Szanka A, Szarka Gy, Iván B
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JOURNAL OF MACROMOLECULAR SCIENCE-PURE AND APPLIED CHEMISTRY 51: pp. 125-133. (2014)

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Poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) four-arm star functional copolymers by quasiliving ATRP: equivalent synthetic routes by protected and nonprotected HEMA comonomers

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Keywords: PMMA; HEMA; copolymer; quasiliving ATRP; star polymer; hydroxyl functionality

Abstract

Comprehensive investigations were carried out on the synthesis of well-defined poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) P(MMA-*co*-HEMA) copolymers, i. e PMMA with predetermined average number of pendant hydroxyl functionalities, by using HEMA and trimethylsilyl-protected HEMA (TMS-EMA) under quasiliving ATRP conditions by a tetrafunctional initiator and CuCl/2,2'-bipyridyl(bpy) catalyst system in methanol at 10 ^{o}C. It was found that these two synthetic routes, that is the direct and protected approaches, are equivalent in terms of yields, hydroxyl functionality and molecular weight distribution (MWD). Bulk copolymerization of MMA and HEMA by ATRP led to broad multimodal MWD in contrast to copolymers with narrow MWD in the presence of methanol. A two-step purification method applying silica-alumina chromatography followed by treatment with an acidic ion-exchange resin, used also as the deprotecting agent, was found to provide copolymers free of catalyst contamination. At higher monomer conversions, GPC analyses indicate the occurrence of chain-chain coupling by recombination of the macroradicals resulting in lower than theoretical apparent initiating efficiencies. According to the results on the effect of reaction time on monomer conversion, relatively short reaction times, less than 2 hours, are sufficient to obtain high yields and PMMA with desired functionalities and MW under the applied ATRP conditions. The resulting four-arm star hydroxyl-functional P(MMA-*co*-HEMA) copolymers offer a variety of new possibilities for the preparation of a variety of novel PMMA-based macromolecular architectures.

1. Introduction

Well-defined synthetic macromolecules with predetermined average molecular weights, narrow molecular weight distribution (MWD), and especially with desired functional groups and topology (linear or branched) are of significant academic and industrial interest because the functionalities make the same polymer backbones useful for a large variety of subsequent modifications and thus applications. Quasiliving polymerizations (1-3) proceeding via dynamic equilibrium between propagating (living) and nonpropagating (nonliving, mostly terminated) polymer chains in the absence of permanent chain breaking reactions have become the major synthetic tools for the preparation of such macromolecular assemblies (see e.g. Refs. 4 for reviews and references therein). Among functional polymers, hydroxyl-functional macromolecules, especially hyrdoxy-telehelics, have gained significant academic and industrial interest and a variety of applications (see e. g. Refs. 4 and 5 references therein). In the group of such polymers, homo- and block copolymers of 2-hydroxyethyl methacrylate (HEMA) are of special importance due to their useful properties and applications in a variety of technological and biomaterial fields (see e.g. Refs. 6a-d for recent reviews). For instance, in addition to contact lenses (7), peptide/polymer conjugates (8a,b), cross-linked polymers (8c-g), graft copolymers (8h,i) and complex polymer architectures (8j) based on HEMA as the functional component are attractive biomaterials for drug and gene delivery and a variety of other applications. Photoluminescent, europium coordinating hybrids of polymers with HEMA units are expected to be alternatives to radioactive probes and organic dyes (8k). In these examples, copolymers of HEMA with methyl methacrylate (MMA) are of significant interest due to the biocompatibility and other advantageous properties of both constituents (8b,c,h,i). However, there are only sporadic reports on attempts to prepare well-defined poly(methyl methacrylate-*co*-2-

hydroxyethyl methacrylate) (P(MMA-*co*-HEMA) copolymers and their chemically modified analogs (8c,h,9).

