Atom Transfer Radical Polymerization of 2-Hydroxyethyl Methacrylate

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ABSTRACT: Atom transfer radical polymerization (ATRP) has been used to directly prepare linear pHEMA of controlled molecular weight and low polydispersity. Reaction conditions were adjusted to successfully polymerize the functional, polar methacrylate monomer. These adjustments included the use of a mixed solvent system consisting of methyl ethyl ketone and 1-propanol, lowering the temperature to 50 °C or less and using an alkyl bromide initiator with a copper chloride catalyst. The Cu/2,2′-bipyridyl (bpy) complex, normally a heterogeneous mixture in nonpolar, organic solvents, was completely soluble in the above solvent system. A block copolymer was prepared with a poly(methyl methacrylate) macroinitiator. The monomer can also be protected and polymerized under conditions very similar to those used for the ATRP of methyl methacrylate.

Introduction

The development of the means to control radical polymerization has provided the ability to synthesize a vast number of architecturally and compositionally new materials that were heretofore unattainable. Among the virtues of controlled radical polymerization is its potential for application to a large variety of monomers, including those with polar or functional groups. One such monomer is 2-hydroxyethyl methacrylate (HEMA). HEMA is a major component in materials for contact lenses, drug delivery, and hydrogels used for a variety of applications,[1,2] but until now its polymerization has not been effectively controlled.

HEMA cannot be polymerized by anionic and group transfer polymerizations due to the labile proton on the hydroxyl group. Little success has been accomplished in polymerizing methacrylates with nitroxide derivatives.[3] Carbamate-modified iniferters have been used to regulate polymerization of HEMA, but in this case, cross-linking agents were added to the polymerization as well, which prohibit the preparation of materials that can be characterized in terms of molecular weight and polydispersity.[4] Control of these two properties in addition to preservation of functionality has become the standard measure of control in the synthesis of well-defined polymeric materials in the emerging field of controlled radical polymerization.[5] Recently, a class of dithioesters have been developed that successfully control the polymerization of HEMA in low content statistical copolymers[6] as well as block copolymers.[7] Reported here is the controlled linear homopolymerization of HEMA and the preparation of a block copolymer with methyl methacrylate (MMA) by atom transfer radical polymerization (ATRP).

Results and Discussion

The use of ATRP has resulted in the controlled synthesis of not only many homopolymers[5] but also combinations of copolymers and novel architectures[8] which could not previously be made. Recently, ATRP has been applied to the polymerization of 2-hydroxyethyl acrylate (HEA), a polar monomer.[9] One key difference between acrylate and methacrylate polymerizations, which can have a pronounced effect on ATRP of HEMA, is that, like methyl methacrylate (MMA), the propagating radicals of HEMA are more stable and propagate more slowly. Unlike MMA, however, HEMA and the solvents required to dissolve the polymer are very polar which may dramatically effect the structure and function of the catalytic species,[10] in this case Cu(bpy)$_2$X/Cu(bpy)$_2$X$_2$ (where X = Cl or Br),[11] and may also lead to increased apparent rates of polymerization relative to MMA.[12] Therefore, simply applying the same conditions used for acrylates or methacrylates to the ATRP of HEMA may not necessarily result in the same successful polymerization.

In fact, when similar conditions to the ATRP of HEA were used for the ATRP of HEMA in bulk, including the use of a homogeneous catalyst with the unsubstituted 2,2′-bipyridine (bpy) ligand, CuBr, and a molar ratio of monomer to initiator to catalyst of 100:1:1, the solution boiled when initiated at room temperature and was solid in 20 min. The resulting polymer had both high molecular weight and polydispersity: $M_n = 63\,000$ ($M_{n,th} = 13\,000$, based on $DP_n = [M]/[I]$), $M_w/M_n = 1.5$.

The choice of initiator in this reaction was ethyl 2-bromoisobutyrate (BriB). Though typically the best initiators for ATRP of methacrylates include *p*-toluenesulfonyl chloride and diethyl 2-bromo-2-methylmalonate, neither of these could be used successfully.[5,13] Condensation of the tosyl chloride with the hydroxy functionality of the monomer is a side reaction that must be avoided. Reactions performed using the brominated malonate as the initiator turned bright green immediately and permanently upon its addition, suggesting complete, irreversible oxidation of the catalyst. Propionates were not used because they are less than ideal initiators for methacrylate polymerizations.[14] The initiator used in all of these reactions was BriB since it is closest in imitating the structure of the propagating methacrylate chain end.

