 1,2-epoxy-5-hexene and allylalcohol as nonreactive monomers to introduce corresponding functionalities.[25]

Herein, we report several examples of addition reactions, classified as four different approaches, that introduce a specific functional group at the ω terminus of poly(methacrylate)s (PMMAs) prepared via copper(I)bromide/pyridinalimine-mediated atom transfer polymerization (see Scheme 1).

The first approach (Method 1) involves the homolysis of the ω-C—Br bond with a subsequent reaction, via coupling or disproportionation, with an external radical species. For example, the previously mentioned reactions carried out with organotin compounds[24] are classified under this approach. Our work comprises the use of 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) as a scavenger for the carbon-centered radical species formed subsequent to carbon–halogen-bond homolysis. For tertiary carbon-centered radicals with an α-methyl group, trapping via disproportionation is competitive with coupling with TEMPO, the latter of which is a reversible process. This ultimately leads to the quantitative formation of a macromonomer and the corresponding hydroxylamine.

Method 2 utilizes monomers that are able to undergo radical addition followed by subsequent fragmentation. Trimethylsilyl enol ethers as quenchers for this type of reaction, previously reported by Sawamoto et al.[22] to yield polymers with ω-ketone functionality and the corresponding trimethylsilyl halide as a byproduct, are examples of this. Following this approach, we prepared a functional silyl enol ether, trimethyl[1-(trimethylsiloxy)phenylethenyloxy]-silane, that ultimately yields, after removal of the trimethylsilane protective group, phenolic end-functional polymers.

The use of allyl bromide as a quencher for atom transfer polymerization is based on the work of Kharasch and coworkers, who proposed the addition-fragmentation mechanism for allyl bromide to explain their results (1) in photochemical studies on the addition of trichloromethyl radicals to olefins[26] and (2) in studies on the thermal decomposition of diacetyl peroxide in refluxing allyl bromide.[27] Their work suggested that vinylic compounds with an α-CH_2Br substituent could be used as chain-transfer agents in free-radical polymerizations. Meijs et al.[28–32] and Yamada et al.[33–35] showed that allyl bromide, methyl α-bromo methacrylate, and ethyl α-bromo methacrylate can be used to synthesize α-bromo ω-vinyl functionalized poly(styrene) and poly(methyl methacrylate) by chain transfer in conventional free-radical polymerization. The reaction with allyl bromide under similar conditions yields an allyl-functionalized polymer material as a result of its addition and subsequent fragmentation, that is, the elimination of a bromide radical.

Method 3 involves the reaction of a functional monomer that yields a relatively more stable secondary, or primary, carbon–halogen bond, which is unable to undergo propagation/homolysis under the polymerization conditions. A marked difference in the rate of dissociation of the starting tertiary C—Br species and a secondary or primary C—Br that is formed after monomer addition allows a single propagation step when the reaction conditions are optimized at ambient temperatures. The aforementioned use of 1,2-epoxy-5-hexene and allyl alcohol falls under this category.[25]

Method 4 is closely related to method 3; in this case, however, monomers are used that are not capable of homopropagation under normal free-radical polymerization conditions, such as maleic anhydride and *N*-phenylmaleimide.

EXPERIMENTAL

Analysis and General

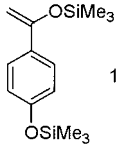
All manipulations were performed with standard Schlenk or syringe techniques under an atmosphere of nitrogen. NMR spectra were recorded on Bruker AC250, DPX 300, and AC400 spectrometers. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer fitted with an attenuated total reflection cell, and mass spectra were measured on a Kratos MS80 spectrometer. The catalyst was removed from the samples for molecular weight analysis by being passed through a column of activated basic alumina. MWDs were measured with size exclusion chromatography (SEC) on a system equipped with a guard column and one mixed E column (Polymer Laboratories) via differential refractive index detection with tetrahydrofuran (THF) at 1 mL min^{-1} as an eluent. PMMA standards ranging from 6×10^4 to 200 g mol^{-1} were used to calibrate the SEC.

