Amide Functional Initiators for Transition-Metal-Mediated Living Radical Polymerization

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ABSTRACT: Amide initiators were used successfully for copper-mediated living radical polymerization (often called ATRP) of a range of methacrylates to narrow molecular weight homopoymers and block copolymers from initiator species containing a bromo-2-methylpropionamide. The polymerization of methyl methacrylate (MMA) occurs efficiently with a copper chloride (Cu(I)Cl)/*N*-*n*-octyl-2-pyridylmethanimine catalyst by maintaining a relatively low temperature for initiation and slowly increasing to the reaction temperature. By keeping the reaction at 25 °C for 30 min before heating to 90 °C, a number-average molecular weight (M_n) of 12 900 g mol^{-1} and a polydispersity of (PDI) = 1.24 at 70% conversion (where [MMA]/[initiator] = 100) were obtained. The polymers produced showed molecular weights in good agreement with the theoretical and polydispersities of 1.20. Where the reaction was heated to 90 °C, immediately high mass was obtained (26 600 g mol^{-1}) in low yield (33%). When copper bromide (Cu(I)Br) was used in place of Cu(I)Cl, the obtained mass was much higher than the theoretical values. Polymerization from an initiator based on L-alanine under these conditions gave poly(methyl methacrylate) (PMMA) with M_n = 8100 g mol^{-1} (PDI = 1.23) as compared to the theoretical value of 5900 at this conversion (58% after 7 h). Polymerization of a other methacrylates including butyl methacrylate (M_n = 8700 (PDI = 1.27), $M_{n,theo}$ = 7000), benzyl methacrylate (M_n = 11 400 (PDI = 1.25), $M_{n,theo}$ = 9700), dimethylaminoethyl methacrylate (DMAEMA) (M_n = 10 900 (PDI = 1.24), $M_{n,theo}$ = 8100), and also poly(ethylene glycol) methacrylate (M_n = 8100 (PDI = 1.24), $M_{n,theo}$ = 6500) were also polymerized. The successful polymerization of styrene using bromo-2-methylpropionamide initiators is also reported with optimum conditions needing 110 °C in the presence of Cu(I)Br and *N*-*n*-octyl-2-pyridylmethanimine yield polymer with M_n = 5800 (PDI = 1.27). Poly(methyl methacrylate) was also used as macroinitiator with DMAEMA to form an AB block copolymer, confirming the living nature of the polymers (M_n = 34 700 (PDI = 1.25)). A triblock polymer of methyl methacrylate and poly(dimethylsiloxane) (PDMS) was also prepared from a difunctional bromo-2-methylpropionamide poly(dimethylsiloxane) initiator (M_n = 29 600 (PDI = 1.27)).

Introduction

Transition-metal-mediated living radical polymerization (LRP) (often called ATRP) has emerged as an effective technique for the controlled polymerization of styrenics, methacrylates, acrylates, and acrylonitrile.[1−3] This technique has been the subject of many papers as it offers the opportunity to prepare a diverse range of functional polymers. A wide variety of moieties have been utilized as initiators including alkyl halides,[4−7] benzylic halides,[8−10] haloesters,[6,7,11,12] haloketones,[7,13,14] halonitriles,[15,16] and sulfonyl halides[17−19] as well as polyhalogenated compounds.[20−23] This type of living radical polymerization requires an activated C−X bond (where X is usually a halogen) alpha to an electron-withdrawing group; initiation occurs following homolytic fission of the C−X bond. The choice of initiator is important in controlling the rate of initiation; if the C−X bond is too strong, initiation, and thus polymerization, will not take place, and if the C−X bond is too weak, a free radical will be produced that results in a high concentration of radicals leading to either premature termination or polymer with broadened polydispersity. To maintain the characteristics of a useful living polymerization with narrow polydispersity, the ability for reinitiation to give block copolymers it is important to maintain the rate of initiation at least comparable to the rate of propagation.

There have been many reported examples of the transformation of hydroxyl functionality into polymerization initiators via an appropriate esterification resulting in molecules with one initiator site per hydroxyl group. Derivatives of cholesterol,[20] sugars,[21,24] cyclodextrins,[25] Wang resins,[22,26] fluorinated molecules,[27] and various preformed polymers such as poly(ethylene glycol),[23,28] poly(dimethylsiloxane),[29] and poly(tetrahydrofuran)[30] have been used to prepare many novel structures including block and star copolymers. Conversely, there have been few examples of primary amines being converted into initiators to give 2-bromo-2-methylpropionamide-based initiators. Sawamoto et al. reported the use of *N*,*N*-dimethyl-2-chloropropanamide in the polymerization of dimethylacrylamide in an attempt to mimic the structure of the propagating polymer structure with a similar initiator composition.[31] Polymeric products were of desired molecular weight, although polydispersity was relatively broad (∼1.6). Only one report by Kang et al. describes the conversion of a primary amine into an initiator for ATRP.[32] An amino functional silicone surface was reacted with 2-bromoisobutyryl bromide to create initiator sites which was used for the polymerization of poly(ethylene glycol)methyl ether methacrylate (PEGMA) and *N*-isopropylacrylamide. However, no attempt was made to determine the molecular weight properties of the polymer produced. Indeed, in a paper describing the polymerization of (meth)acrylamides by ATRP, Matyjaszewski utilized ester derived initiators.[33] Previous investigations have shown that polymers formed using bromo-2-methylpropionamide initiators have tended to be of low polydispersity but with molecular weights differing considerably from the predicted. This is most likely caused by large amounts of termination occurring at the start of the reaction during the initiation phase. The result of this is a polymer with a molecular

