Phenolic Ester-Based Initiators for Transition Metal Mediated Living Polymerization

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ABSTRACT: A range of phenolic esters derived form the esterification of substituted phenols with 2-bromoisobutyryl bromide and 2-chloroisobutyryl chloride have been demonstrated to be effective atom transfer polymerization initiators in conjunction with *N*-(*n*-octyl)-2-pyridylmethanimine and copper(I) chloride and bromide. All initiators have been fully characterized. Methoxy, phenyl ether, primary aryl amino, aldehyde, nitro, and benzyl ether functional initiators lead to efficacious atom transfer polymerization without imparting any detrimental effects on the polymerization. Polymerizations have been shown to proceed with excellent first-order kinetics with small amount of termination, as seen by narrow polydispersity indices, often below 1.10. Rates of polymerization are of the of the order of 1×10^{-4} s^{-1}, which gives PMMA of approximately 10 000 g mol^{-1} after 4 h under typical polymerization conditions. M_n increases linearly with conversion. Polymerization of a range of alkyl methacrylates is demonstrated including ethyl methacrylate, butyl methacrylate (iso- and *n*-) while *tert*-butyl methacrylate terminates early in the reaction, with the production of a broad molar mass distribution polymer. Polymerization of styrene proceeds effectively, but at a much slower rate than for MMA. Polymerization of MMA with a chloro functional initiator and CuCl proceeds at approximately half the rate of the bromo analogues with a broadening of PDI. Difunctional and trifunctional initiators are derived from the appropriate polyphenols. The multifunctional initiators are shown to be effective atom transfer initiators to give narrow PDI polymer with controlled M_n. The role of deactivating copper(II) species is further seen by the effect of the polymerization rate in a range of kinetic experiments. Esterified phenols are an extremely versatile and simple route into α-functional polymers via atom transfer polymerization.

Introduction

Controlled vinyl addition polymerization giving a wide range of polymer structures is continuing to receive widespread attention.[1] This allows the controlled synthesis of a range of polymeric structures, e.g., block copolymers, graft copolymers, α and α,*ω* (telechelic) functional polymers, star polymers,[2,3] etc. The use of radicals, or systems that behave in a fashion similar to free radical polymerization, to achieve these aims has the potential to remove many of the constraints of anionic/group transfer polymerization, where very pure reagents/solvents are usually required, as are low temperatures and a limited range of solvents.

The use of low valent, late transition metal complexes as halogen transfer agents is being widely developed following the initial ground-breaking work of both Matyjaszewski[4,5] and Sawamoto.[6] This approach is based on the atom transfer cyclization chemistry developed in small molecule organic synthesis, the Kharash reaction.[7,8] Sawamoto described the use of $Ru^{II}(PPh_3)_3Cl_2$ in conjunction with aluminum alkoxides for the living polymerization of styrene and methyl methacrylate while Matyjaszewski illustrated living polymerization of a range of vinyl monomers catalyzed by copper(I) bipyridine complexes. Since these initial reports, many other well-controlled systems have been described based on a number of other transition metals, e.g., nickel,[9−11] copper(0),[12] palladium,[13] rhodium,[14] and iron.[15] The exact mechanism of this type of reaction is not yet fully elucidated, and indeed it seems likely that different metals/ligands have different important fundamental interactions involved, e.g., the role of coordination of monomer to the active metal species.[16] However, several studies have looked at different aspects of the polymerization, and to all intents the system behaves very similar to conventional free radical polymerization[17,18] in terms of stereochemistry of polymers,[10,19] reactivity ratios in statistical co-polymerization,[20,21] etc. Many of these studies have been carried out on copper(I)-based chemistry, the subject of the current work. For example, the reaction order of each component has been determined,[22−24] EPR measurements carried out,[25,26] the role of solvents, additives looked at,[27−29] etc. A range of effective ligands have been used in conjunction with copper(I) salts including multidentate alkylamines, such as tris[2-(dimethylamino)ethyl)amine], which even allow effective living polymerization under ambient conditions.[30]

This chemistry is currently being employed to prepare a range of polymers with a wide diversity of structure and intended applications under diverse conditions.[31] Macroinitators have been used to prepare block copolymers,[32,33] calixaranes,[34,35] simple sugars,[36] and metal-centered initiators have been used to give star polymers,[37] and multifunctional initiators have used to prepare comb polymers.[38,39] Indeed even a new type of block copolymer has been introduced, *gradient copolymers*,[40] based on atom transfer radical polymerization. Fukuda and Ohno have used both atom transfer[41] and living nitroxide mediated polymerization[42] to give carbohydrate-containing polymers, *glycopolymers*. Insoluble supports have also been used to prepare anchored polymers with a range of structures.[43,44]

An effective method of introducing useful functionality into polymers by living polymerization is by the use of functional initiators. The use of a range of initiators

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was illustrated by Percec who has developed sulfonyl chlorides as so-called "*universal-initiators*", which give polymers with very narrow polydispersity when used in conjunction with copper-based catalysts.[23,45,46] Functional carbon−halide initiators have been used by Matyjaszewski with copper(I) bipyridyl complexes[47−49] and macroinitiators derived from condensation polymers have also been used effectively.[32,33] We have been developing the use of copper(I) Schiff base complexes using pyridinal imine ligands for the effective atom transfer controlled polymerization of vinyl monomers, in particular methacrylates.[24,50,51] This paper reports a comprehensive study on the use of different initiators with this chemistry to prepare poly(methacrylates) with a range of well-characterized end functionalities.

Experimental Section

Analysis and General Data. All manipulations were performed using standard Schlenk or syringe techniques under an atmosphere of nitrogen. NMR spectra were recorded on Bruker AC250, DPX 300, and AC400 spectrometers. FTIR spectra were recorded on a Bruker Vector 22 spectrometer with fitted an attenuated total reflection (ATR) cell, and mass spectra were measured on a Kratos MS80 spectrometer. Crystal data was collected on a Siemens three-circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated radiation Mo Kα radiation (λ = 0.710 73 Å) was used. Polymer conversions were measured by gravimetry by drying to constant weight in a vacuum oven at 70 °C. The catalyst was removed from the samples for molecular weight analysis by passing the samples through a column of activated basic alumina. Molecular weight distributions were measured using size exclusion chromatography (SEC), on a system equipped with a guard column and one mixed E column (Polymer Laboratories) with differential refractive index detection using tetrahydrofuran at 1 mL min^{-1} as an eluent. Poly(MMA) standards in the range 6×10^4 to 200 g mol^{-1} were used to calibrate the SEC.