Reagents

Methyl methacrylate (Aldrich; 99 %) was purified by being passed through a column of activated basic alumina to remove the inhibitor. Copper(I)-bromide (Aldrich; 98 %) was purified according to the method of Keller and Wycoff;[36] *N*-(*n*-propyl)-2-pyridylmethanimine and *N*-(*n*-octyl)-2-pyridylmethanimine were prepared as described earlier.[14] All other reagents were obtained from Aldrich and used without further purification.

Synthesis of Trimethyl[1-(trimethylsiloxy)phenylethenyloxy]silane (1)

4′-hydroxyacetophenone (1.00 g) in 100 mL of THF was cooled to −78 °C, and 2.3 molar equivalents of 2 M lithium diisopropyl amide in THF/hexane was added dropwise. The mixture was stirred for 2 h, after which 2.3 molar equivalents of chlorotrimethylsilane was added slowly. After addition, the mixture was stirred overnight and allowed to reach room temperature. The product was isolated by being passed through the solution over celite, and subsequently the solvents were removed *in vacuo*. The crude product was dissolved in anhydrous pentane and passed over celite a second time. The volatiles were removed *in vacuo*, and the product was finally obtained in its pure form by distillation:



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^{1}H NMR ($CDCl_3$, 298 K, 300 MHz, δ): 7.53 (d, 2H, J = 8.85 Hz), 6.84 (d, 2H, J = 8.85), 4.84 (s, 1H), 4.38 (s, 1H), 0.31 (s, 18H). ^{13}C NMR ($CDCl_3$, 298 K, δ): 155.8, 131.0, 128.2, 126.7, 119.8, 90.0, 0.3.

Preparation of Tertiary Bromide-Terminated PMMA

This was synthesized with standard atom transfer polymerization methodology with a targeted degree of polymerization of 30; with 50 mL of [M]/[I]/[Cu]/[L], 8.1 mL of ethyl-2-bromoisobutyrate, 4.47 g of Cu(I)Br, and 8.8 mL of *N*-(*n*-propyl)-2-pyridylmethanimine (30/1/1/2, respectively); at 90 °C; for 110 min; and with a 78% conversion. The reaction was quenched via freezing in liquid nitrogen. After removal of the copper catalyst through passing over activated basic aluminum oxide and subsequent precipitation into pentane, gel permeation chromatography analysis showed that the polymer had an $\langle M_n \rangle$ of 3450 and a PDI of 1.16.

^1H NMR ($CDCl_3$, 323 K, 400 MHz, δ, ppm): 3.95–4.10 (m, 2H, α-OCH_2CH_3), 3.65–3.80 (s, 3H, ω-OCH_3), 3.45–3.60 (s, 3nH, OCH_3), 1.65–2.05 (m, 3nH, CH_3), 1.15–1.23 (s, 3H, α-OCH_2CH_3), 0.86–1.07 (s, 2x, CH_3 of initiator), 0.5–1.5 (m, CH_2 backbone).

Less than 5% of the ω-unsaturated material was observed [there were resonances at δ 6.16–6.22 (s, 1H, *H*HC=), 5.43–5.54 (m, 1H, H*H*C=) ppm] because of permanent chain stopping reactions, such as ordinary bimolecular termination by disproportionation.

Reaction of PMMA from Atom Transfer Polymerization with TEMPO

TEMPO (1.42 g), Cu(I)Br (0.132 g), *N*-(*n*-propyl)-2-pyridylmethanimine (0.28 mL), and ω-bromo PMMA (3.0 g) in 10 mL of toluene were stirred at 90 °C for 3 h.

^1H NMR ($CDCl_3$, 323 K, 400 MHz, specific resonances, δ, ppm): 6.16–6.22 (s, 1H, *H*HC=, $I = 15.17$), 5.43–5.54 (m, 1H, H*H*C=, $I = 16.15$), 4.00–4.25 (m, 2H, α-OCH_2CH_3, $I = 39.99$), 3.70–3.75 (s, 3H, ω-OCH_3), 3.35–3.85 (s, 3nH, OCH_3), 2.42–2.71 (m, 2H, ω-CH_2 backbone, $I = 30.97$). Yield: 77.9%.