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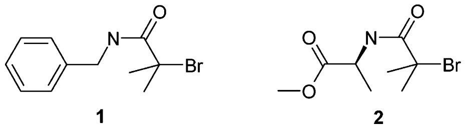
Scheme 1. Initiators Used in This Work



weight considerably greater than the theoretical value. It must also be noted that the two complementary living radical polymerization techniques have also been extensively developed for the synthesis of complex polymer architectures. Poly(dimethylsiloxane) triblock copolymers have been reported by Davis as well as more complex architectures,[34,35] while Perrier has developed a facile route to quite complex initiators, which in turn give rise to diverse polymer structures[36,37] including supported initiators.[38] Nitroxide-mediated radical polymerization also been widely developed, especially for styrenes and acrylate monomers[39,40] but not so successfully for methacrylates.

This present work describes the preparation of bromo-2-methylpropionamide initiators for methacrylate polymerization via copper-mediated LRP. Reaction conditions have been optimized for the synthesis of poly(methacrylates) and poly(styrene) of desired molecular weight with low polydispersity. Two initiators were used based on benzylamine and the amino acid L-alanine. The synthesis of both homopolymers and block copolymers is reported. The synthesis of block copolymers from a preformed amino-functional polymeric macroinitiator is also described.

Experimental Section

General Characterization. ^{1}H (300 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX300 spectrometer using deuterated solvents from Aldrich. Infrared spectra were recorded on a Bruker Vector 22 FTIR spectrometer using a Golden Gate attenuated total reflection (ATR) cell. Elemental analysis was conducted using a Leeman Labs CE400 elemental analyzer.

Size exclusion chromatography (SEC) was carried out using a Polymer Laboratories modular system equipped with a differential refractive index (DRI) and UV/vis detectors calibrated with linear poly(methyl methacrylate) standards ($M_p = 200-1.577 \times 10^6$ g mol^{-1}) and linear poly(styrene) standards ($M_p = 540-1.640 \times 10^6$ g mol^{-1}). The mobile phase used was 95% tetrahydrofuran (THF) and 5% triethylamine, and the elution time was standardized against that of toluene. The flow rate was set at 1.0 mL/min. The system was equipped with a PL-gel 5 μm (50 × 7.5 mm) guard column and two PL-gel 5 μm (300 × 7.5 mm) mixed C (suitable for separations up to M_w 2 000 000 g mol^{-1}) columns thermostated at 25 °C.

Materials. Methyl methacrylate (Aldrich, 99%), butyl methacrylate (BMA) (Aldrich, 99%), benzyl methacrylate (BzMA) (Aldrich, 96%), and styrene (Lancaster; 99%) were purified by passage through a short column of activated basic alumina before use to remove inhibitors and acidic impurities. This was deoxygenated by purging with dry nitrogen gas for ∼30 min prior to being stored at 0 °C. (Dimethylamino)ethyl methacrylate (DMAEMA) (Aldrich, 98%) was bubbled with dry nitrogen gas for 30 min prior to use. Toluene (BDH, 98%) was degassed by bubbling with nitrogen for 30 min and stored in a sealed flask under nitrogen. Copper(I) bromide (Aldrich, 99%) and copper(I) chloride (Aldrich, 98%) were purified according to the method of Keller and Wycoff.[41] Benzylamine (Aldrich, 99%), triethylamine (Aldrich, 99.5%), 2-bromoisobutyryl bromide (Aldrich, 98%), L-alanine methyl ester (Fluka, 99%), aminopropyl-terminated poly(dimethylsiloxane) (ABCR), and d_8-methyl methacrylate (Aldrich, 99%) were used as received. Diimine ligands were prepared as described previously.[42] All other materials were obtained from Aldrich and were used without any further purification unless otherwise stated.