In general, for obtaining functional copolymers, including copolymers of MMA and HEMA as well, there are two major synthetic routes to build special functional groups into polymer chains. The first applies copolymerization of the selected functional group containing monomers (direct or unprotected route), while the second one proceeds via postpolymerization polymer analog modifications of macromolecules prepared by copolymerizing of precursor or protected monomers (indirect or protected route). Due to the presence of the hydroxyl group in HEMA, its copolymerizations by processes sensitive to protic entities, such as group transfer polymerization (GTP) and anionic polymerization, require the use of protected monomers with groups like acetals (10) or trialkylsilyl (11) groups. Recently, several attempts have been reported on the preparation of a variety of block and random copolymers of HEMA with MMA mainly by quasiliving atom transfer radical polymerization (ATRP) (8c,h,9,12). However, in most of these cases, direct copolymerizations of HEMA with MMA require special solvents or solvent mixtures (e.g. anisole, butyl acetate, methylethyl ketone, toluene, DMF, acetonitrile, cyclohexanone etc. and mixtures thereof), high temperatures and long reaction times. Moreover, the reported ATRP processes usually led to low yields, low initiating efficiencies or copolymers with broad MWD. Attempts for the polymerization of 2-(trimethylsilyloxy)ethyl methacrylate (TMS-EMA), a widely used protected HEMA (11,13) by ATRP were also carried out at high temperatures (70-110 °C) with results and problems similar to the direct route with the unprotected HEMA (9g-k,12b-d). The synthesis of PHEMA homopolymer by ATRP in methanol or in its mixtures with other solvents in the range of 20-70 °C was also investigated (8k,14). An interesting approach was recently reported by Yagci et al. (9a) for the preparation of P(MMA-*co*-HEMA) linear random copolymers by ATRP in methanol at low temperature, i. e. at 10 °C. In the reported two

cases, long reaction times (5 and 15 hours) were applied and copolymers with low yields and lower than theoretical initiating efficiencies (I_{eff}) were obtained (9a). However, systematic experiments with this promising copolymerization reaction, that is detailed studies on the fundamental aspects of this process aiming at the synthesis of well-defined P(MMA-*co*-HEMA) copolymers, i. e. PMMA with desired number of pendant hydroxyl functionalities, are lacking. Herein, we report on our comprehensive investigations for the synthesis of P(MMA-*co*-HEMA) four-arm star copolymers by quasiliving ATRP with both HEMA and TMS-EMA, the broadly applied silyl-protected HEMA, in order to reveal the differences or equivalence of the nonprotected and protected synthetic routes for obtaining PMMA with well-defined structure, especially predetermined number of pendant hydroxyl groups along the chains.

2. Experimental

2.1. Materials. Methyl methacrylate (MMA, 99%, Aldrich) was stirred with CaH_2 for 3 hours, then passed through neutral alumina column and distilled under reduced pressure to remove the inhibitor. 2-Hydroxyethyl methacrylate (HEMA, 97%, Aldrich) was distilled before use under reduced pressure. 2-(Trimethylsilyloxy)ethyl methacrylate (TMS-EMA) (10a) and 1,1,1,1-tetrakis(2'-bromo-2'-methylpropionyloxymethyl)methane (TBMPMM) (9c) were synthesized according to the literature procedures. Methanol (lab. use, Molar Chemicals) was stirred with 3 Å molecular sieves for 3 hours and distilled under reduced pressure. CuBr (98%, Aldrich) and CuCl (99+%, Aldrich) were purified by stirring overnight in acetic acid, then filtered and washed with abs. ethanol and diethyl ether and finally dried. 2,2'-Bipyridyl (bpy, 99%, Aldrich), N,N,N',N",N"-pentamethyldiethylentriamine (PMDETA, 99%, Aldrich), tetrahydrofuran (THF, lab. use, Molar Chemicals) and hexane (lab. use, Molar Chemicals) were used as received. Amberjet 1200-H ion-exchange resin (Aldrich) was washed with THF before use.

2.2. Bulk copolymerization of MMA and HEMA. 2.00 g of TBMPMM initiator (2.73 mmol), 1.57 g of CuBr (10.94 mmol), 11 mL of MMA (107.54 mmol) and 2.7 mL of HEMA (25.73 mmol) were added into a 50 mL round bottom flask. This mixture was degassed under vacuum followed by argon backfilling three times for deoxygenation. Then, it was immersed into an oil bath at 60 °C and after 10 minutes 0.8 mL of PMDETA (11.49 mmol) was added. After 10 minutes reaction time it was cooled to room temperature. The reaction mixture was dissolved in THF, passed through a neutral alumina column and precipitated into hexane. The solvents were decanted, the polymer was redissolved in THF, and the chromatography and precipitation were repeated. The final product was dried until constant weight under vacuum at room temperature.