Reaction of PMMA from Atom Transfer Polymerization with 1

1 (2.25 g), Cu(I)Br (0.132 g), *N*-(*n*-propyl)-2-pyridylmethanimine (0.28 mL), and ω-bromo PMMA (3.0 g) in 10 mL of toluene were stirred at 90 °C for 3 h.

^1H NMR (DMSO-d_6, 323 K, 400 MHz, specific resonances, δ, ppm): 9.45 (s, 1H, OH), 7.75–7.85, 6.80–6.90 (each d, 2H, Ph), 4.01–4.12 (m, 2H, α-OCH_2CH_3). Yield: ca. 100%.

Reaction of PMMA from Atom Transfer Polymerization with Allyl Bromide

Copper powder (0.30 g), Cu(I)Br (0.1316 g), *N*-(*n*-propyl)-2-pyridylmethanimine (0.28 mL), and ω-bromo PMMA (3.0 g) in 10 mL of toluene and 8 mL of allyl bromide were stirred at 50 °C for 24 h.

^1H NMR ($CDCl_3$, 323 K, 400 MHz, specific resonances, δ, ppm): 5.42–5.72 (m, 1H, $H_2C{=}CH$—, $I = 2.53$), 4.84–5.06 (m, 2H, $H_2C{=}CH$—, $I = 4.53$), 3.93–4.13 (m, 2H, α-OCH_2CH_3, $I = 8.23$), 3.35–3.90 (s, 3nH, OCH_3). Yield: 57.2%.

Reaction of PMMA from Atom Transfer Polymerization with Divinylbenzene

Cu(I)Br (0.132 g), *N*-(*n*-octyl)-2-pyridylmethanimine (0.42 mL), and ω-bromo PMMA (3.0 g) in 20 mL of toluene and 13 mL of divinylbenzene were stirred at 25 °C for 24 h.

^1H NMR (DMSO-d_6, 323 K, 400 MHz, specific resonances, δ, ppm): 6.91–7.60 (m, 4H, Ph) and 6.61–6.86 (m, 1H, $H_2C{=}CH$—) total $I = 2.50$, 5.68–5.95 (m, 1H, *H*HC=CH—), 5.10–5.39 (m, 1H, H*H*C=CH—, $I = 0.52$), 4.00–4.14 (m, 2H, α-OCH_2CH_3, $I = 1.00$). Yield: ca. 100%.

Reaction of PMMA from Atom Transfer Polymerization with Benzyl Acrylate

Cu(I)Br (0.132 g), *N*-(*n*-octyl)-2-pyridylmethanimine (0.42 mL), and ω-bromo PMMA (3.0 g) in 20 mL of toluene and 14 mL of benzyl acrylate were heated at 25 °C for 24 h. Experiment 2 was performed as experiment 1 with 1.4 mL of benzyl acrylate, experiment 3 was performed as experiment 1 with 0.100 g of Cu(I)Br and 0.0442 g of Cu(II)Br_2 for 4 h at 60 °C, and experiment 4 as was performed as experiment 1 with 0.065 g of Cu(I)Br and 0.1005 g of Cu(II)Br_2 for 4 h at 60 °C.

^1H NMR ($CDCl_3$, 323 K, 400 MHz, specific resonances, δ, ppm): 7.06–7.41 (m, 5H, Ph), 5.05–5.20 (s, 2H, benzylic), 4.14–4.34 (m, 1H, ω-C*H*Br), 3.93–4.13 (m, 2H, α-OCH_2CH_3, $I = 1.00$). Yield (experiment 1): 266.6%. Yield (experiment 2): 56.9%. Yield (experiment 3): 62.3%. Yield (experiment 4): 23.4%. (Note that a 100% yield means, on average, the addition of one single unit of benzyl acrylate.)