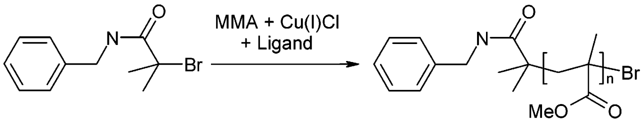
Synthesis of *N*-Benzyl-2-bromo-2-methylpropionamide, 1 (Scheme 1). Benzylamine (30 mL, 0.27 mol), triethylamine (76.5 mL, 0.55 mol), and anhydrous THF (1000 mL) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (50.9 mL, 0.41 mol) was added slowly at 0 °C with stirring. A white precipitate, of triethylammonium bromide, was formed, and the reaction was left for 20 h at ambient temperature with stirring. The precipitate was removed by filtration prior to removal of volatiles in vacuo to leave a brown liquid. The product was redissolved in dichloromethane and was subsequently isolated following washing with two 200 mL portions of saturated sodium carbonate solution, 0.5 M HCl(aq), and deionized water. The dichloromethane solution was dried over $MgSO_4$ and the volatiles removed in vacuo to give a light brown solid. ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz) δ: 7.31 (M, 5 H, Aro), 7.02 (S, 1 H, NH), 4.46 (d, $J = 5.8$ Hz, 2H, Aro−CH_2−NH), 1.99 (s, 6H, C═O−CMe_2). ^{13}C NMR ($CDCl_3$, 298 K, 100.6 MHz) δ: 171.95(C═O), 137.77, 128.81, 127.55, 127.40 (Aro), 62.90 (C═O−CMe$_2$), 44.38 (Aro−CH$_2$−NH), 32.62 (C═O−CMe_2). IR (solid, ATR cell) υ (cm^{-1}): 3291 (amide N−H stretch), 1642 (amide −CONH stretch), 1534 (Aro −H vibration), 1354, 1293, 1102, 693, 638. CHN Analysis: calculated, C = 51.58%, H = 5.51%, N = 5.47%. Found: C = 51.39%, H = 5.48%, N = 5.51%

Synthesis of L-Alanine Methyl Ester−2-Bromo-2-methylpropionamide, 2 (Scheme 1). L-Alanine methyl ester (19.5 g, 0.14 mol), triethylamine (76.5 mL, 0.51 mol), and anhydrous dichloromethane (700 mL) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (36.5 mL, 0.30 mol) was added slowly at 0 °C with stirring. A white precipitate, of triethylammonium bromide, was formed, and the reaction was left for 20 h at ambient temperature with stirring. The precipitate was removed by filtration prior to removal of volatiles in vacuo to leave a brown liquid. The product was redissolved in dichloromethane and was subsequently isolated following washing with two 200 mL portions of saturated sodium carbonate solution, 0.5 M HCl(aq), and deionized water. The dichloromethane solution was dried over $MgSO_4$ and the volatiles were removed in vacuo to give an orange liquid. Yield = 82.4%. ^{1}H NMR ($CDCl_3$, 298 K) δ: 7.20 (S, 1 H, NH), 4.52 (m, 1H, C═OCHCH$_3$NH), 3.77 (s, 3H, C═O−OMe), 1.96 (s, 6H, C═O−CMe_2), 1.45 (d, $J = 7.3$ Hz, 3 H, C═OCHCH_3-NH). ^{13}C NMR ($CDCl_3$, 298 K) δ: 172.95 (C═O−OMe), 171.57 (C═O−NH), 61.77 (C═O−CMe$_2$), 52.51 (O−CH$_3$), 48.87 (C═OCHCH$_3$-NH), 32.27 (C═O−CMe_2), 17.98 (C═OCHCH$_3$NH). CHN Analysis: calculated: C = 38.11%, H = 5.60%, N = 5.56%: Found, C = 38.02%, H = 5.57%, N = 5.58%.

Preparation of Difunctional α-Bromoamide−Poly(dimethylsiloxane) Macroinitiator. Aminopropyl-terminated poly(dimethylsiloxane) with a molecular weight of ∼5000 g mol^{-1} (PDI = 1.65 as determined by ourselves using SEC calibrated with PMMA standards) was used. Aminopropyl-terminated PDMS (30 g, 6 mmol), triethylamine (4 mL, 28 mmol), and anhydrous tetrahydrofuran (300 mL) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (2.6 mL, 20 mmol) was added slowly at 0 °C with stirring. A white precipitate, of triethylammonium bromide, was formed, and the reaction was left for 20 h at ambient temperature with continued stirring. The precipitate was removed by filtration prior to removal of volatiles in vacuo to leave a brown oil. The product was redissolved in dichloromethane and was subsequently isolated following washing with two 200 mL portions of saturated sodium carbonate solution, 0.5 M HCl(aq), and deionized water. The dichloromethane solution was dried over $MgSO_4$, and the volatiles removed in vacuo to give an orange oil. ^{1}H NMR ($CDCl_3$, 298 K) δ (ppm): 6.78 (s, 1H, NH), 3.22 (t, $J = 7.2$, 2H, CH_2NH), 1.97 (s, 6H, C(CH_3)$_2$Br), 1.55 (m, 2H, CH$_2$CH_2-CH$_2$), 0.53 (m, 2H, CH_2SiO), 0.06 (s, 6H, nSi(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 298 K) δ (ppm): 176.0 (C═O), 62.0 (NH−CH$_2$), 56.1 NH−CH$_2$$CH_2$), 43.7 ($CH_2$−Si), 44.9 (CBr($CH_3$)$_2$), 31.2 ($C$(CH$_3$)$_2$-Br), 0.1 (Si($CH_3$)$_2$)$_n$, ($n = 40$). IR absorption ν (cm^{-1}): 2963 (alkyl C−H stretch), 1670 (amide −CONH stretch), 1260 (−Si(CH$_3$)$_2$) and 1095−1025 (Si−O).