In preliminary experiments (i.e., bulk, 90 °C), polydispersities were fairly broad ($M_w/M_n \geq 1.5$), and a low molecular weight tail was regularly observed in the SEC traces. Cu(bpy)$_2$X$_2$ was added to the reaction mixtures to increase the concentration of the deactivating species in solution, so as to reduce the concentration of propa-

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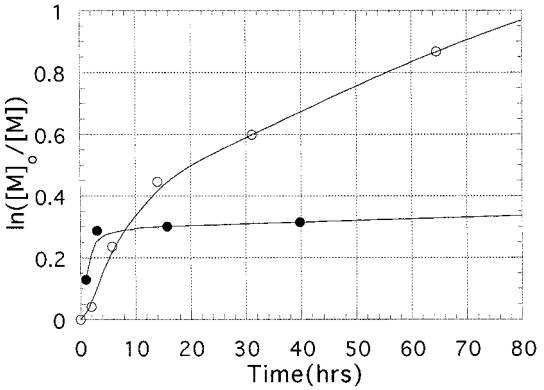


Figure 1. Kinetic plot for ATRP of HEMA in DMF at room temperature and 50 °C. (●, 50 °C; ○, ambient temperature). [HEMA] = 1.6 M, [BriBu] = 4.1 mM, [CuBr] = 8.1 mM, [$CuBr_2$] = 1.0 mM, [bpy] = 20.7 mM.

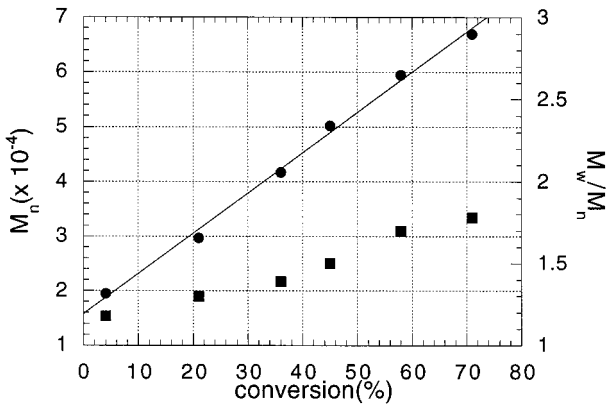


Figure 2. Molecular weight and polydispersity data for ATRP of HEMA in DMF at room temperature. [HEMA] = 1.6 M, [BriBu] = 4.1 mM, [CuBr] = 8.1 mM, [$CuBr_2$] = 1.0 mM, [bpy] = 20.7 mM.

gating radicals and the amount of irreversible termination (vide infra).

To approach the conditions used in ATRP of MMA, the use of a good solvent was necessary. Unfortunately, pHEMA is soluble only in extremely polar solvents such as DMF, DMSO, and HMPA, none of which have been shown to be overly successful as solvents for ATRP. Polymerizations of HEMA were carried out in DMF as a solvent with some success, however. For example, at 80 vol % dilution in DMF, the reaction was slow enough at room temperature to follow its kinetics.

The kinetic plot in Figure 1 for reactions that were carried out in DMF clearly shows curvature indicative of termination possibly due to competing side reactions. This effect was magnified by an increase in temperature to 50 °C such that the reaction stopped at less than 30% conversion. Corresponding molecular weight data are plotted in Figure 2. Molecular weights increased linearly, but the plot did not pass through the origin. Polydispersities were low initially but increased steadily with conversion.

Another possibility for dissolving pHEMA is the use of mixed solvents.[15] Similar reactions were carried out in a combination of methyl ethyl ketone (MEK) and 1-propanol (70/30 v/v). Figures 3 and 4 show data for reactions in this solvent system (50 vol %) and using a mixed halogen catalyst/initiator, i.e., an alkyl bromide initiator and CuCl/2bpy with added $CuCl_2$/2bpy. The advantages of using this combination were reported independently by Haddleton and Matyjaszewski and are