Reaction of PMMA from Atom Transfer Polymerization with Ethylene

Cu(I)Br (0.132 g), *N*-(*n*-octyl)-2-pyridylmethanimine (0.42 mL), and ω-bromo PMMA (3.0 g) in 20 mL of toluene were heated and stirred at 90 °C while being purged with ethylene gas for 45 min. The yield was about 100% on the basis of the complete disappearance of both the ω-OCH_3 and C—Br resonances of the starting PMMA.

^{13}C NMR ($CDCl_3$, 323 K; specific resonances, δ, ppm): 30.2, 30.4 (CH_2Br), 29.6–29.8 (CH_2CH_2Br).

Reaction of PMMA from Atom Transfer Polymerization with Maleic Anhydride

Maleic anhydride (1.78 g), Cu(I)Br (0.13 g), *N*-(*n*-propyl)-2-pyridylmethanimine (0.28 mL), and ω-bromo PMMA (3.0 g) in 20 mL of toluene were stirred at 90 °C for 4 h. The yield was about 100% (^1H NMR analysis). According to FTIR (specific), there was carbonyl stretching of the anhydride at 1781 cm^{-1}.

RESULTS AND DISCUSSION

Method 1: Reaction of Activated Polymer with TEMPO

Tertiary alkoxyamines with an α-methyl group next to the alkoxyamine C—O bond undergo competitive irreversible trapping via β-hydrogen radical abstraction versus reversible trapping via coupling after C—O-bond homolysis. This accounts for the fact that TEMPO-mediated living radical polymerization of methacrylates has not yet proven possible, with proper control of the MWD, as a direct result of permanent termination of chain growth. However, the irreversible process of trapping via disproportionation has an advantage in the synthesis of macromonomers under atom transfer polymerization conditions. The addition of TEMPO to a propagating polymerization solution should terminate the polymerization process to yield macromonomers of structure **2**. Methacrylate macromonomers of similar structures are prepared via catalytic chain transfer polymerization and find commercial applications in pigment dispersants and the synthesis of polyols and inks.[37] A characteristic of the polymers produced by this process is that the MWD is relatively broad as a result of the conventional free-radical polymerization mechanism. Macromonomers prepared via living radical polymerization with method 1, however, would yield products with narrow MWDs. To illustrate this, PMMA prepared via atom transfer polymerization ($\langle M_n \rangle$ = 3460; PDI = 1.16) was reacted with TEMPO under the standard polymerization conditions at 90 °C. The reaction was allowed to proceed for 3 h. The product was purified by precipitation into pentane. ^1H NMR analysis clearly confirmed the presence of the characteristic vinylic protons from structure **2** at 6.16–6.22 and 5.43–5.54 ppm, the ω-methoxy carbonyl protons at 3.70–3.75 ppm, and the ω-methylene protons at 2.45–2.55 ppm (see Fig. 1). A comparison of the PMMA starting material with the product via the CH_3CH_2O protons of the α-initiating group and the specific resonances of the product shows a high conversion (>78%) of the ω-bromo PMMA chains into their corresponding macromonomer analogues. The near complete disappearance of the original ω-methylester (at ca. 3.71 ppm, which should appear in Fig. 1 at ca. 3.77 ppm because of the presence of small amounts of TEMPO) suggests that the remainder (<22%) of the material has not reacted via the desired pathway. A tentative explanation is termination by disproportion-

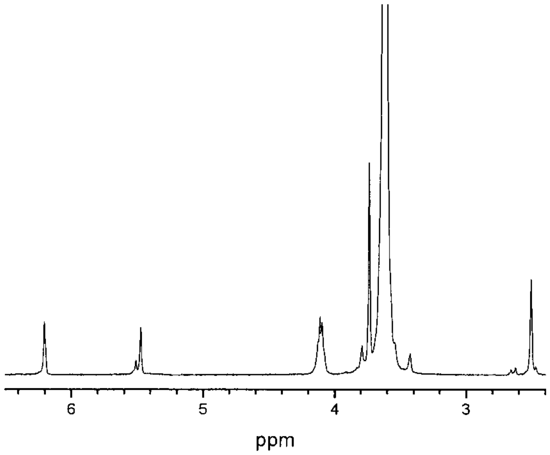

Figure 1. Section of the ^1H NMR ($CDCl_3$) spectrum of the reaction of ω-bromo PMMA with TEMPO to yield macromonomers of structure **2**, showing the presence of the characteristic vinylic at 6.16–6.22 and 5.43–5.54 ppm, the ω-methoxy carbonyl protons at 3.70–3.75 ppm, and the ω-methylene protons at 2.45–2.55 ppm.

ation or reaction of the hydroxylamine with the generated carbon-centered radical to yield the saturated PMMA species.