Polymerization of Methyl Methacrylate. Methyl methacrylate was polymerized with both **1** and **2** as initiators as well as Cu(I)Cl and *N*-*n*-octyl-2-pyridylmethanimine as catalysts. Typically, Cu-

Scheme 2



(I)Cl (0.138 g, 1.39 × 10^{-3} mol) and **1** (0.356 g, 1.39 × 10^{-3} mol) were added to a Schlenk tube which was fitted with a rubber septum and pump-filled with nitrogen three times. Subsequently, deoxygenated and inhibitor-free MMA (15 mL, 0.14 mol), deoxygenated toluene (15 mL), and *N*-*n*-octyl-2-pyridylmethanimine (0.67 mL, 2.9 × 10^{-3} mol) were added to the Schlenk tube under nitrogen. The solution was further deoxygenated by three freeze−pump−thaw cycles before being heated to 25 °C for 30 min. The solution was subsequently heated to 90 °C. Samples were removed periodically for conversion and GPC analysis via syringe. The final polymer was purified by the passage of the solution over a basic alumina column and was isolated by precipitation in cold petroleum ether (40−60) and drying in vacuo. M_n = 48 200 g mol^{-1} (PDI = 1.18) in 87.9% conversion after 4.5 h.

Polymerization of Styrene. Styrene was polymerized with both **1** and **2** as initiators as well as Cu(I)Br and *N*-*n*-octyl-2-pyridylmethanimine as catalysts. Typically, Cu(I)Br (0.227 g, 1.58 × 10^{-3} mol) and **1** (0.404 g, 1.58 × 10^{-3} mol) were added to a Schlenk tube that was fitted with a rubber septum and pump-filled with nitrogen three times. The mixture was subsequently deoxygenated, and inhibitor-free styrene (15 mL, 0.16 mol), deoxygenated toluene (15 mL), and *N*-*n*-octyl-2-pyridylmethanimine (0.76 mL, 3.2 × 10^{-3} mol) were added to the Schlenk tube under nitrogen. The solution was further degoxygenated by three freeze−pump−thaw cycles before being heated to 25 °C for 30 min. The solution was heated to 110 °C. Samples were removed periodically for conversion and GPC analysis via syringe. The final polymer was purified by the passage of the solution over a basic alumina column and was isolated by precipitation in cold methanol and drying in vacuo. M_n of 6800, polydispersity = 1.24, and 65% conversion in 12 h.

Preparation of PMMA−PDMAEMA Block Copolymer. Cu(I)Br (0.024 g, 1.67 × 10^{-4} mol) and PMMA (2 g, 1.67 × 10^{-4} mol) were added to a Schlenk tube that was fitted with a rubber septum and pump-filled with nitrogen three times. Subsequently, deoxygenated DMAEMA (5.85 mL, 0.034 mol), deoxygenated toluene (20 mL), and *N*-*n*-propyl-2-pyridylmethanimine (0.056 mL, 3.7 × 10^{-4} mol) were added to the Schlenk tube under nitrogen. The solution was further degassed by three freeze−pump−thaw cycles before being heated to 25 °C for 20 h. Samples were removed periodically for conversion and GPC analysis via syringe. The final polymer was purified by the passage of the solution over a basic alumina column and was isolated by precipitation in cold petroleum ether (40−60) and drying in vacuo. M_n = 11 500, polydispersity = 1.18 (SEC).

Preparation of PMMA−PDMS−PMMA Triblock Copolymer. Cu(I)Cl (0.158 g, 1.59 × 10^{-3} mol) and PDMS initiator (4 g, 8 × 10^{-4} mol) were added to a Schlenk tube that was fitted with a rubber septum and pump-filled with nitrogen three times. Subsequently, deoxygenated and inhibitor-free MMA (17.16 mL, 0.16 mol), deoxygenated toluene (20 mL) and *N*-*n*-octyl-2-pyridylmethanimine (0.76 mL, 3.2 × 10^{-3} mol) were added to the Schlenk tube under nitrogen. The solution was further deoxygenated by three freeze−pump−thaw cycles before being heated to 25 °C for 30 min. The solution was subsequently heated to 90 °C. Samples were removed periodically for conversion and GPC analysis via syringe. The final polymer was purified by the passage of the solution over a basic alumina column and was isolated by drying in vacuo. M_n = 29 600 g mol^{-1}, polydispersity = 1.27.