Reagents. Methyl methacrylate (Aldrich, 99%), ethyl methacrylate (Aldrich, 98%), isopropyl methacrylate (Aldrich, 99%), *n*-butyl methacrylate (Aldrich, 99%), isobutyl methacrylate (Aldrich, 99%), and *tert*-butyl methacrylate (TCI, 98%) were purified by passing through a column of activated basic alumina to remove inhibitor. Copper(I) bromide (Aldrich, 98%) was purified according to the method of Keller and Wycoff,[52] *N*-(*n*-octyl)-2-pyridylmethanimine, **18**, was prepared as described earlier.[24,53,54] 2-Bromo-2-methylpropionic acid phenyl ester, **2**, 2-chloro-2-methylpropionic acid phenyl ester, **3**, 2-bromo-2-methylpropionic acid 4-nitrophenyl ester, **8,** and 4-(2,2-dimethylpropionato)phenol were synthesized by modified literature procedures (see Supporting Information for full details).

Typical Polymerization. $Cu^{I}Br$ (0.1342 g, 9.34×10^{-4} mol) was placed in a oven-dried Schlenk tube. The tube was fitted with a rubber septum, and the tube was evacuated (rotary pump) and flushed with dry nitrogen three times. Methyl methacrylate (10 mL, 9.34×10^{-2} mol) and xylene (20 mL) were transferred to the tube via degassed syringe. The mixture was stirred rapidly under nitrogen and *N*-(*n*-octyl)-2-pyridylmethanimine, **18** (0.4082 g, 1.86×10^{-3} mol), was added, which imparted a deep red/brown color to the solution. Phenyl-2-bromoisobutyrate (0.2272 g, 9.34×10^{-4} mol) was added, and the resulting solution was degassed by three freeze−pump−thaw cycles. The resulting mixture was placed in a thermostatically controlled oil bath at 90 °C. Samples were taken periodically for conversion and molecular weight analysis. Conversion was measured by gravimetry by drying to constant weight in a vacuum oven at 70 °C. The catalyst was removed from the samples by passing the samples through a column of activated basic alumina prior to molecular weight analysis.

2-Bromo-2-methylpropionic Acid 4-Methoxyphenyl Ester, 4. 4-Methoxyphenol (24.83 g, 0.2 mol), triethylamine (30.6 mL, 0.22 mol), and THF (400 mL) were placed in a three-neck round-bottomed flask. Bromoisobutyryl bromide (27.2 mL, 0.22 mol) was added slowly with stirring. A white precipitate, of triethylammonium bromide, was formed, when the reaction was left for 6 h with stirring. The insolubles were removed by filtration prior to removal of solvent in vacuo to leave a yellow liquid. The product was isolated following washing with 2 × 200 mL portions of saturated Na_2CO_3(aq), dilute HCl(aq), and distilled water. The dichloromethane solution was dried with $MgSO_4$ and the solvent removed by rotary evaporation to give a yellow oily liquid. On overnight cooling, the product crystallized. The product was recrystallized three times from ethanol at 5 °C. Yield = 33.9 g (62%); mp, below ambient.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.04 (d, J = 9.1 Hz 2 H), 6.90 (d, J = 9.1 Hz 2 H), 3.80 (s, 3H), 2.05 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 100.6 MHz): δ 170.45, 157.38, 144.15, 121.68, 114.38, 55.45, 30.54. IR (solid, ATR cell): 3011, 2975, 2842, 1749, 1595, 1503, 1454, 1272, 1249, 1181, 1160, 1137, 1100, 1026, 941, 872, 816, 744 cm^{-1}. Mass spectrometry (+EI) (*m*/*z*): 274, 272 (mass peaks) 151, 149, 123, 121, 109, 95, 81, 70, 65, 52, 41. Anal. Calcd for $C_{11}H_{13}O_3$ Br: C, 48.37; H, 4.80. Found: C, 48.38; H, 4.79.

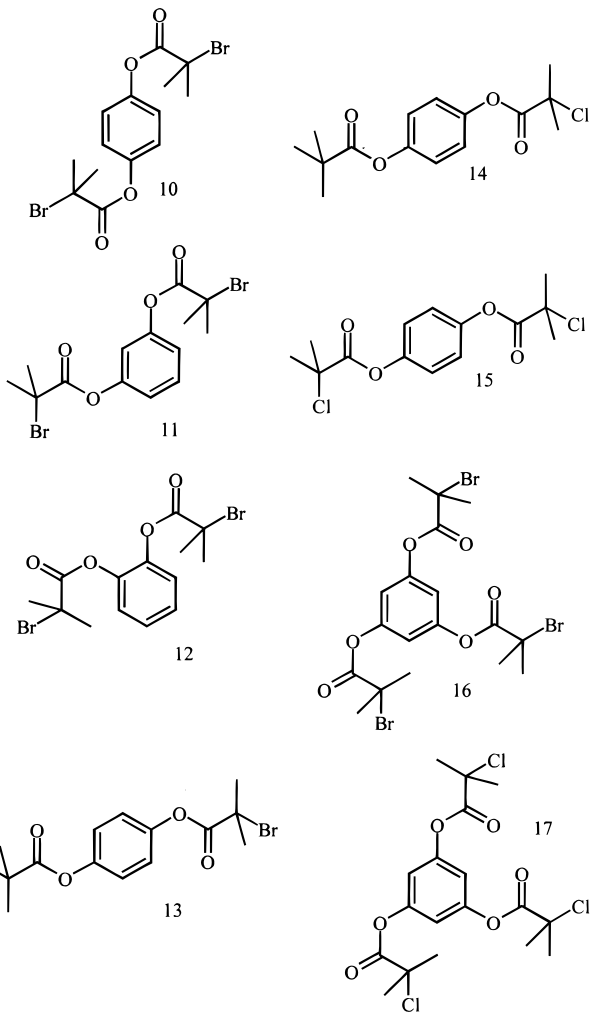
Synthesis of Phenyl 4-(2′-Bromo-2′-methylpropionato)-benzoate, 5. Benzyl-4-hydroxy benzoate (22.82 g, 0.1 mol), triethylamine (15.3 mL, 0.11 mol), and THF (400 mL) were placed in a 1 L three-neck round-bottom flask. Bromoisobutyryl bromide (13.6 mL, 0.11 mol) was added slowly with stirring to the mixture and the reaction was allowed to react for 6 h. The triethylammonium bromide was removed by filtration and the solvent removed by rotary evaporation. The product was isolated as an orange/brown oil, which crystallized upon standing. The product was recrystallized from methanol−water (90:10) and dried to give a slightly yellow crystalline product. Yield = 32.05 g (85%); mp, 49.8 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 8.13 (d, J = 8.8 Hz, 2 H), 7.39 (m, 5 H), 7.20 (d, 8.8 Hz, 2H), 5.36 (s, 2 H), 2.06 (s, 6H). ^{13}C $\{^1H\}$ NMR ($CDCl_3$, 298 K 100.6 MHz): δ 169.6 (C-3), 165.4 (C-8), 154.3, 135.8, 131.3, 128.5, 128.2, 128.1, 128.0, 121.1, 66.8, 55.0 (C-2), 30.4 (C-1). IR (solid, ATR cell) 2977, 1750 (C═O), 1504, 1452, 1380, 1268, 1246, 1185, 1134, 1101, 1015, 875, 741, 698,. EI MS 378, 376 (mass peaks), 271, 269, 151, 149, 123, 121 cm^{-1}. Anal. Calcd for $C_{18}H_{17}BrO_4$: C, 57.31; H, 4.54. Found: C, 57.30; H, 4.54.