Method 2a: Reaction of Activated Polymer with Silyl Enol Ethers

Trimethyl[1-(trimethylsiloxy)phenylthenyloxy]-silane (**1**) was synthesized from 4′-hydroxyacetophenone through the reaction with chlorotrimethylsilane with lithium diisopropyl amide at −78 °C. The addition of a 10-fold excess of this compound to PMMA, produced by atom transfer polymerization, under standard atom transfer polymerization conditions at 90 °C yielded the ω-ketone-terminated polymer chain in quantitative yields. The trimethylsilyl (TMS) phenol-protecting group could be removed by dissolution of the product in a toluene/methanol mixture to yield the final PMMA product with a phenolic end-functional group (**3**), as confirmed by ^{1}H NMR analysis.

Method 2b: Reaction of Activated Polymer with Allyl Bromide

The modification of the standard reaction conditions was required for allyl bromide to be used as a quenching agent. This arises because of the elimination of a bromine radical and the potential formation of a Cu(II)Br$_2$ complex by reaction with the Cu(I)Br complex. This would result in an increase in Cu(II) concentration, so the increase in the rate of chain deactivation would reduce the probability of the addition of allyl bromide, thus strongly limiting the outcome of the modification of the ω terminus. In an attempt to overcome this problem, Cu(0) was added to the system, which can disproportionate with Cu(II) to regenerate Cu(I).[38,39] To minimize the occurrence of ordinary bimolecular termination by disproportionation as a side reaction, the temperatures were lowered to 50 °C to keep the rate of generation of carbon-centered radicals low. Under these conditions, ^{1}H NMR analysis showed a functionalization of about 57%, thereby clearly showing the characteristic resonances of the introduced allyl group from structure **4** at 5.42–5.72 and 4.84–5.06 ppm (see Fig. 2).

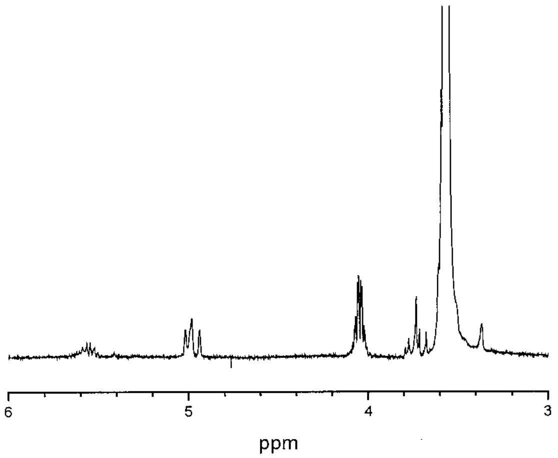

Figure 2. Section of the ^{1}H NMR spectrum (CDCl$_3$) of the reaction of ω-bromo PMMA with allyl bromide to yield **4**, showing the characteristic resonances of the introduced allyl group at 5.42–5.72 ppm and 4.84–5.06 ppm.