Results and Discussion

Preparation of Poly(methacrylate)s. The polymerization of MMA was investigated under a range of reaction conditions (Scheme 2). The nature of the catalyst and the reaction temperature were varied. All reactions were conducted in toluene (50% v/v) with a target theoretical molecular weight of 10 000 g mol^{-1} ([MMA]:[initiator] = 100), with **1** as initiator. When Cu(I)Br was used to form the catalyst and the reaction was carried out by rapid heating to 90 °C at the start of the reaction gave PMMA with M_n = 48 200 g mol^{-1} (PDI = 1.18) in 87.9% conversion after 4.5 h. When the reaction was started at 25 °C and held at this temperature for 30 min prior to slow heating to 90 °C, the resulting PMMA had M_n = 45 700 g mol^{-1} (PDI = 1.18) in 90% conversion after 3 h. When the reaction was catalyzed by Cu(I)Cl, a conversion of 33.5% with M_n = 26 600 g mol^{-1} (PDI = 1.13) was obtained, again significantly greater than the predicted value. When the polymerization was carried out with Cu(I)Cl with the initial 30 min of the reaction at 25 °C, followed by slowly heating (over 15 min) to 90 °C, 79% conversion was achieved in 6 h (M_n = 10 700 g mol^{-1} (PDI = 1.23)); the polymerization data are summarized in Table 1. Figure 1 shows the kinetic plot for the Cu(I)Cl-mediated polymerization of MMA with T_0 = 25 °C and Figure 2 the increase of M_n with conversion. In Figure 1 an induction period is observed at the start of the reaction which is due to the 30 min period at 25 °C and the time taken to heat the oil bath to reaction temperature. Under these conditions the polymerization shows characteristics of a living polymerization resulting in polymer with controlled molecular weight and narrow PDI, which narrows on increasing conversion as expected.

Table 1. Polymerization Data for the Polymerization of MMA with CuX/*N*-*n*-Octyl-2-pyridylmethanimine (1:2) as Catalyst with 1 as Initiator in Toluene Solution (33 vol %)

catalyst	T_0[a]	$M_{n,theo}$[b]	M_n (g mol^{-1})	PDI	conv[c] (%)	time (h)
CuBr	90	8800	48 200	1.18	88	4.5
CuBr	25	9000	45 700	1.18	90	3
CuCl	90	3300	26 600	1.13	33	10.5
CuCl	25	7900	10 700	1.23	79	6

[a] Where T_0 = 25 °C reaction held at 25 °C for 30 min prior to heating to 90 °C over 15 min. [b] $M_{n,theo}$ = [MMA]/[**1**] (100) × M_0 (100) × % conversion. [c] Conversion from ^{1}H NMR.

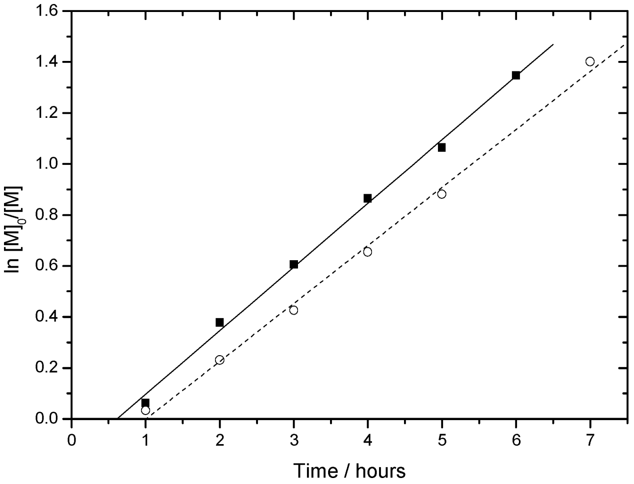


Figure 1. First-order kinetic plot for the polymerization of MMA using a Cu(I)Cl catalyst [MMA]/[CuCl]/[ligand]/[**1**] = 100/1/2/1 in toluene solution (50 vol %). T_0 = 25 °C, held for 30 min, and then heated to and subsequently held at 90 °C for 6/7 h. ■ and solid line = initiator **1**; ○ and dashed line = initiator **2**.

Polymerization of MMA with an initiator derived from L-alanine, **2**, with Cu(I)Cl catalyst gave polymers of with M_n close to the theoretical value, assuming each initiator starts one polymer chain, with low polydispersity. This polymerization was started at 25 °C and held at this temperature for 30 min prior to slowly raising to 90 °C. A conversion of 58% was

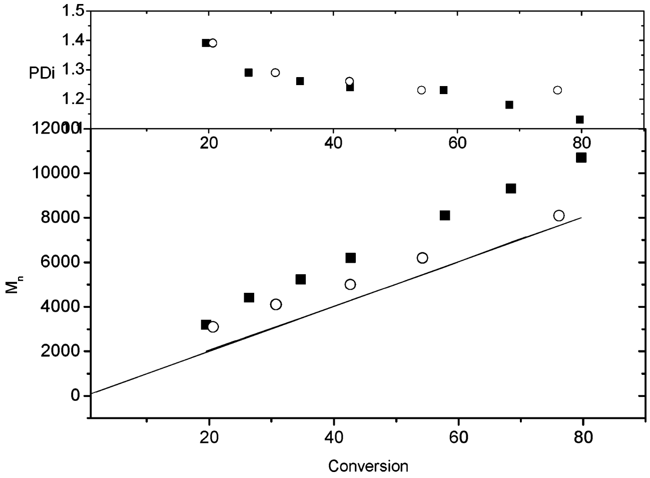


Figure 2. M_n vs conversion for the preparation of PMMA using a Cu(I)Cl catalyst [MMA]/[CuCl]/[ligand]/[**1**] = 100/1/2/1 in toluene solution (50 vol %). T_0 = 25 °C, subsequently held at 90 °C for 6 h. ■ = initiator **1**; ○ = initiator **2**.