2-Bromo-2-methylpropionic Acid 4-Aminophenyl Ester, 6. 2-Bromo-2-methylpropionic acid 4-nitrophenyl ester, **8**, **(**11.52 g, 0.04 mol) and $Sn^{II}Cl_2 \cdot 2H_2O$ (0.2 mol) were dissolved in ethyl acetate (200 mL). The mixture was heated under reflux for 1 h at 80 °C, cooled, and made basic (pH 8−9) using 5% sodium bicarbonate aqueous solution. Distilled water (200 mL) was added and the ethyl acetate layer separated. The organic layer was washed with saturated brine solution (3 ×

200 mL) followed by distilled water (2 × 200 mL). The organic layer was dried with magnesium sulfate, and the solvent was removed in vacuo. This gave a slightly brown crystalline product. Yield = 8.2 g (79%); mp, dec prior to melting.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 6.9 (d, J = 8.5 Hz, 2 H), 6.67 (d, J = 8.8 Hz, 2 H), 2.04 (s, 6 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 170.68, 144.47, 142.53, 121.36, 115.36, 55.59, 30.49. IR (solid ATR cell): 3445, 3357 (N−H stretch), 3008, 2969, 1740 (C═O), 1621 (N−H bend), 1506, 1266 (C−N stretch), 1184, 1162, 1139, 1103, 867, 810 cm^{-1}. EI MS (m/z): 259, 257 (mass peaks), 150, 148, 123, 121. Anal. Calcd for $C_{10}H_{10}NO_4$ Br: C, 46.53; H, 4.69; N, 5.43. Found: C, 46.54; H, 4.69; N, 5.27.



1,4-(2′-Bromo-2′-methylpropionato)benzene, 10. 1,4-Dihydroxybenzene (11.01 g 0.1 mol), triethylamine, (30.6 mL, 0.22 mol), and THF (400 mL) were placed in a 1 L flask. Bromoisobutyryl bromide (27.2 mL, 0.22 mol) was added slowly with stirring and left for 6 h with stirring. On completion of the reaction, triethylammonium bromide was removed by filtration and the solvent removed in vacuo. The product was isolated as a white crystalline product that was recrystallized twice from methanol. Yield = 33.7 g (82.6%); mp, 127.7 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.16 (s, 4 H), 2.05 (s, 12 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 169.95, 148.27, 121.99, 55.17, 30.34; IR (solid, ATR cell): 3010, 2981, 2934, 1744 $\upsilon_{C=O}$ (s), 1499, 1456, 1388, 1372, 1263, 1204, 1171, 1134, 1102, 1012, 940, 885, 809, 779, 747, 636 cm^{-1}. Mass spectrometry (+CI/NH_3) (m/z): 429, 427, 425 (mass peaks + NH_3), 410, 408, 406, 348, 346, 344, 330, 328, 326. Anal. Calcd for $C_{14}H_{16}O_4Br_2$,: C, 41.21; H, 3.95. Found: C, 41.10; H, 3.86.

1,3-(2′-Bromo-2′-methylpropionato)benzene, 11. This compound was prepared as for **10**, purified by recrystallization twice from 90:10 methanol−water. Yield = 30.8 g (75.5%); mp, 61.1 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.39 (t, J = 8.1 Hz, 1 H), 7.08−6.99 (m, 3H) 2.05 (s, 12 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 169.57, 151.03, 129.78, 118.75, 114.49, 55.05, 30.40. IR (solid, ATR cell): 3007, 2981, 1754 $\upsilon_{C=O}$, 1597, 1482, 1460, 1388, 1373, 1242, 1134, 1092, 1006, 960, 938, 917, 892, 836, 787, 767, 682, 650 cm^{-1}. Mass spectrometry (+EI) (m/z): 410, 408, 406, (mass peaks) 331, 329, 327, 301, 299, 260, 258, 151, 149, 123, 121, 110. Anal. Calcd for $C_{14}H_{16}O_4Br_2$,: C, 41.21; H, 3.95. Found: C, 41.23; H, 3.90.

1,2-(2′-Bromo-2′-methylpropionato)benzene, 12. This compund was prepared as for **10**, isolated as a yellow oil. Yield = 19.95 g (49%).

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.27 (m, 4 H), 2.05 (s, 12 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 168.77, 141.86, 126.82, 122.75, 54.96, 30.52. IR (solid, ATR cell): 2978, 2931, 1758 $\upsilon_{C=O}$, 1598, 1493, 1460, 1389, 1371, 1258, 1239, 1170, 1129, 1091 cm^{-1}. Mass spectrometry (+EI) (m/z) 410, 408, 406 (mass peaks), 260, 258, 221, 220, 205, 189, 177, 151, 149, 123, 121, 101. Anal. Calcd for $C_{14}H_{16}O_4Br_2$: C, 41.21; H, 3.95. Found: C, 41.14; H = 3.92.

1-(2′-Bromo-2′-methylpropionato)-4-(2″,2″-dimethylpropionato)benzene, 13. 4-(2,2-dimethylpropionato)phenol (7.77 g, 0.04 mol), triethylamine (6.2 mL, 0.044 mol), and tetrahydrofuran (250 mL) were placed in a three-neck round-bottomed flask. 2-Bromoisobutyryl bromide (5.5 mL, 0.044 mol) was added slowly with stirring, and the reaction was left for 6 h at ambient temperature with stirring. Triethylammonium bromide was removed by filtration and the solvent removed in vacuo. The product was recovered as an orange/white solid that was recrystallized three times from methanol to give a white solid, which was dried, under vacuum. Yield = 10.2 g (74.3%); mp, 136.9 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.16−7.06 (m, 4 H), 2.05 (s, 6 H), 1.35 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 176.69, 169.96, 148.67, 147.85, 122.33, 121.74, 55.20, 38.96, 30.49, 27.00. IR (solid, ATR cell): 2977, 2932, 2872, 1746 $\upsilon_{C=O}$ 1500, 1476, 1460, 1387, 1369, 1263, 1176, 1098, 1009, 935, 898, 872, 832, 794, 774 cm^{-1}. Mass spectrometry (+EI) (m/z): 344, 342 (mass peaks), 260, 258, 151, 149, 123, 121, 110, 85, 70, 57, 41. Anal. Calcd for $C_{15}H_{19}O_4Br$: C, 52.49; H, 5.58. Found: C, 52.20; H, 5.53.