2.3. Solution copolymeriziation of MMA and HEMA. In a typical experiment, a mixture of TBMPMM (0.91 g, 1.24 mmol) as a tetrafunctional initiator, bpy (1.56 g, 9.98 mmol), MMA (10.6 mL, 100.10 mmol), HEMA (1.4 mL, 10.02 mmol) and 8 mL distilled methanol were charged into a 50 mL round bottom flask equipped with a magnetic stirrer. The solution was deoxygenated with three freeze-thaw cycles. Subsequently, the reaction mixture was warmed to ambient temperature and CuCl (0.49 g, 4.95 mmol) was added under argon. The solution was immediately freezed, and the deoxygenation was repeated. Then the flask was warmed to 10 °C, and after predetermined times samples were taken. Methanol was removed on a rotary evaporator, and the remaining mixture was dissolved in THF and passed through a chromatography column filled with silica and neutral alumina to remove the complex salts. The resulting copolymer was precipitated into hexane, collected by filtration and dried in a vacuum oven at room temperature until constant weight.

2.4. Copolymerization of MMA and TMS-EMA. The copolymerizations of MMA with TMS-EMA were carried out the same way as described for HEMA. In comparative experiments, the feed molar ratios of MMA/HEMA and MMA/TMS-EMA were in the same range as shown in Table 1.

2.5. Deprotection of P(MMA-*co*-TMS-EMA). The P(MMA-*co*-TMS-EMA) copolymers were dissolved in THF, and then shaken with Amberjet 1200-H ion-exchange resin for 4 hours. Then the resulting polymers were precipitated into hexane, collected by filtration and dried in a vacuum oven at room temperature until constant weight.

2.6. Characterization. The molecular weight distributions and average molecular weights were determined by gel permeation chromatography (GPC). The GPC equipment was composed of an in-line degasser, 515 HPLC Pump and 717 Autosampler, all supplied by Waters, three GPC columns (type MIXED C, Varian), an Agilent 390 dual detector (RI and differential viscometry) and WinGPC Unichrom software (PSS GmbH). THF was used as eluent with 1 ml/min elution rate at 30 °C. Nuclear magnetic resonance (NMR) spectra were recorded in chloroform-*d* on a 200 MHz Varian spectrometer.

3. Results and discussion

In order to obtain P(MMA-*co*-HEMA) star polymers with well-defined average number of pendant hydroxyl functionalities per macromolecule, two approaches via quasiliving ATRP were investigated by using 1,1,1,1-tetrakis(2'-bromo-2'-methylpropionyloxymethyl)methane (TBMPMM) tetrafunctional initiator. As shown in Scheme 1, the first method applied direct copolymerization of MMA and HEMA with the CuCl/2,2'-bipyridyl (bpy) catalyst system in

methanol at 10 ^{o}C. Under the same conditions, the second synthetic route utilized silyl-protected HEMA, i. e. TMS-EMA, and the desired P(MMA-*co*-HEMA) was obtained by subsequent removal of the protecting group by an acidic ion-exchange resin. For comparison, the MMA/HEMA and MMA/TMS-EMA molar ratios were in the same range within the same series of experiments.

In contrast to literature claims (8k), it was surprisingly found by us in the course of the purification of the resulting polymers that passing their methanol solution through a column filled with silica and neutral alumina is insufficient for removing the catalyst residues because methanol deactivates the column fillings. Therefore, another way was attempted by us to obtain pure products. First, methanol was removed under reduced pressure, the colored copolymers were redissolved in THF, and then these solutions were chromatographed. However, even this process was not sufficient to remove all of the catalyst residues in most of the cases, and products with slight green color were obtained. It was found by us that treating the chromatographed THF solutions of the copolymers with an acidic ion-exchange resin (Amberjet 1200-H), which was also used for removing the acid sensitive trimethylsilyl protecting groups, led to pure products. This means that this process results simultaneously in deprotection for the P(MMA-*co*-TMS-EMA) and removal of the remaining catalyst impurities from both kind of copolymers. This combined purification process, that is chromatography by silica and alumina containing columns followed by treatment with a recoverable acidic ion-exchange resin, may be broadly applied process to purify polymers prepared by quasiliving ATRP.