Table 2. Molecular Mass Data for the Polymerization of Methacrylates with 1 in the Presence of Cu(I)Cl, [Ligand]/[1]/[Ligand]/[CuCl], in Toluene Solution 50%[a]

monomer	$M_{n,theo}$ (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	PDI
MMA	8000	10 400	10 700	1.13
BMA	7000	8 700	13 000	1.27
BzMA	9700	11 400	17 200	1.25
DMAEMA	8100	10 900	21 100	1.24
PEGMA 300	6500	8 100	12 900	1.24

[a] See the Supporting Information.

achieved in 7 h with M_n = 8100 g mol^{-1} (PDI = 1.23) ($M_{n,theo}$ = 5900 g mol^{-1}). Thus, when CuCl is used with bromo-2-methylpropionamide-based initiators and the reaction mixture is allowed to react for 30 min at ambient temperature prior to slow heating to reaction temperature, living polymerization ensues, and the previous observations confirm the conditions that are ideally suited for copper-mediated polymerization of methacrylates. With amide initiators the initial initiation step likely occurs rapidly leading to a high concentration of free radicals, which results in radical−radical coupling/disproportionation in competition with initiation/propagation. A low temperature at the start of the reaction to 25 °C still allows initiation to proceed, but more slowly.[43] The use of Cu(I)Cl as opposed to Cu(I)Br also reduces the rate of homolytic bond fission.[44] Following initiation, the halogen is alpha to an ester as is normal in this type of polymerization and reaction proceeds more efficiently at higher temperature, resulting in living polymerization.

A range of methacrylate monomers were polymerized—butyl methacrylate, benzyl methacrylate (BzMA), (dimethylamino)ethyl methacrylate (DMAEMA), and poly(ethylene glycol)methyl ether methacrylate (PEGMA)—using Cu(I)Cl and *N*-benzyl-2-bromo-2-methylpropionamide to verify the versatility of the polymerization system. All reactions were started at 25 °C and held at this temperature for 30 min prior to increasing the temperature slowly to 90 °C (Table 2). Although in some cases there is significant difference between the theoretical and SEC values (it is noted that the SEC was calibrated with linear PMMA standards), the M_n values determined by NMR agree well with the theoretical values. In the case of BMA the initiator efficiency can be calculated at each conversion point and was found to vary between 0.58 and 0.74 throughout the reaction. The M_n from ^{1}H NMR was calculated using the aromatic signals of the initiating end group (δ 7.31 and 7.02) and the polymer backbone $CH_2{-}CH_2\mathit{CH_3}$ signals at δ 1.2−0.8. The differences between the SEC molecular weights and the theoretical M_n are in part due to calibration errors associated with calibrating the SEC with PMMA; however, we are reassured by the good agreement with the NMR M_n values which could only be measured at the end of the reaction.

Polymerization of d_8-MMA allowed the nature and the presence of the initiator in the final polymer to be observed more clearly than with protonated MMA due to the absence of peaks from the repeat unit (Figure 3). Three resonances from the initiator can be seen in both spectra with a shift in chemical shift as a C−Br bond is replaced with a C−C bond. Figure 3 shows the shifts for the benzene ring which have shifted 0.1 ppm (δ 7.22−7.33) and also the CH_2 group between the benzene ring and the amide group. The signal for the amide group (δ 7.03) itself has also disappeared in the polymer spectra. ^{13}C NMR spectroscopy confirmed the presence of a carbon chlorine bond at the ω-chain end, δ 67.1 and 66.3 (Figure 4), and also the presence of the initiator at the α-chain end. Thus, polymers have both alpha and omega termini derived from the initiator as would be expected for an analogous ester-derived initiator.

Polymerization of Styrene. The polymerization of styrene was also investigated under a range of conditions. All reactions were conducted in toluene (50% v/v) with a target molecular weight of 9000 g mol^{-1} with **1** as initiator. First, a polymerization was conducted using Cu(I)Br as catalyst with the reaction started with all of the reagents heated to 90 °C. A second polymerization was carried out using Cu(I)Br in which the reaction was started at 25 °C and held at this temperature for 30 min prior to raising to 90 °C. The experiments were repeated