1-(2′-Chloro-2′-methylpropionato)-4-(2″, 2″-dimethylpropionato)benzene, 14. This compound was prepared as for **13** except that chloroisobutyryl chloride was used. The product was recovered as a yellow/white solid that was recrystallized three times from methanol to give a white solid, which was dried, under vacuum. Yield = 9.02 g (75.4%); mp, 132 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.14−7.05 (m, 4 H), 1.90 (s, 6 H), 1.34 (s, 9H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 176.66, 169.85, 148.68, 147.78, 122.33, 121.79, 64.22, 38.94, 29.49, 26.97. IR (solid, ATR cell): 2979, 2934, 2873, 1746, 1500, 1477, 1460, 1369, 1267, 1176, 1106, 1010, 899, 875, 834, 794 cm^{-1}. Mass spectrometry (+EI) (m/z): 300, 298 (mass peaks) 216, 214, 110, 87, 85, 83, 77, 57, 47. Anal. Calcd for $C_{15}H_{19}O_4$ Cl: C, 60.30; H, 6.41. Found: C, 60.08; H, 6.36.

1,4-(2′-chloro-2′-methylpropionato)benzene, 15. This compound was prepared as for **10** except that chloroisobutyryl chloride was used; the product was recovered as a white crystalline solid and was recrystallized three times from methanol. Yield = 20.9 g (65.6%); mp, 122.2 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 7.16 (s, 4 H), 1.91 (s, 12 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 170.32, 148.71, 122.55, 64.69, 30.00. IR (solid ATR cell): 2977, 1752 $\upsilon_{C=O}$ (s) 1501, 1455, 1265, 1175, 1144, 1108, 1015, 935, 892, 810, 667. Mass spectrometry (+CI/NH_3) (m/z): 322, 320, 318 (mass peaks), 304, 302, 300, 216, 214, 127, 110, 71, 58, 35. Anal.Calcd for $C_{14}H_{16}O_4Cl_2$: C, 52.68; H, 5.05. Found: C, 52.37; H, 5.01.

1,3,5-(2′-Bromo-2′-methylpropionato)benzene, 16. 1,3,5-Trihydroxybenzene (6.3055 g, 0.05 mol), triethylamine (23 mL,

0.165 mol), and THF (250 mL) were placed in a 500 mL three-neck round-bottom flask. Bromoisobutyryl bromide (20.4 mL, 0.165 mol) was added slowly. The triethylammonium bromide was removed by filtration and the solvent removed in vacuo. The product was recovered as a white/yellow powder that was recrystallized three times from methanol to give white crystalline powder: yield 25.9 g (90.6%); mp, 187.0 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 6.95 (s, 3 H), 2.04 (s, 18 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 169.41, 151.28, 112.49, 54.78, 30.50. IR (solid, ATR cell): 2980, 1750, 1608, 1452, 1388, 1256, 1134, 1093, 1010, 988, 921, 888, 819, 752, 678 cm^{-1}. Mass spectrometry (+EI) (*m*/*z*): 576, 574, 572, 570 (mass peaks), 467, 465, 463, 424, 422, 276, 274, 151, 149, 123, 121, 83, 69. Anal. Calcd for $C_{18}H_{21}O_6Br_3$: C, 37.73; H, 3.69. Found: C, 37.75; H, 3.68.

1,3,5-(2′-Chloro-2′-methylpropionato)benzene, 17. This compound was prepared as for **16** except that chloroisobutyryl chloride was used. The product was recovered as a pale yellow powder that was recrystallized three times from methanol. The product was dried under high vacuum to give a white crystalline powder. Yield = 35.4 g (62.9%); mp, 175.5 °C.

^{1}H NMR ($CDCl_3$, 298 K, 250.13 MHz): δ 6.95 (s, 3 H), 1.89 (s, 18 H). ^{13}C {^{1}H} NMR ($CDCl_3$, 298 K 100.6 MHz): δ 169.04, 151.06, 112.52, 63.97, 29.31. IR (solid ATR cell): 3099, 2985, 2938, 1755 $\upsilon_{C=O}$, 1610, 1454, 1389, 1371, 1261, 1143, 1118, 1100, 1012, 989, 919, 890, 824 cm^{-1}. Mass spectrometry (+EI) (*m*/*z*): 444, 442, 440, 438 (mass peaks), 338, 336, 334, 230, 232, 126, 105, 83, 77, 70, 47. Anal. Calcd for $C_{18}H_{21}O_6Cl_3$: C, 49.17; H, 4.81. Found: C, 49.13; H, 4.78.

Results and Discussion

A range of atom transfer polymerization initiators was synthesized by the condensation of phenols with 2-bromoisobutyryl bromide and 2-chloroisobutyryl chloride. This generic approach is very versatile and allows a wide range of functionality to be incorporated within linear and branched polymers. The synthesis of multifunctional initiators was achieved by condensation of di- and triphenols. All initiators were achieved in good yield and were fully characterized prior to polymerization studies. Spectroscopic data is given in all cases where it does not previously appear in the literature; see Supporting Information for data and procedures that overlap with previous literature work.

Polymerization of Methyl Methacrylate and Styrene with Monofunctional Phenolic Ester Bromo Initiators with CuBr-Based Catalysts. Methyl methacrylate was polymerized in xylene solution at 90 °C with a complex formed between copper(I) bromide and *N*-(*n*-octyl)-2-pyridylmethanimine, **18**. The reactions were carried out with a monomer to initiator molar ratio of 100 targeting a final DP_n of 100, giving a theoretical M_n of approximately 10 000 g mol^{-1} at 100% conversion. The reactions were sampled periodically with time and molecular mass and conversion measured in each instance. Figure 1 shows the first-order plots for the ethyl ester initiator, **1**, and the bromophenol ester **2**. There is a small increase in the rate of polymerization with **2** with respect to **1**. Table 1 reports the M_n and PDI of the polymers after 4 h. When the polymerization was stopped after 45 min and the polymer isolated by precipitation, the presence of the terminal aromatic ring was observed across the entire molecular mass distribution, by UV detection SEC; see Supporting Information. Characteristic triplets at 7.29 and 7.17 ppm and a doublet at 6.99 ppm were observed by ^{1}H NMR; see Supporting Information. The M_n was determined by integration of the ω-methoxy group relative to the remaining methoxy groups and found to be 3140 g mol^{-1}, comparing very favorably with $M_{n(SEC)}$ of 3160 and $M_{n(theoretical)}$ of 3050. The ω-terminal C−Br group was seen as three peaks between 58.0 and 59.5 ppm in the ^{13}C NMR spectrum. Attempts to characterize the polymer by MALDI−TOF resulted in fragmentation with loss of CH_3Br and HBr, which will be discussed in detail in a future publication.