The efficient deprotection by the acidic ion-exchange resin was verified by ^{1}H NMR spectroscopy. As shown in Figure 1, the signal at 0.15 ppm characteristic of the trimethylsilyl protons in P(MMA-*co*-TMS-EMA) (Figure 1B) is absent in the deprotected copolymer, and the resulting NMR spectrum (Figure 1C) is the same as that of the P(MMA-*co*-HEMA) produced by

direct ATRP copolymerization of MMA and HEMA (Figure 1A). It has to be noted that the intensity of the trimethylsilyl protons of the TMS-EMA monomer units in the P(MMA-*co*-TMS-EMA) copolymers is lower than expected, which is due to partial deprotection during workup.

Table 1 summarizes the feed ratios, the resulting P(MMA-*co*-HEMA) copolymer compositions, the number average molecular weights (M_n) and polydispersity (M_w/M_n) data. Bulk copolymerization of MMA and HEMA was also attempted. As shown in Table 1, three series of comparative copolymerization experiments were carried out in methanol with 19 hours polymerization time. The initiator/comonomer (HEMA or TMS-EMA) were the same (~1/8) in all cases, while the MMA/initiator ratios increased in the order of 40, 60, 80 in experiment series 1, 2 and 3, respectively. The conversions were near to 100% in every copolymerization experiments. The data in Table 1 also reveal that the compositions of the resulting P(MMA-*co*-HEMA) for both type of copolymers, i. e. for those obtained by direct copolymerization of MMA and HEMA and by the protected route with TMS-EMA match well with the feed ratios and with each other within the same series (the P(MMA-*co*-HEMA) copolymers formed by deprotection of P(MMA-*co*-TMS-EMA) are assigned as "Deprotected"). These results indicate that the unprotected and TMS-protected copolymerization routes by quasiliving ATRP in methanol at 10 ^{o}C for obtaining P(MMA-*co*-HEMA) copolymers are equivalent from composition point of view.

As shown in Table 1, the number average molecular weights determined by GPC are the same for the same series of copolymers within experimental error. The polydispersities (M_w/M_n) lies in the region of 1.26-1.40 indicating fairly narrow molecular weight distributions (MWD) with one exception, P(MMA-*co*-TMS-EMA)-2, which is most likely due to insufficient stirring during the polymerization. As displayed in Figure 2, the GPC curves are close to identical for the P(MMA-*co*-HEMA)-3, the P(MMA-*co*-TMS-EMA)-3 and the Deprotected-3 samples. Similar GPC curves were obtained for all the other sample series, that is, the nonprotected and protected

routes lead to copolymers with practically the same MWDs and average molecular weights, on the one hand. On the other hand, Figure 2 also shows that there is no observable change in the GPC curve upon deprotection, that is the applied deprotection process does not result in either chain scission or chain-chain coupling.

Table 1 also shows that the apparent initiating efficiencies (I_{eff}) fall in the region of 0.5-0.75 for sample series 1 and 2, while 100% initiating efficiencies are obtained for samples with the highest MMA concentration (samples 3). In the course of quasiliving ATRP, the relative rates of chain termination (R_t) and propagation (R_p) increases with increasing polymerization time, i. e. with increasing conversion, due to the following relationship:

$$R_t/R_p = k_t r/(k_p m) \qquad (1)$$

This relation comes from the rate equations for propagation ($R_p = k_p m r$) and termination ($R_t = k_t r^2$) in free radical polymerizations, where R_p, R_t, k_p, k_t, m and r are the rate of propagation, rate of termination, rate constant of propagation, rate constant of termination, concentrations of monomer and radicals, respectively. Therefore, the increase of chain termination by both recombination and disproportionation can be expected at high monomer conversions, i. e. with decreasing monomer concentrations, and as well as under monomer starved conditions after complete monomer consumption. Recombination leads to chain-chain coupling which would decrease the apparent initiating efficiencies below 100%. This is in accordance with results reported earlier for similar polymerizations of MMA and HEMA or TMS-EMA under ATRP conditions, i. e. molecular weight (MW) increase at high monomer conversions above the expected theoretical MWs due to recombination (9j-l). At higher monomer concentrations

(sample series 3) the R_t/R_p ratio becomes lower resulting in relatively less termination, i. e. in apparent initiating efficiencies close to 100%.