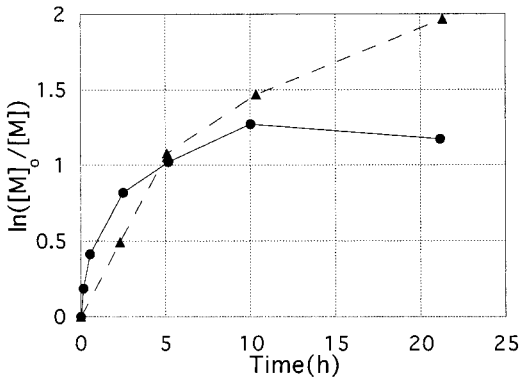


Figure 3. Kinetic plot for ATRP of HEMA in methyl ethyl ketone/1-propanol 70/30 v/v at 50 and 70 °C. [HEMA] = 4.1 M, [BriBu] = 0.04 M, [CuCl] = 0.02 M, [$CuCl_2$] = 4×10^{-3} M, [bpy] = 0.05 M (●, 70 °C; ▲, 50 °C).

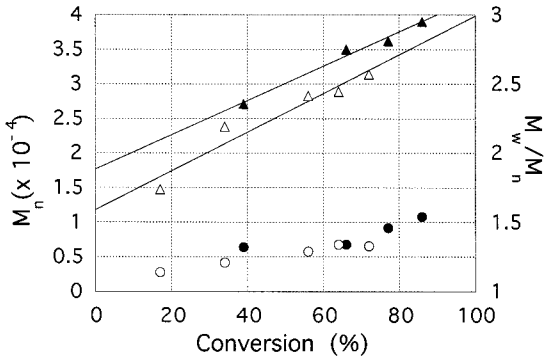


Figure 4. Molecular weight and polydispersity data for ATRP of HEMA in methyl ethyl ketone/1-propanol 70/30 v/v at 50 and 70 °C. [HEMA] = 4.1 M, [BriBu] = 0.04 M, [CuCl] = 0.02 M, [$CuCl_2$] = 4×10^{-3} M, [bpy] = 0.05 M (●, M_n (50 °C); ○, M_n (70 °C); ▲, M_w/M_n (50 °C); △, M_w/M_n (70 °C)).

discussed elsewhere.[16,17] The difference between these reaction conditions and those in DMF were clearly demonstrated by the high conversions reached at 50 °C (Figure 3). In this case, the curvature of the kinetic plots became more apparent again at higher temperatures (70 °C). Molecular weights still increased with conversion, but polydispersities leveled off and were not as high ($M_w/M_n \leq 1.5$) as in DMF.

Data for similar polymerizations in the absence of $CuCl_2$ are plotted in Figures 5−7. Different molecular weights were obtained by varying the concentration of initiator, [BriB]. Kinetic data (Figure 5) showed less termination, but at low [BriB] (10 mM) the polymerization was still limited to about 50% conversion after 6 h. Polydispersities (Figure 7) at this concentration of initiator also increased with conversion above 20%. Hence, under these conditions, high molecular weights (M_n above 20 000) could not be achieved. There are still other possibilities for achieving higher molecular weights such as protecting the hydroxyl group and polymerizing the less polar monomer as discussed below.

Molecular weight data obtained by SEC for all pHEMA samples were measured versus polystyrene standards in DMF. Because the hydrodynamic volumes of these polymers at the same molecular weights are not the same, the molecular weights that are reported may not be accurate. Polydispersities may also be higher due to peak broadening of the eluted polystyrene on SEC columns in DMF. Figure 6 illustrates the dependence of molecular weight on conversion for several different

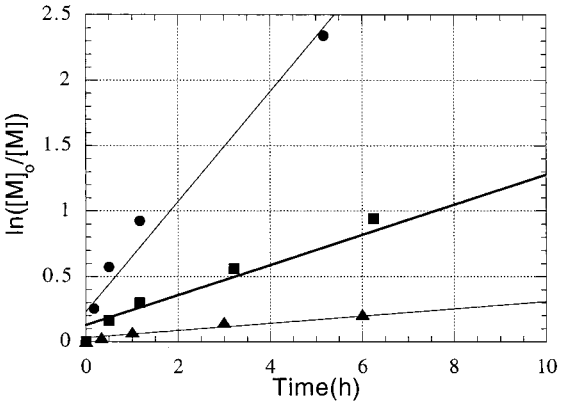


Figure 5. Kinetic plot of ATRP of HEMA in methyl ethyl ketone/1-propanol 70/30 v/v. 50 °C, [HEMA] = 4.1 M, [CuCl] = 0.01 M, [bpy] = 0.02 M (●, [BriBu] = 41 mM; ■, [BriBu] = 21 mM; ▲, [BriBu] = 10 mM).