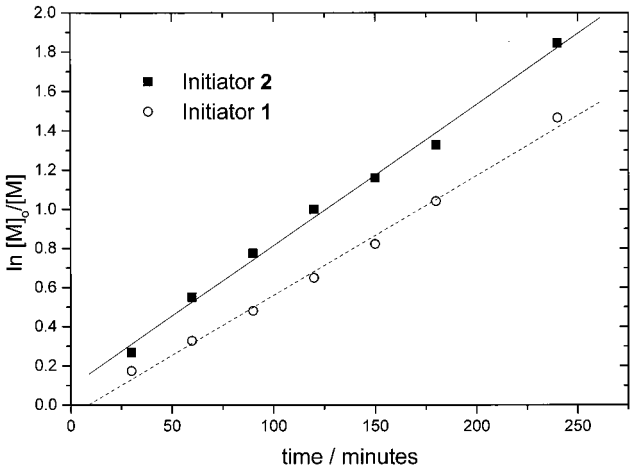


Figure 1. Kinetic plot for the polymerization of MMA with initiators **1** and **2** polymerized in xylene solution (33% v/v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1. Lines drawn are linear regression best fits.

Table 1. Atom Transfer Polymerization with Phenolic Ester-Based Monofunctional Initiators in Xylene Solution (33% v/v) at 90 °C [MMA]/[CuBr]/[18]/[initiator] = 100/1/2/1, Sampled at *t* = 4 h

initiator	monomer	convn, %	M_n	PDI	k_p[Pol*] × 10^4, s^{-1}	I_{eff}
1	MMA	76.9	6350	1.19	1.02	0.82
2	MMA	84.2	6620	1.11	1.20	0.79
3[a]	MMA	72.8	7780	1.35	0.43	1.07
4	MMA	66.9	5430	1.14	1.29	0.81
5	MMA	82.2	6710	1.10	1.37	0.82
6	MMA	86.6	9340	1.19	1.34	1.08
7	MMA	76.7	6440	1.10	1.03	0.84
8	MMA	85.2	6350	1.09	1.35	0.77
13	MMA	80.6	7220	1.09	1.16	0.89
14[a]	MMA	64.6	7410	1.23	0.72	1.15
2[b]	STY	29.5	1950	1.10	0.21	0.66
2[c]	STY	52.8	5000	1.11	0.57	0.91
2[d]	STY	56.2	5240	1.10	0.61	0.90

[a] CuCl used as catalyst. [b] Styrene in xylene (50% v/v) at 110 °C, 44% conversion after 8 h; see Supporting Information. [c] Styrene in xylene (50% v/v) at 110 °C, [MMA]/[CuBr]/[**18**]/[initiator] = 100/2/4/1, 80% conversion after 8 h, see Supporting Information. [d] Styrene in xylene (50% v/v) at 110 °C.

Initiators **4**−**9** are all effective initiators for atom transfer polymerization all showing linear first-order kinetic plots, Figure 3, and a linear increase of M_n with conversion, Figure 4. In all cases the PDI remains narrow throughout the polymerization, Table 1, and the aromatic α-terminal aromatic group is observed in the UV detection SEC across the entire mass envelope; see Supporting Information. There is no detectable effect on the rate of polymerization as a function of the electronic effects of the 4-substutuent, as might have been expected. Thus alkyl ethers, primary aromatic amines, aromatic nitro, and aldehyde groups can be used to introduce a range of functionality within the polymer, without the need for protecting group chemistry with no detrimental effects on the polymerization.

Initiator **1** is also effective for the atom transfer polymerization of styrene, under similar conditions,

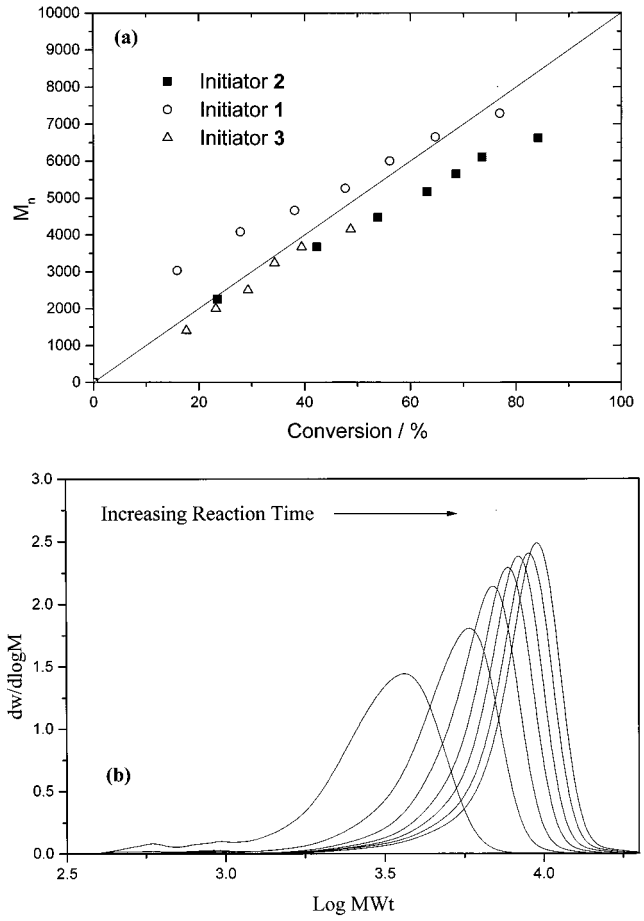


Figure 2. (a) Evolution of M_n with conversion for the polymerization of MMA in xylene solution (33% v/v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1 with initators **1**−**3**. The line is theoretical M_n. (b) SEC traces for the polymerization with **2.** The area under each curve has been normalized so as to be directly proportional to conversion.

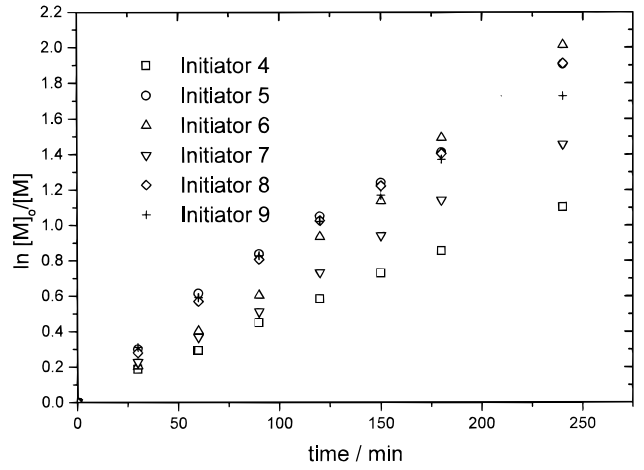


Figure 3. Kinetic plots for the polymerization of MMA with monofunctional phenolic ester initiators **1**−**9**, xylene solution (33% v/v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1.