The last entry in Table 1 shows the results of the solventless bulk copolymerization of MMA with HEMA with the CuBr/PMDETA initiating system. Although P(MMA-*co*-HEMA) copolymer with 95% yield was obtained by the bulk ATRP, the GPC curve (not shown) and the data in Table 1 indicate that this copolymer possesses broad, multimodal MWD. These results mean that there is significant difference between the MWDs of the copolymers obtained by bulk and in methanol. These findings also verify that diluting the MMA/HEMA (or TMS-EMA) copolymerization system by methanol under ATRP conditions lead to copolymers with remarkably narrower MWDs.

Every copolymerization experiment with long (19 hours) polymerization time led practically to complete monomer conversions as shown in Table 1. Therefore, copolymerizations were also carried with different reaction times in order to determine the optimal duration of these copolymerizations. As Table 2 indicates, much shorter reaction times, i. e. 2 hours or less is sufficient to obtain high, near to 100% yields. The data in Table 2 also show that the molecular weights increase with increasing time, that is with increasing monomer conversion. The initiating efficiency was found to be close to theoretical (~100%) at 67% monomer conversion after 30 minutes reaction time. However, the decreasing apparent initiating efficiencies and broadening of MWD (increasing polydispersity, i. e. M_w/M_n) indicate the occurrence of chain-chain coupling in line with Equation 1 at higher yields. Indeed, the GPC curves in Figure 3 corroborate this conclusion. As shown in this Figure, a copolymer with narrow MWD is obtained at 30 minutes, and the GPC curves shift to higher molecular weights (lower elution volumes) as the copolymerization proceeds. It is noteworthy that the shift in the GPC curves for copolymers prepared with 1.5 and 2 hours reaction time is significantly higher in the higher molecular weight

region than that in the lower one in comparison to the sample obtained at 1 hour reaction time. This clearly indicates that the MWD broadening at this stage of the copolymerization process, i. e. at low monomer concentrations, is due to chain-chain coupling by recombination.

4. Conclusions

The results of these investigations aiming at revealing the synthetic possibilities to obtain well-defined PMMA four arm star copolymers with desired number of pendant hydroxyl functionalities prove that ATRP copolymerizations of MMA with HEMA and with TMS-EMA, the protected HEMA, in methanol at 10 ^{o}C are equivalent synthetic routes, i. e. using protected HEMA is not required for obtaining the targeted copolymers under the applied conditions. Both the direct and protected (indirect) copolymerization processes under identical conditions lead to copolymers with the same compositions of P(MMA-*co*-HEMA) after deprotection of the P(MMA-*co*-TMS-EMA) copolymers by treating it with an acidic ion exchange resin. The results of our study also indicate that P(MMA-*co*-HEMA) copolymers with high yields, designed average number of pendant hydroxyl functionalities and narrow molecular weight distribution can be prepared during relatively short reaction times (less than 2 hours) by using the polymerization conditions applied by us. This means that these ATRP circumstances, i. e. diluting the MMA/HEMA copolymerization system with methanol at 10 ^{o}C, afford the synthesis of well-defined P(MMA-*co*-HEMA) copolymers by direct copolymerization of MMA with HEMA, that is using HEMA without a protecting group. In this context, it should be mentioned that the preparation of PMMA with multiple terminal functionalities by ATRP was recently reported by Gadwal and Khan (15) indicating the interest in avoiding the protection/deprotection steps in the syntheses of functional PMMAs. In accordance with previous literature reports (9j-l),

the GPC analyses of the P(MMA-*co*-HEMA) copolymers and the dependence of M_n on monomer conversion indicate that chain-chain coupling by recombination of the macroradicals occurs, especially at higher conversions and/or under monomer starved conditions, resulting in lower than theoretical apparent initiating efficiencies.