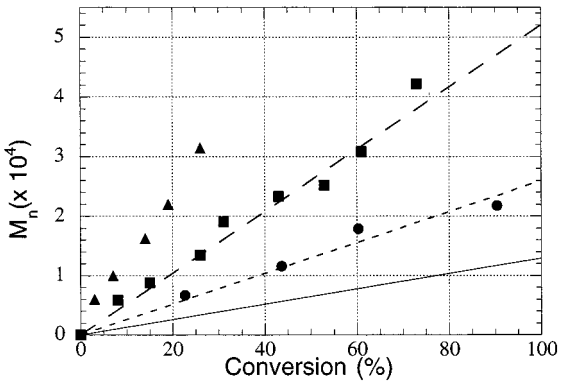


Figure 6. Experimental and theoretical molecular weight data for ATRP of HEMA in methyl ethyl ketone/1-propanol 70/30 v/v. 50 °C, [HEMA] = 4.1 M, [CuCl] = 0.01 M, [bpy] = 0.02 M ([BriBu] = 41 mM; experimental M_n (●), theoretical M_n (—); [BriBu] = 21 mM; experimental M_n (■); theoretical M_n (- - -); [BriBu] = 10 mM; experimental M_n (▲), theoretical M_n (- - -).

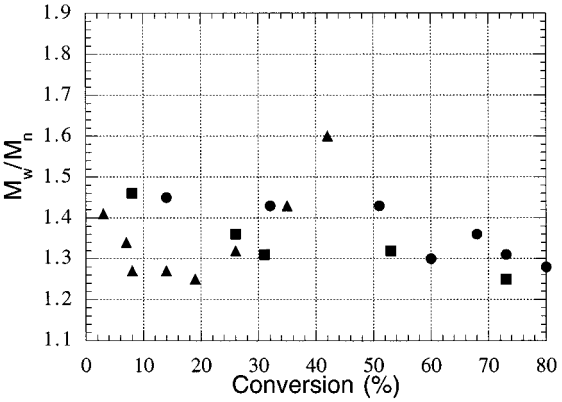


Figure 7. Polydispersities for ATRP of HEMA in methyl ethyl ketone/1-propanol 70/30 v/v. 50 °C, [HEMA] = 4.1 M, [CuCl] = 0.01 M, [bpy] = 0.02 M (●, [BriBu] = 41 mM; ■, [BriBu] = 21 mM; ▲, [BriBu] = 10 mM).

initiator concentrations. The theoretical line for $M_{n,th}$ = 26 000 fits the experimental data targeting M_n = 13 000, and the same is true of $M_{n,th}$ = 52 000 and the data for M_n = 26 000. This suggests that either the efficiency of initiation is only 50% or the molecular weights obtained by SEC could be close to twice the actual value. This could not be confirmed using NMR for low molecular weight samples because the end group resonances are overlapped by resonances of the polymeric repeat units. Although poly(methyl methacrylate) (pMMA) standards are more commonly used in DMF, the molecular weights of pHEMA scaled more closely to twice the values obtained using polystyrene standards than those using pMMA.

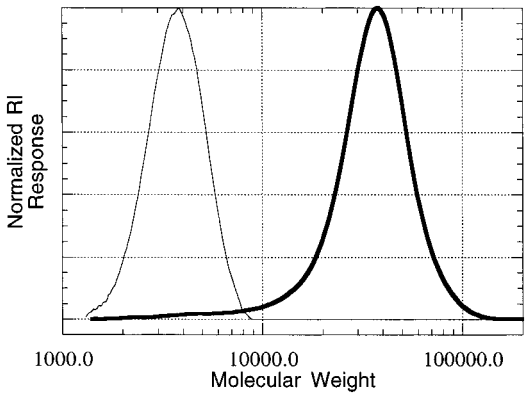


Figure 8. SEC traces for pMMA−Cl macroinitiator and p(MMA-*b*-HEMA).