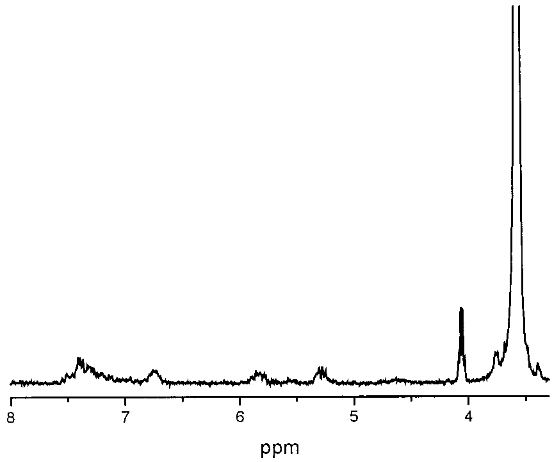

Figure 3. Section of the ^{1}H NMR (DMSO-d_6) spectrum of the reaction of ω-bromo PMMA with divinylbenzene to yield **5**, showing the aromatic protons at 6.91–7.60 ppm, the three pendant vinyl protons at 6.61–6.86, 5.68–5.95, and 5.10–5.39 ppm, and the disappearance of the distinct signal for the ultimate methoxycarbonyl group of the starting material at 3.65–3.80 ppm.

Method 3a: Reaction of Activated Polymer with Divinylbenzene

Divinylbenzene has a relatively low rate coefficient of homopropagation and thus guarantees an easy control of polymer chain growth. In this case, the temperature was lowered to ambient conditions to increase the difference in the rate of C—Br homolysis induced by the difference in activation energies for secondary and tertiary C—Br species. A reaction at 25 °C for 24 h resulted in a quantitative addition of one single divinylbenzene monomeric unit onto the PMMA starting material, **5**. ^{1}H NMR (DMSO-d_6) analysis confirmed a quantitative conversion and showed the presence of the aromatic protons at 6.91–7.60 ppm, the three pendant vinyl protons at 6.61–6.86, 5.68–5.95, and 5.10–5.39 ppm, and the disappearance of the distinct signal for the ultimate methoxycarbonyl group of the starting material at 3.65–3.80 ppm (see Fig. 3).

Method 3b: Reaction of Activated Polymer with Benzylacrylate

Benzylacrylate has a high rate coefficient of homopropagation, so the control of chain growth is more problematic. A comparison of the benzylic resonances at 5.05–5.18 ppm and the ω-C*H*Br at 4.15–4.36 ppm with the CH_3CH_2O protons of the α-initiating group at 3.95–4.10 ppm in the ^{1}H NMR spectrum gave, on average, about three monomer units added to the starting polymer spectrum under the same polymerization conditions used with divinylbenzene. To circumvent this, the initial monomer concentration was reduced by a factor of 10 to favor reversible chain deactivation over monomer addition. This resulted in only 55% functionalization. For optimization of the conditions under which the reaction was carried out, different amounts of Cu(II)Br_2 were charged into the system to increase the probability of reversible chain deactivation. The addition of 22% Cu(II)Br_2, with respect to Cu(I)Br, with the reaction at 60 °C for 4 h resulted in a 62% transformation, whereas the addition of 50% Cu(II)Br_2 only reached a 23% conversion, as indicated by ^{1}H NMR analysis (see Fig. 4).

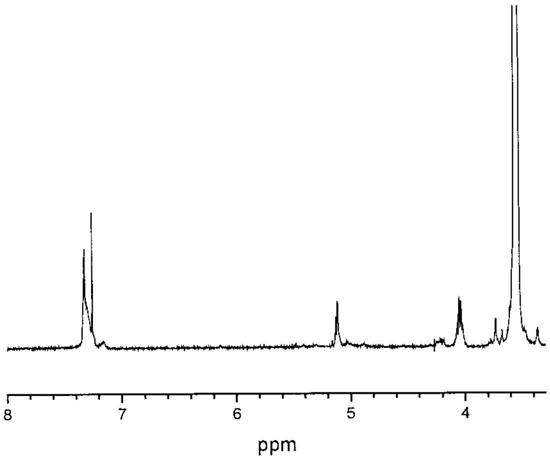

Figure 4. Section of the ^{1}H NMR ($CDCl_3$) spectrum of the reaction of ω-bromo PMMA with benzyl acrylate to yield **6**.