Because applications of polymers obtained by ATRP requires pure products, a combined purification process was developed by us to obtain P(MMA-*co*-HEMA) copolymers without catalyst residues. Column chromatography by silica-alumina fillings of THF solutions of the copolymers followed by treatment with an acidic ion exchange resin proved to be very efficient for obtaining copolymers free of catalyst contamination, on the one hand. On the other hand, the applied resin (Amberjet 1200-H ion-exchange resin) served as the catalyst for efficient deprotection of the TMS groups of the TMS-EMA units in the P(MMA-*co*-TMS-EMA) copolymers. It was also found that the applied ATRP conditions, that is copolymerization of MMA with either HEMA or TMS-EMA under ATRP conditions with the TBMPMM tetrafunctional initiator and CuCl/bpy catalyst system in methanol at 10 ^{o}C yield P(MMA-*co*-HEMA) copolymers with narrow MWD and predetermined molecular weights up about 60-70% monomer conversion due to suppressed termination in the presence of higher concentration of monomer, while at higher monomer conversions chain-chain coupling takes place due to the increase of the relative rate of chain termination by recombination. The resulting copolymers can be utilized as starting functional PMMAs for obtaining a variety of novel complex polymer architectures with potential applications from healthcare to engineering polymers by designed subsequent processes.

Acknowledgements

The authors thank Mr. Tamás Ignáth for technical assistance with the GPC measurements.

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Table 1. Feed molar ratios of TBMPMM initiator, MMA and HEMA or TMS-EMA, conversions (X_c), M_n, M_w/M_n, copolymer compositions of the P(MMA-*co*-HEMA) copolymers obtained by direct or protected routes (samples assigned as Deprotected) and the apparent initiating efficiencies (I_{eff}). (Polymerization conditions: TBMPMM/CuCl/bpy = 1/4/8, Ar atmosphere, 10 ^oC, 19 hours reaction time in methanol as solvent except in bulk copolymerization; conversions and compositions were determined by ^1H NMR; bulk copolymerization was carried out with the CuBr/PMDETA catalyst system at 60 ^oC for 10 minutes.)

Sample	Feed ratio TBMPMM/MMA / (HEMA or TMS-EMA)	X_c (%)	M_n (g/mol)	M_w/M_n	Copolymer composition (MMA/HEMA)	I_{eff}
P(MMA-*co*-HEMA)-1	1/39.9/8.2	100	8700	1.36	39.9/8.8	0.67
P(MMA-*co*-TMS-EMA)-1	1/40.6/8.2	100	9100	1.40		0.71
Deprotected-1			9300	1.36	40.6/8.2	
P(MMA-*co*-HEMA)-2	1/59.2/7.9	100	10400	1.35	59.2/8.6	0.74
P(MMA-*co*-TMS-EMA)-2	1/59.7/8.2	100	16700	2.26		0.50
Deprotected-2			17700	2.22	59.7/8.3	
P(MMA-*co*-HEMA)-3	1/80.8/8.1	97	9900	1.26	80.8/10.6	0.97
P(MMA-*co*-TMS-EMA)-3	1/80.4/8.0	96	9400	1.33		1.00
Deprotected-3			9400	1.33	80.4/11.7	
Bulk copolymerization (MMA and HEMA)	1/39.9/9.4	95	13300	4.17	39.9/14	0.43

Table 2. The monomer conversions (X_c), M_n, M_w/M_n and the apparent initiating efficiencies (I_{eff}) at different polymerization times during copolymerization of MMA with HEMA. (Polymerization conditions: TBMPMM/CuCl/bpy/MMA/HEMA = 1/4/8/44/8, Ar atmosphere, methanol as solvent,10 ^{o}C.)

Polymerization time (min)	X_c (%)	M_n (g/mol)	M_w/M_n	I_{eff}
30	67	4300	1.23	0.98
60	87	6600	1.27	0.83
90	94	7200	1.30	0.81
120	99	7500	1.35	0.81

SCHEME AND FIGURE CAPTIONS

Scheme 1. Nonprotected and silyl-protected synthesis routes for obtaining four-arm star random poly(methyl methacrylate-*co*-2-hydroxyethyl methacrylate) copolymers by quasiliving ATRP in methanol at 10 ^{o}C.