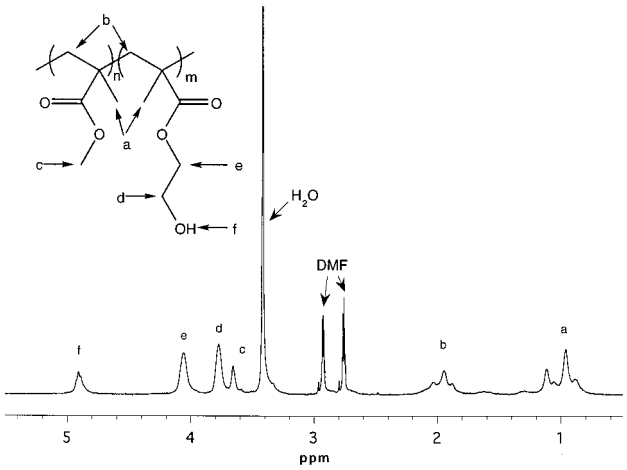
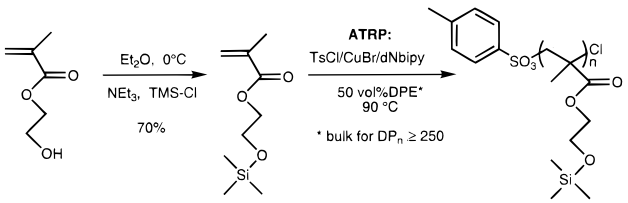


Figure 9. ^{1}H NMR of p(MMA-*b*-HEMA) in d_7-DMF.

Determination of the real molecular weight of pHEMA obtained by ATRP was obtained by preparing a block copolymer of HEMA and MMA and comparing the molar ratios of the two blocks as determined by ^{1}H NMR. The molecular weight of the first block, pMMA terminated with chlorine (p(MMA−Cl)), was measured by SEC (M_n = 3400, M_w/M_n = 1.12) and ^{1}H NMR (M_n = 3300). The second block was then polymerized and the resultant copolymer isolated and analyzed again by SEC (M_n = 32 900, M_w/M_n = 1.17) and ^{1}H NMR in d_7-DMF (Figure 9; M_n = 15 000). SEC traces in Figure 8 show efficient initiation from the first block. On the basis of the only slight differences in refractive index increments for the two homopolymers (at 25 °C in DMF, dn/dc_{pMMA} = 0.058; dn/dc_{pHEMA} = 0.076),[18] any residual pMMA should be indicated in the detector response. The theoretical M_n for the block copolymer based on conversion of HEMA (65%) was 13 200. This confirmed that the molecular weights of the pHEMA prepared by ATRP were close to their theoretical values based on the ratio of consumed monomer to initial inititator concentrations ($DP_n = \Delta[M]/[I]_0$). Thus, initiator efficiency is much greater than 50%, and the molecular weight determined by SEC is nearly twice the actual value as confirmed by the ^{1}H NMR data.

An alternative to directly preparing well-defined pHEMA is to protect the hydroxy group with a tri-

Scheme 1



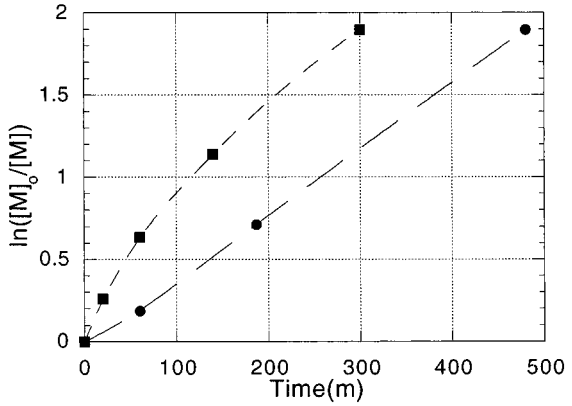


Figure 10. Kinetic data for ATRP of HEMA−TMS (■, [HEMA−TMS] = 5 M, [TsCl] = 0.01 M, [CuBr] = 0.01 M, [dNbpy] = 0.02 M, bulk, 90 °C; ●, [HEMA−TMS] = 2.5 M, [TsCl] = 0.02 M, [CuBr] = 0.02 M, [dNbpy] = 0.04 M, 50 vol % DPE, 90 °C).