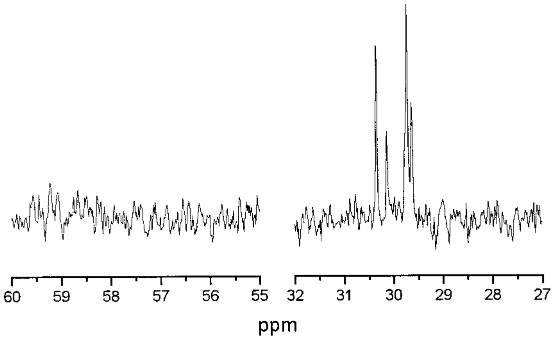

Figure 5. Sections of the ^{13}C NMR ($CDCl_3$) spectrum showing the complete disappearance of the quaternary *C*—Br (δ 58–59 ppm) and the presence of the CH_2CH_2Br resonances after the reaction of ω-bromo PMMA with ethylene to yield **7**.

Method 3c: Reaction of Activated Polymer with Ethylene

From a synthetic point of view, the reaction of an activated polymer chain with ethylene under atom transfer polymerization conditions is beneficial, as the end group will become a relative sterically nonhindered primary bromide. The latter can be transformed into a great variety of different functional groups with well-known organic synthetic reactions, such as nucleophilic substitution reactions. The purging of an atom transfer polymerization at a high monomer conversion (>85%) with ethylene, that is, for methyl methacrylate (MMA) as a monomer with our standard polymerization conditions for a period of 45 min, resulted in a complete ω-CH_2CH_2Br functionalization, **7**. This was confirmed by NMR analysis, as the resonances of both the ω-OCH_3 (δ 3.65–3.80 ppm) and the *C*—Br (δ 58–59 ppm) of the starting PMMA disappeared completely, and the ^{13}C NMR spectrum showed the presence of the ω-CH_2CH_2Br end group (see Fig. 5).

Method 4: Reaction of Activated Polymer with Nonhomopropagating Monomers

Maleic anhydride is a common monomer that is not able to homopropagate under free-radical polymer-

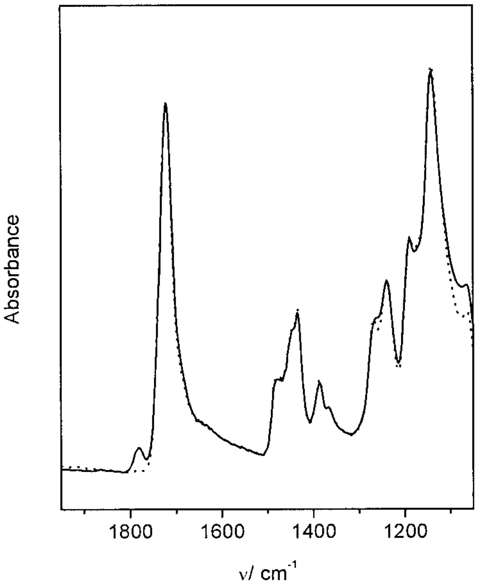

Figure 6. Section of the FTIR spectrum before (dotted line) and after (solid line) the reaction of ω-bromo PMMA with maleic anhydride to yield **8**, showing the appearance of the carbonyl stretching of the anhydride at 1781 cm^{-1} adjacent to the C=O stretching of the methoxycarbonyl at 1721 cm^{-1}.

ization conditions because of an exceptionally low rate coefficient of propagation.[40] Therefore, the addition of one monomer unit is carried out easily to give a polymer of structure **8**. FTIR analysis clearly confirmed the presence of the targeted end group, showing the carbonyl stretching of the anhydride at 1781 cm^{-1} adjacent to the C=O stretching of the methoxycarbonyl at 1721 cm^{-1} (see Fig. 6). Furthermore, ^1H NMR analysis showed the complete disappearance of the resonance of the original ω-methylester at 3.75 ppm in DMSO-d_6, thereby indicating a high conversion.

CONCLUSIONS

Modifications of the ω-bromo end group of methacrylate polymers prepared by copper-mediated living radical polymerization to produce ω-functional polymers can be performed in high yields with four different approaches: the use of TEMPO to induce disproportionation, the use of compounds that undergo addition fragmentation, the single addition of both fast and slow propagation monomers producing a secondary C—Br bond, and the addition of nonhomopropagating monomers.

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