Table 1. However, polymerization of styrene is slower than MMA with reactions being carried out at 110 °C and 50% concentration in order to achieve approximately 80% conversion after 8 h. The presence of small amounts of polar impurities/additives has been previously shown to effect catalyst efficiency. This is due to coordination of donor atoms at the copper catalyst. To investigate this, polymerization was carried out in the

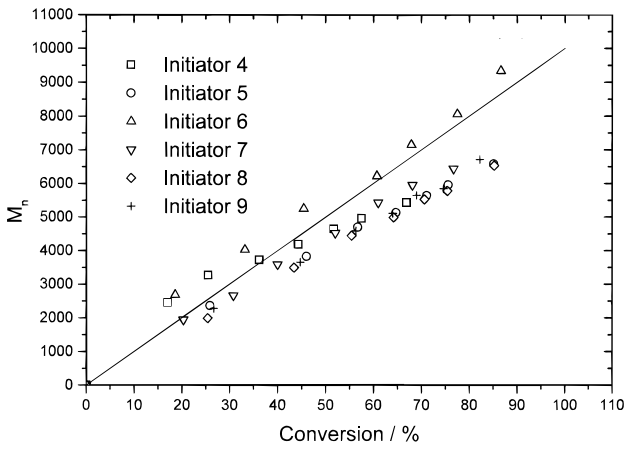


Figure 4. Evolution of M_n with conversion for the polymerization of MMA in xylene solution (33%v /v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1 with initators **4**−**9**. The line is theoretical M_n.

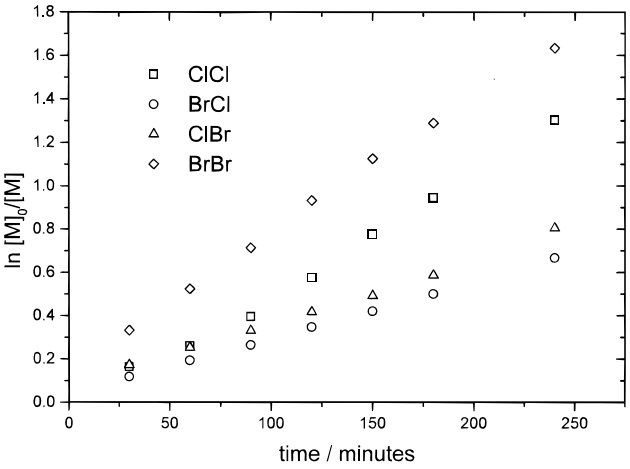


Figure 5. Kinetic plots for the polymerization of MMA with monofunctional phenolic ester initiators **1** and **3** with both CuBr and CuCl, xylene solution (33% v/v) at 90 °C [MMA]/[CuX]/[**18**]/[initiator] = 100/1/2/1.

presence of 1,4-(2′,2-dimethylpropionato)benzene in equimolar quantity with respect to initiator, maintaining [initiator]:[CuBr]:[**18**] = 1:2:1. No effect on rate was observed, Table 1. In all cases M_n increased fairly linearly with conversion, while maintaining narrow PDI, with good linearity shown in the first-order kinetics; see Supporting Information for full details.

Polymerization of Methyl Methacrylate with Monofunctional Phenolic Ester Chloro Initiators with CuBr/CuCl-Based Catalysts. It has been previously shown that the presence of a chloride originating from either the initiator or the catalyst becomes the ω-terminus of the polymer. This results in a lowering of the rate of polymerization. Polymerization of MMA was carried out with 2-chloro-2-methylpropionic acid phenyl ester, **3**, initiator, and the equivalent bromide initiator, **2**, with both copper(I) chloride and copper(I) bromide. Polymerization proceeds efficiently in all cases, Figure 5.

When the chloride initiator, **3**, is used, the rate of polymerization decreases. The M_n increases fairly linearly with conversion and follows the theoretical line quite well, Figure 2, and the polydispersity index, PDI, is less than 1.2 for both bromide initiators but increases significantly with the chloride initiator, **3**. Initiators **13** and **14** were synthesized for two reasons. First they

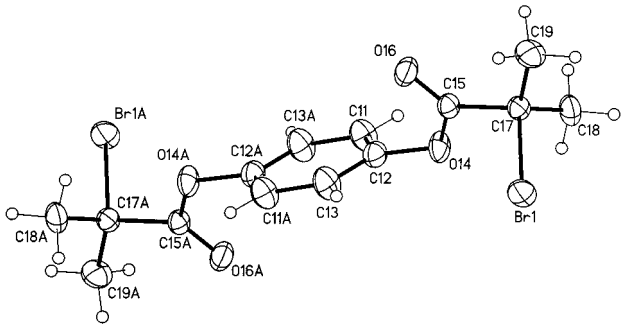


Figure 6. ORTEP diagram of 1,4-(2′-bromo-2′-methylpropionato)benzene, **10**.

Table 2. Data for the Polymerization of MMA with Difunctional Initiators at 90 °C in 33% Xylene Solution after 4 h

initiator	[MMA]:[CuBr]:[**18**]:[initiator]	M_n	PDI	convn, %	k_p[Pol*] × 10^4, s^{-1}
10a	100:1:2:1	7900	1.09	85.8	1.30
10b	100:2:4:1	7500	1.08	98.1	2.57
10c	100:2:4:2	4740	1.13	99.7	3.96
11	100:2:4:1	8600	1.09	97.8	2.56
12	100:2:4:1	8970	1.10	96.1	2.23
15	100:2:4:1[a]	8350	1.21	84.6	1.27

[a] CuCl used in catalyst with chloro initiator.

provide an additional experiment to compare the effect of changing the halogen in the system and second they are very similar, in structure, to the difunctional initiators **10**−**12** and were thus used for comparative purposes. Polymerization of MMA with both **13** and **14** with CuBr and CuCl respectively proceeds with a linear increase in M_n and PDI's of 1.09 and 1.23 after 4 h. The rate of polymerization for **13** is identical to the parent initiator, **2**, with a decrease in rate from 1.16 × 10^{-4} to 0.72 × 10^{-4} s^{-1} for **14**, Table 1. This decrease is of a similar magnitude to other experiments where bromide is changed to chloride.