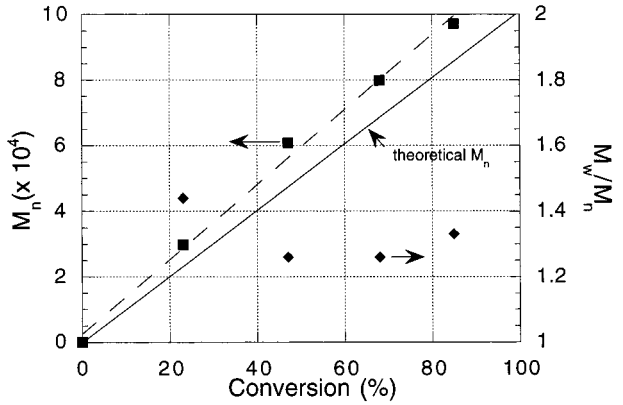


Figure 11. Molecular weight data for ATRP to prepare high molecular weight pHEMA−TMS ([HEMA−TMS] = 5 M, [TsCl] = 0.01 M, [CuBr] = 0.01 M, [dNbpy] = 0.02 M, bulk, 90 °C).

methylsilyl group (HEMA−TMS) as shown in Scheme 1. The less polar, protected monomer has a similar solubility as MMA and can be polymerized readily using conditions very similar to those used to prepare pMMA by ATRP. This method has been used by DeSimone et al. to prepare block copolymers with HEMA for surfactants in supercritical CO_2.[19]

Shown in Figures 10 and 11 are the kinetic and molecular weight data for the ATRP of HEMA−TMS ($M_{n,th}$ = 100 000). There was some termination observed in the first-order kinetic plot (Figure 10), but the molecular weights increased linearly and polydispersities were low (Figure 11). The kinetic plot also shows a similar polymerization targeting a lower molecular weight (M_n = 25 000) and in 50 vol % solvent (DPE). This reaction proceeded with less observed termination. The reaction targeting higher molecular weight was performed in bulk because in solvent the reaction was slower and conversion was limited to 80%. Stirring these samples in wet THF under acidic conditions, at room temperature, yielded pHEMA. Thus, higher molecular weight pHEMA was obtained using this method.

To investigate the source of error in the molecular weight data, pHEMA−TMS was hydrolyzed to prepare pHEMA, and the molecular weight determined by SEC for pHEMA was compared to the predicted value based on the SEC data for the protected monomer. For pHEMA−TMS with M_n = 18 300 (M_w/M_n = 1.10), the number-average molecular weight of the deprotected polymer (pHEMA) should be 11 800. The value obtained by GPC was 22 500 (M_w/M_n = 1.11). This also supports the earlier observation that molecular weights of pHEMA are roughly half of those indicated by SEC values determined versus polystyrene standards.

Conclusion

ATRP has been used to prepare pHEMA with controlled molecular weights and low polydispersities. Various molecular weights were obtained by varying the ratio of monomer to initiator. The best conditions for these reactions included the use of a mixed solvent system consisting of MEK and 1-propanol (70/30), low reaction temperatures (50 °C), and a mixed halogen initiator/catalyst system. A block copolymer, p(MMA-*b*-HEMA), was also prepared by ATRP from a macroinitiator of pMMA. The protected monomer, HEMA−TMS, was polymerized by ATRP using conditions similar to those used for MMA.

Experimental Section

2,2′-Bipyridine (bpy) from Aldrich was recrystallized from ethanol to remove impurities. CuBr was washed with acetic acid followed by methanol to remove impurities. $CuBr_2$ was ground with a mortar and pestle to improve the rate of dissolution. 4,4′-Di(5-nonyl)-2,2-bipyridyl (dNbpy) was prepared as described previously.[20] All other reagents except HEMA were used as received from Aldrich.

Characterization. A Waters 510 LC pump connected to a Waters 410 differential refractometer with DMF as the carrier solvent and linear 500 and 1000 Å Phenogel columns were used for gel permeation chromatography (GPC). Kinetic samples were diluted up in DMF, passed over a small plug of alumina to remove catalyst, filtered through a 0.2 μm syringe filter, and injected directly onto the columns. All molecular weights are listed versus polystyrene standards unless otherwise indicated. Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Bruker spectrometer.

Purification of Monomer. The first procedure involved washing an aqueous solution (25 vol % HEMA) of monomer with hexanes (4 × 200 mL), salting the monomer out of the aqueous phase by addition of NaCl, drying over $MgSO_4$, and distilling under reduced pressure. The second procedure included passing monomer through a neutral silica column, eluted with 30/70 benzene/ethyl acetate, and distilling under reduced pressure. Both methods yielded monomer that polymerized readily and without cross-linking as shown by SEC.