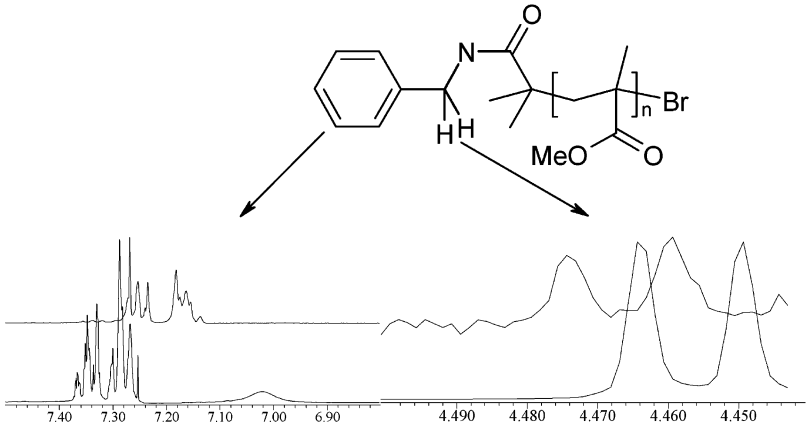


Figure 3. ^{1}H NMR spectra of initiator 1 (bottom) and d_8-MMA polymer initiated with 1 (top).

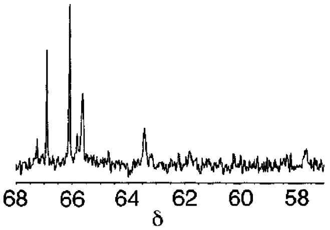


Figure 4. ^{13}C NMR spectra of carbon chlorine bond at ω-chain end.

using Cu(I)Cl as catalyst. The products of the reactions started at 90 °C had molecular weights similar to the predicted values. The reaction catalyzed by Cu(I)Br achieved 65% conversion in 12 h; M_n = 6800, polydispersity = 1.24. The reaction catalyzed by Cu(I)Cl achieved a conversion of 80% in 24 h; M_n of 7600, polydispersity = 1.56. The polymerizations started at 25 °C exhibited similar results. The polymerization conducted using Cu(I)Br achieved 62% conversion in 12 h; the resulting polymer had an M_n = 7900 with polydispersity = 1.24. When the same polymerization was repeated using Cu(I)Cl, 76% conversion was achieved in 24 h. The resulting polymer had an M_n of 7400 and a polydispersity = 1.46. These results are in contrast to the observations made with methacrylate monomers with Cu(I)Br-mediated polymerizations yielding better results than those catalyzed by Cu(I)Cl. It also appears that starting the reaction at a lower temperature has no benefit in this case. This may be explained be the slower rate of polymerization of styrene compared to MMA due to the creation of a secondary radical in styrene, which is stabilized by the aromatic ring. Styrene was also polymerized with L-alanine methyl ester−2-bromo-2-methylpropionamide as initiator. The reaction was catalyzed with Cu(I)Br and started at 90 °C. The polymerization achieved 72% conversion in 12 h; analysis of the final product showed M_n of 5800 with a polydispersity = 1.27.

Preparation of Block Copolymers. To further investigate the living characteristics of polymers prepared from *N*-benzyl-2-bromo-2-methylpropionamide initiator, a block copolymer was prepared via sequential addition. Initially, a homopolymer block of MMA was prepared using Cu(I)Cl as catalyst. The reaction was commenced at 25 °C and held at this temperature for 30 min prior to heating to 90 °C. The isolated and purified polymer had M_n = 11 500 with polydispersity = 1.18 (SEC). This polymer was subsequently used as a macroinitiator for the polymerization of DMAEMA at 100 °C using Cu(I)Br as catalyst. The resulting block copolymer had M_n = 34 700 and a polydispersity = 1.25 (SEC). Figure 5 shows the SEC traces of the PMMA macroinitiator and the resulting PMMA-*b*-PDMAEMA block copolymer, confirming the formation of a block copolymer.

To demonstrate further the robust nature of this polymerization technique, an ABA triblock copolymer was prepared from a diaminopropyl-functional poly(dimethylsiloxane) (PDMS) difunctional macroinitiator prepared from the reaction of diaminopropyl-terminated PDMS with 2-bromoisobutyryl bromide (Scheme 3). Subsequent polymerization of MMA, Cu(I)Cl catalyst with an initial temperature of 25 °C, and subsequently slow heating to 90 °C led to 62% conversion after 5.75 h (M_n = 29 600 g mol^{-1}, polydispersity = 1.27 (SEC)). ^{1}H NMR spectroscopy indicated an M_n = 13 100 g mol^{-1}, in good agreement with the theoretical value of 11 200 g mol^{-1}. Figure 6 shows the linear first-order kinetic plot for the preparation of an ABA PMMA−PDMS−PMMA triblock copolymer. In Figure 6 an induction period is observed at the start of the reaction which corresponds to the 30 min period at 25 °C and the time taken to heat the oil bath to reaction temperature. Further analysis by SEC indicates that molecular weight increases with conversion and polydispersity is reduced with increasing conversion.