Polymerization of Methyl Methacrylate with Difunctional Phenolic Ester Initiators. Diphenols offer an attractive route to difunctional initiators and the potential for ABA triblock copolymers by sequential addition and/or telechelic polymers by appropriate termination reactions. Esterification of hydroquinone to give **10** proceeds in high yield to give a difunctional initiator where the two initiating sites are well separated and able to initiate independently of each other; the crystal structure of **10** was determined, Figure 6.[55] Polymerization of MMA with the 1,4-disubstituted initiator **10** proceeds with first-order kinetics to give high conversion polymer with narrow PDI and M_n as targeted, which increases linearly with conversion, Table 2. When the polymerization was stopped after 1 h, at low conversion, the polymer isolated ^{1}H NMR clearly shows that both sites initiate. This is seen by the disappearance of the sharp singlet at 7.16 ppm and the appearance of a broad singlet upfield at 6.95 ppm; see Supporting Information. The reaction has been previously shown to be first order in both catalyst and initiator.[24] When the polymerization is carried out with the same ratio of catalyst to initiator sites and monomer to initiator, **10b**, we have a doubling of both the catalyst concentration and of the initiator concentration. We observe a doubling of the rate of polymerization and not an increase by a factor of 4. The reaction scheme for the reaction is given by eq 1 where R is the active propagation center. A doubling of the concentration of copper(I) can also be expected to be accompanied by a doubling of the deactivating copper(II), hence the observation of the observed doubling of the rate and not an increase by a factor of 4 as would be expected if Cu(II) species were not formed, Figure 7. When the initiator concentration is further increased by a factor of 2, then the rate is again doubled. A very similar rate of polymerization is achieved when the concentration of copper(I) is reduced to 50% of the concentration of initiating sites, Figure 7. Initiators based on resorcinol, **11**, and catchecol, **12**, also prove effective difunctional initiators, Table 3, showing essentially identical kinetics to **10**. Figure 8 shows the evolution of molecular mass with conversion for initiators **10**−**12**. As with monofunctional initiators when the chloro difunctional initiator, **15**, is used with a CuCl-based catalyst a decrease in the rate of polymerization is observed, by a factor of approximately 2, from 2.57 × 10^{-4} to 1.27 × 10^{-4} s^{-1} under identical reaction conditions, Table 3.

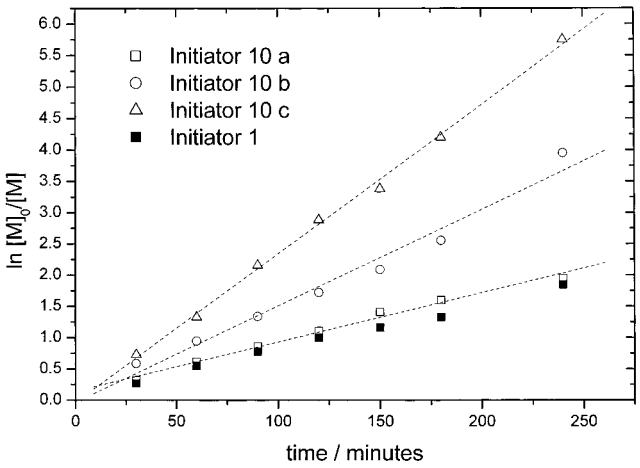


Figure 7. Kinetic plots for the polymerization of MMA with difunctional phenolic ester initiator **10** under different reaction conditions a−c, see Table 3, xylene solution (33%v/v) at 90 °C, lines drawn are linear regression best fits. Polymerization with initiator **1** given for comparison, xylene solution (33% v/v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1.

$$\mathrm{C{-}Br + Cu^{I}Br \xrightarrow{k_{act}} R + Cu^{II}Br_2}$$

$$\mathrm{R + Cu^{II}Br_2 \xrightarrow{k_{deact}} C{-}Br + Cu^{I}Br}$$

$$\frac{d[R]}{dt} = k_{act}[C{-}Br][Cu^{I}Br] - k_{deact}[R][Cu^{II}Br_2] \overset{S.S.}{=} 0$$

$$[R] = \frac{k_{act}[C{-}Br][Cu^{I}Br]}{k_{deact}[Cu^{II}Br_2]} \qquad (1)$$

where R = active propagation center.

Polymerization of Alkyl Methacrylates and Styrene with Difunctional Phenolic Ester Initiators. Ethyl (EMA), isopropyl (*i*-PMA), *n*-butyl (*n*-BMA), isobutyl (*i*-BMA), and benzyl methacrylate (BzMA) all polymerized with initiator **10** under atom transfer polymerization conditions. All showed good first-order kinetics with a linear increase of M_n with conversion. The rate of polymerization is considerably enhanced in the case of benzyl methacrylate and also increases with *n*-BMA and *i*-BMA. This effect is ascribed to changes in solubility of the active true catalyst or a decrease in solubility of any copper(II) deactivators formed in the system as

Table 3. Polymerization of Vinyl Monomers Initiator 10 in Xylene Solution (33% v/v) at 90 °C [MMA]/[CuBr]/[18]/[initiator] = 100/1/2/1

monomer	time	convn, %	M_n	PDI	k_p[Pol*] × 10^4, s^{-1}
EMA	240	94	8460[a]	1.10[a]	1.98
i-PMA	240	68	6320[a]	1.12[a]	0.82
t-BMA	240	57	7130[a]	1.31[a]	
n-BMA	240	100	10800[a]	1.15[a]	4.32
i-BMA	240	100	10400[a]	1.13[a]	3.88
BzMA	60	100	11440[a]	1.13[a]	11.7
STY[b]	240	30	1950[c]	1.10[c]	0.21
STY[b]	480	44	2870[c]	1.12[c]	0.21

[a] Molecular mass determined by SEC against PMMA standards. [b] Styrene polymerized at 110 °C in 50% xylene solution. [c] Molecular mass determined by SEC against PSTY standards.

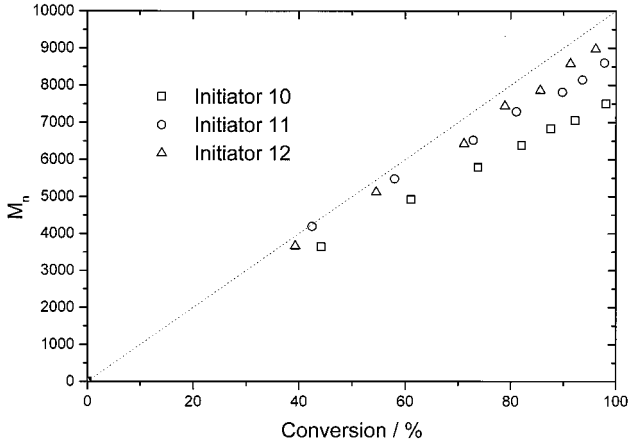


Figure 8. Evolution of M_n with conversion for the polymerization of MMA in xylene solution (33%v/v) at 90 °C [MMA]/[CuBr]/[**18**]/[initiator] = 100/1/2/1 with difunctional bromo initiators **10**−**12**. The line is theoretical M_n.