Figure 1. ^{1}H NMR spectra of P(MMA-*co*-HEMA)-3 (A), P(MMA-*co*-TMS-EMA)-3 (B) and its deprotected derivative (Deprotected-3) (C). (Polymerization conditions: TBMPMM/CuCl/bpy = 1/4/8, Ar atmosphere, 10 ^{o}C, 19 hours reaction time in methanol as solvent; for sample identification see Table 1.)

Figure 2. GPC traces of P(MMA-*co*-HEMA)-3 (——), P(MMA-*co*-TMS-EMA)-3 (----) and its deprotected derivative (Deprotected-3) (••••). (Polymerization conditions: TBMPMM/CuCl/bpy = 1/4/8, Ar atmosphere, 10 ^{o}C, 19 hours reaction time in methanol as solvent.)

Figure 3. GPC traces of P(MMA-*co*-HEMA) copolymers obtained during copolymerization of MMA with HEMA at different polymerization times. (Polymerization conditions: TBMPMM/CuCl/bpy/MMA/HEMA = 1/4/8/44/8, in methanol as solvent, Ar atmosphere, 10 ^{o}C.)

SCHEME 1

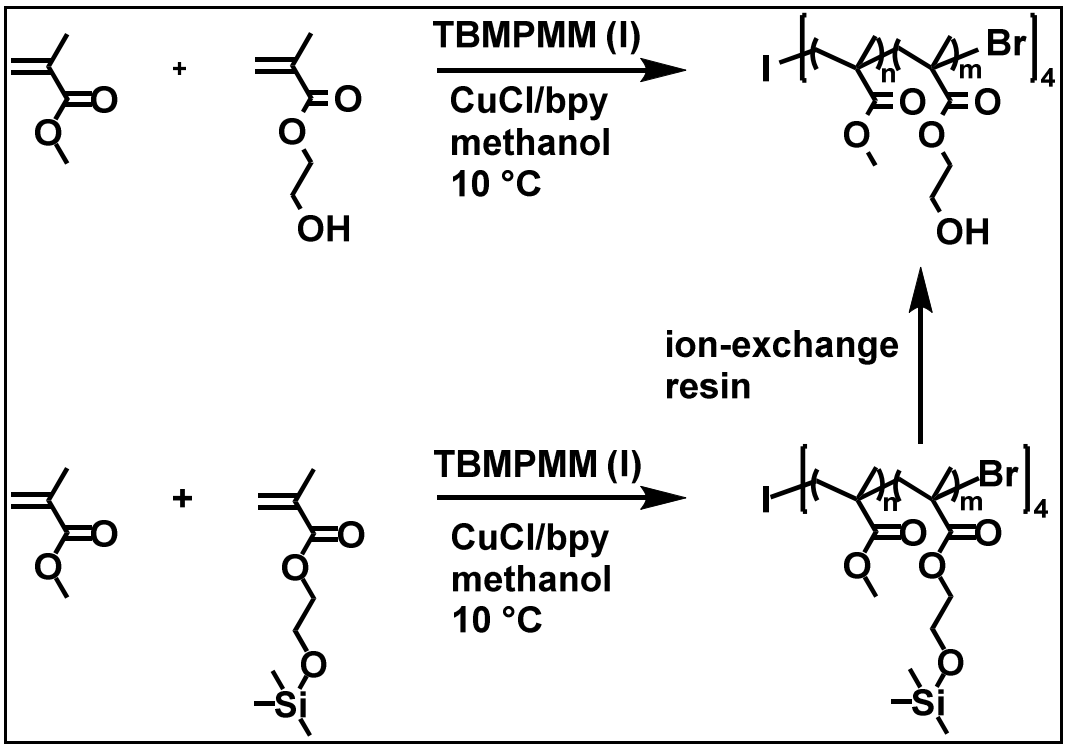
TBMPMM (I)
CuCl/bpy
methanol
10 °C
ion-exchange
resin
TBMPMM (I)
CuCl/bpy
methanol
10 °C