Synthesis of 2-(Trimethylsilyloxy)ethyl Methacrylate (HEMA−TMS). In a dry 500 mL round-bottomed flask filled with argon, sealed with a rubber septa, and vented to the atmosphere, 10 mL (76 mmol) of unpurified HEMA, 10.6 mL (76 mmol) of triethylamine and 250 mL of ethyl ether were chilled to 0 °C. A 9.8 mL (76 mmol) aliquot of TMS−Cl was added dropwise over 10 min. A white precipitate formed immediately. The mixture was stirred at 0 °C for 2 h then filtered to remove the solids. The solid was washed with ether. The filtrate was then washed with deionized water (3 × 100 mL) and dried over $MgSO_4$, and the ether was removed under vacuum. The protected monomer was distilled (50 °C, 0.06 Torr). Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 6.1 (s, 1H); 5.5 (s, 1H); 4.2 (t, 2H); 3.8 (t, 2H); 1.9 (s, 3H); 0.5 (s, 9H).

Synthesis of Low Molecular Weight pHEMA−TMS ($M_{n,th}$ = 10 000). In a 5 mL flask, 0.0566 g (0.2 mmol) of TsCl and 3.0 mL (9.9 mmol) of HEMA−TMS were purged with bubbling argon for a minimum of 45 min. In a 10 mL flask, 0.0214 g (0.1 mmol) of CuBr, 0.1224 g (0.2 mmol) of dNbipy, and 3.0 g of 1,4-dimethoxybenzene (DMB) were degassed by vacuum followed by argon backfill three times. The solution of HEMA−TMS and TsCl was then transferred into the catalyst mixture using a cannula. The solution was stirred at 90 °C. Conversion was determined by ^{1}H NMR. Molecular weights were determined by SEC in THF using PMMA standards. Final conversion was 94%. M_n = 11 800, M_w/M_n = 1.18.

Polymerizations in sparged diphenyl ether (DPE) and in bulk ($M_{n,th}$ = 50 000) were carried out using identical procedures. In some polymerizations, kinetic samples were removed at timed intervals, with conversion determined by GC using DMB/DPE as internal standards.

ATRP of HEMA. The following are typical reaction conditions. In a 10 mL round-bottom flask 0.0123 g (0.12 mmol) of CuCl and 0.0386 g (0.241 mmol) were degassed by vacuum followed by argon backfill three times. Solvent (70/30 v/v MEK/1-propanol; 3.0 mL) and HEMA (3.0 mL; 25 mmol) which had been degassed with bubbling argon for at least 45 min were added by syringe and placed in a thermostated oil bath. An initial sample was taken by syringe, and BriB (36 μL; 0.12 mmol) was added. At timed intervals, kinetic samples were taken by syringe. Conversion was measured by GC.

Synthesis of p(MMA-*b*-HEMA). The poly(methyl methacrylate) with predominantly chlorine end groups (pMMA−Cl) was prepared as discussed previously.[21] In a 5 mL pear-shaped flask, 0.125 g of pMMA (M_n = 3400, M_w/M_n = 1.12) was degassed, and 1.0 mL of previously degassed 1-propanol/MEK (30/70 v/v) was added by syringe. The mixture was stirred until the solution was homogeneous (1 h). In a 5 mL round-bottom flask, CuCl (0.0035 g; 0.035 mmol), and bpy (0.0110 g; 0.07 mmol) were degassed, and sparged HEMA (1.0 mL; 4.1 mmol) was added. The red mixture was stirred until homogeneous (5 min) and then placed in a 60 °C oil bath. The initiator solution was transferred by cannula into the round-bottom flask. The solution was homogeneous and dark red. After 1 h and 15 min, the flask was removed, and conversion was determined to be 65% by ^{1}H NMR in d_6-DMSO. GPC_{DMF}: M_n = 32 900, M_w/M_n = 1.17. The polymer was diluted with an additional 3 mL of 1-propanol/MEK and passed over alumina to obtain a pink solution that was precipitated into water, redissolved in 1-propanol/MEK, and passed over alumina again. The solution was colorless but did not precipitate into water a second time. Instead, it was lyophilized for 4 days at −52 °C and 16 Torr to obtain a white hygroscopic solid (yield: 0.2 g).

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