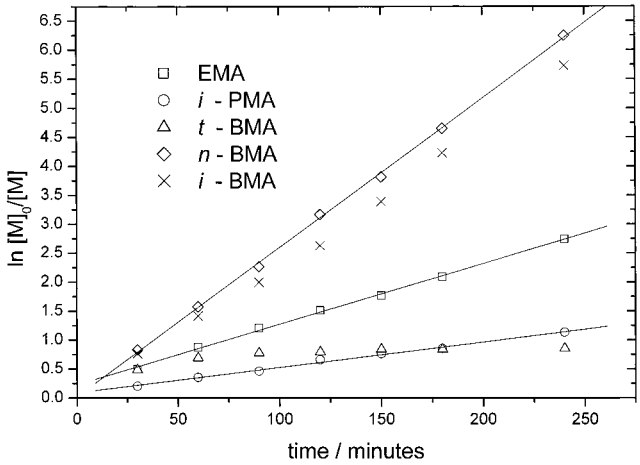


Figure 9. Kinetic plots for the polymerization of alkyl methacrylates with difunctional phenolic ester initiator **10**, xylene solution (33% v/v) at 90 °C. The lines drawn are linear regression best fits for EMA, *t*-BMA, and *i*-PMA, not all drawn for clarity.

a result of the increase in hydrophobicity of the reaction medium. When *t*-BMA is polymerized, the first-order kinetic plot shows an initial fast rate followed by clear termination early in the reaction accompanied by a broadening of the PDI, Figure 9 and Table 3. This is thought to be due to two possible reasons: first an increase in steric bulk at the propagating center slowing propagation relative to termination by normal free radical routes, or more likely the evolution of butene to

Table 4. Polymerization with Trifunctional Initiators [MMA]/[Cu^IBr]/[18]/[initiator] = 100: 3:6:1 Sampled after 4 h

	monomer	catalyst	M_n	PDI	convn, %	k_p[Pol*] × 10^4, s^{-1}
16	MMA[a]	CuBr	9600	1.12	98.8	4.07
17	MMA[a]	CuCl	8570	1.21	87.6	2.03
16	STY[b]	CuBr	7050	1.15	68.2	0.86
17	STY[b]	CuCl	7080	1.35	65.6	0.85

[a] 33% (v/v) xylene at 90 °C. [b] In xylene 50% (v/v) at 110 °C.

leave the free acid which protonates the ligand, leading to a loss in catalytic activity.[24] The rate of polymerization of styrene is again very slow, reaching only 44% conversion after 8 h even after increasing the concentration of the monomer from 33 to 50% and increasing the temperature by 20 °C to 110 °C. This is consistent with our earlier findings with this type of polymerization system.[24]

Polymerization of Methyl Methacrylate with Trifunctional Phenolic Ester Initiators. Multifunctional initiators have been reported based on a range of polyols such as calixaranes[34,35] and carbohydrates;[36] polyphenols offer an attractive alternative. Atom transfer polymerization of MMA and styrene, proceeds effectively with bromo, **16**, and chloro, **17**, trifunctional initiators, Table 4. Again with MMA we observe a decrease in rate by a factor of 2 for the chloride-based chemistry, this is not, however, the case for styrene. Again the chloro-based chemistry produces broader PDI polymers than the bromo initiator/catalyst. The use of polyphenols to produce multifunctional initiators is a facile approach for the core first production of star polymers.

General Discussion and Conclusions

Esterification of phenols with either bromoisobutyryl bromide or chloroisobutyryl chloride is a simple route to a range of initiators for the atom transfer polymerization of methyl methacrylate, alkyl methacrylates and styrene. Phenolic esters lead to efficient living polymerization in conjunction with copper(I) halides and *N*-(*n*-alkyl)-2-pyridylmethanimine in hydrocarbon solution leading to polymers with narrow PDI and targeted M_n, with good initiator efficiency, in times between 4 and 8 h. The use of polyphenols leads to a family of multifunctional initiators, which have been demonstrated to lead to efficient polymerization in from two and three different sites to again give polymers with narrow PDI's. The range of commercially available functional phenols allows the facile use of functional initiators leading to α-functional polymers. Not only do methoxy, phenyl ether, primary aryl amino, aldehyde, nitro, and benzyl ether functional initiators lead to efficacious atom transfer polymerization, but none of these groups impart any detrimental effects on the polymerization. The use of *N*-(*n*-octyl)-2-pyridylmethanimine in xylene leads to homogeneous reaction solutions. The catalyst is removed by passing down a column of basic alumina. Chloro analogues of the bromo initiators are also efficient initiators in conjunction with CuCl with only a factor of 2 decrease in the rate of polymerization in all cases studied. The rate of polymerization of styrene is significantly slower than for alkyl methacrylates. Increasing the length of the alkyl chain in the monomer leads to faster rates of polymerization. However, *tert*-butyl methacrylate is not polymerized effectively which is

believed to be the result of decomposition to the acid leading to a poisoning of the catalyst via protonation of the ligand.

In conclusion, the use of esterified phenols is an extremely versatile and simple route into α-functional polymers via atom transfer polymerization/transition metal mediated living polymerization.

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Supporting Information Available: Text giving further details on the synthetic procedures used to prepare reagents used in this work, figures showing chromatograms and NMR spectra of the initiation reaction, tables giving full polymerization conversion and molecular mass information, and tables giving atomic coordinates and isotropic displacement coordinates, selected bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(55) Crystal data: collected using a Siemens three-circle diffractometer equipped with a SMART CCD area detector; graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), formula $C_{14}H_{16}Br_2O_4$, M = 408.09 g mol^{-1}, size = 0.45 × 0.12 × 0.06 mm, triclinic, space group $P\bar{1}$, a = 6.0400(10) Å, b = 9.611(2) Å, c = 13.931(3) Å, β = 89.678(5)°, V = 789.4(3) Å^3, Z = 2, ρ_{calc} = 1.717 g cm^3, θ range = 2.17−28.56°, temperature = 180(2) K; of 4747 reflections collected, 3461 were independent ($[F_o \geq 4\sigma(F_o)]$). Anisotropic thermal parameters were used for all non-H atoms. Hydrogen atoms were inserted at calculated positions and fixed, with isotropic thermal parameters, U = 0.08 Å^3, riding on the supporting atom. The structure was solved by direct methods using SHELXTL[56] version 5.0 and the refinements were carried out using SHELXTL96[57] software, minimizing on the weighted R factor wR2. R = 0.0451 ($R = \sum|F_o - F_c|/\sum F_o$ (for $F_o \geq 4\sigma(F_o)$)), wR2 = 0.2457 (wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ for all data), a weighting scheme of the form $w^{-1} = \sigma^2(F_o^2) + aP + bP$ was used, where $P = [\max.(F_o^2, 0) + 2F_c^2]/3$, where $\max.(F_o^2, 0)$ indicates that the larger of F_o^2 or 0 is taken, a and b are values set by the program (a = 0.10 b = 0.00). A semiempirical absorption correction was applied using SADABS, where T_{min} = 0.6692 and T_{max} = 0.9273, S = 0.977, Δ/e Å^{-3} (peaks of unassigned residual electron density) maximum = +0.256, minimum = −0.224, Additional material is available from the Cambridge Crystallographic Data Centre, CCDC xxxxxx.
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