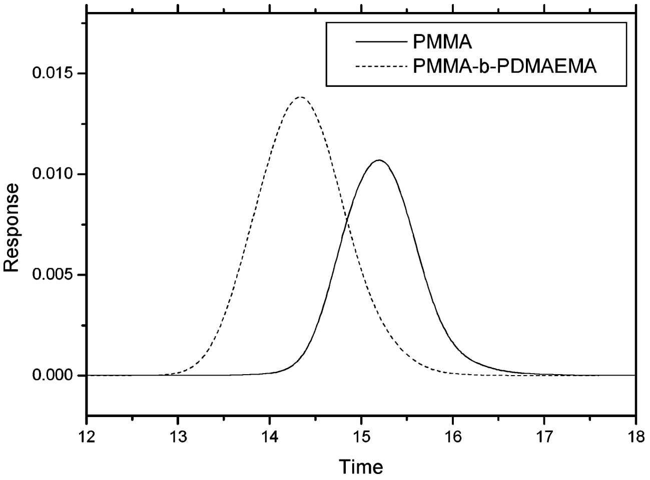
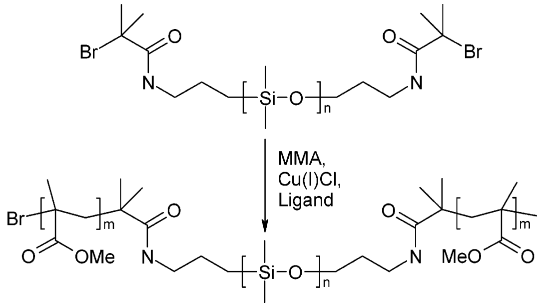


Figure 5. SEC trace of a PMMA macroinitiator and a PMMA-*b*-PDMAEMA block copolymer.

Scheme 3



Conclusions

We have shown that under the appropriate reaction conditions amide functional initiators based on bromo-2-methylpropionamide can be successfully used to prepare a range of poly(methacrylate)s and polystyrene under living radical conditions with M_n approximately equal to [monomer]/[initiator] × M_0 with narrow polydispersity. In the case of methacrylates it is important to reduce the rate of the initiation step in which the halogen alpha to an amide is being transferred to monomer. Following this subsequent propagation steps involve the halide alpha to an ester group. Thus, propagation can be carried out under more conventional reaction conditions. The reduction in rate can also be achieved in part by the use of CuCl in place of CuBr. Block copolymers were also prepared to further demonstrate the robustness of these initiators. It has been accepted for a considerable period of time that many species containing hydroxyl functionality can be transformed into LRP initiators by appropriate esterification. The present results show that this is also true for amines following a relatively straightforward amidation. As amides are more hydrolytically stable than esters, especially in the presence of esterases, this not only increases the range of molecules that may be utilized as initiators but also results in a more stable chemical bond between the chain and the chain terminus.

Supporting Information Available: Ratios, conversions, molecular weights, and NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

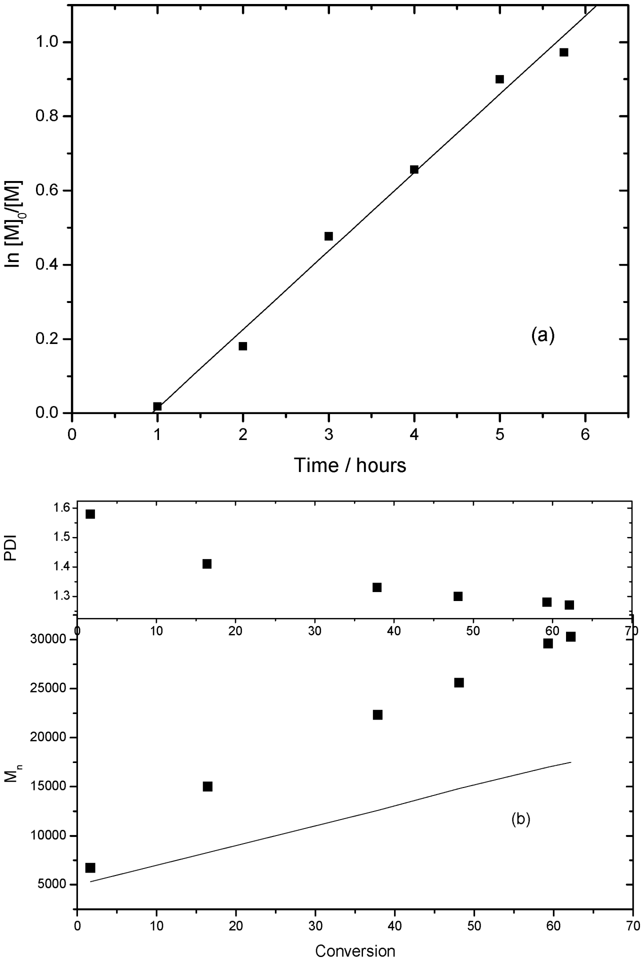


Figure 6. (a) First-order kinetic plot for the preparation of a PMMA−PDMS−PMMA triblock copolymer. (b) Evolution of M_n and PDI with conversion for the polymerization of MMA form PDMS macroinitiator.

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