FIGURE 1

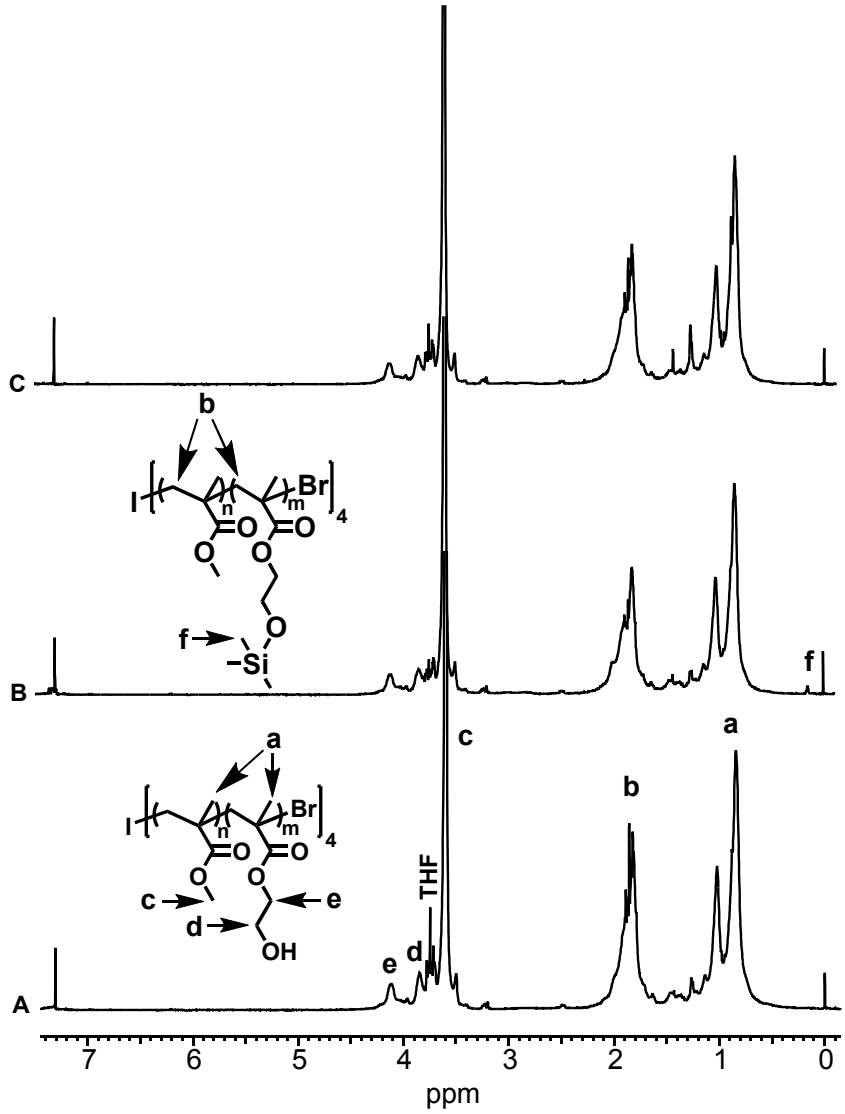

FIGURE 2

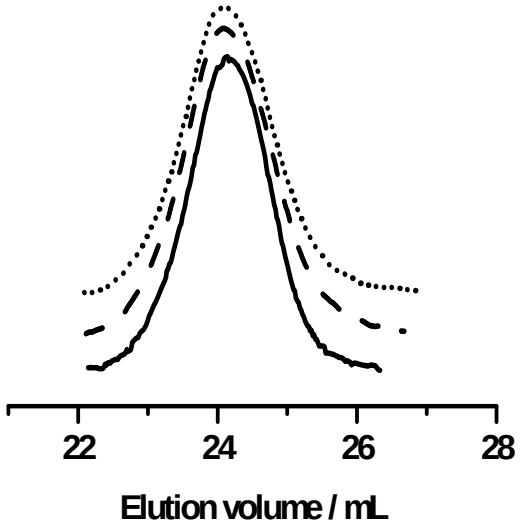

FIGURE 3