Synthesis and Characterization of Star Polymers with Varying Arm Number, Length, and Composition from Organic and Hybrid Inorganic/Organic Multifunctional Initiators

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ABSTRACT: Multifunctional initiators, derived from cyclotriphosphazenes, cyclosiloxanes, and organic polyols, were used in the synthesis of styrenic and (meth)acrylic star polymers by atom transfer radical polymerization (ATRP). Conditions were identified in each system which provided linear first-order kinetics for polymers with narrow, monomodal molecular weight distributions. Molecular weight measurements relative to linear polystyrene standards showed that the star polymers had lower molecular weights than theoretically predicted. Triple detection SEC measured on poly(*n*-butyl acrylate) samples demonstrated that the absolute molecular weight matched the theoretical value—the smaller relative chain length was due to lower hydrodynamic volumes of the star-branched polymers relative to linear analogues. Kinetic arguments were used to demonstrate that each alkyl halide moiety bound to the initiators was participating in ATRP. Well-defined poly(methyl acrylate) stars of molecular weights $M_n > 500\,000$ and low polydispersity ($M_w/M_n < 1.2$) have been prepared. Star−block copolymers with a soft poly(methyl acrylate) core and a hard poly(isobornyl acrylate) shell were also synthesized.

Introduction

The synthesis and characterization of star polymers has been a consistent area of exploration in the ongoing pursuit of structure property relationships in macromolecular science.[1] Star polymers have different hydrodynamic properties and higher degrees of chain end functionality compared to linear polymers of similar composition. Methods toward making star polymers fall into two broad classes. In the “arm first” approach, monofunctional, living linear macromolecules are initially synthesized. Star formation then occurs in one of two ways: a difunctional comonomer is used to provide cross-linking through propagation[2] or a multifunctional terminating agent is added connecting a precise number of arms to a central core molecule.[1] The former, microgel, technique produces macromolecules with a large, often heterogeneous, number of arms while in the latter case separation techniques are used to isolate stars from uncoupled linear polymers.

The second class of star polymers are synthesized by the “core first” approach. Multifunctional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both arm number and length. Furthermore, the reaction consists solely of stars in the absence of linear polymers. However, in many cases the multifunctional initiators must be presynthesized, and limited studies have been documented using this method due to the poor solubility of multiply charged species needed to initiate ionic polymerizations.[3−7]

Regardless of the type of star synthesized, three potential flaws have traditionally been encountered: the synthetic techniques, the variety of monomers available to those techniques, and removal of linear chain contaminants. In terms of well-defined stars, it is essential that a controlled polymerization technique be used that maintains chain functionality. Living ionic,[4,8] metathesis,[9] and group transfer[10,11] polymerizations were adequate for the application, but all required strenuous methods of reagent purification. Also, the processes were only useful for a limited range of monomers. One solution was the advent of controlled/“living” free radical polymerizations.[12] These reactions utilize a dynamic equilibrium between active and dormant species such that the concentration of free radicals is similar to that found in conventional processes but where deactivation competes with termination, thereby limiting the irreversible reaction to low levels. Specifically, atom transfer radical polymerization (ATRP)[13−25] provides control over chain length and functionality by an equilibrium between a dormant alkyl halide and a free radical mediated by an interchange between copper(I)/copper(II) salts and the organic polymeric chain ends. ATRP has been demonstrated to provide controlled polymerizations of styrenes,[13,16−18] (meth)acrylates,[13,15,19−23,25] and acrylonitrile[24] with variations in composition and architecture found in block, graft, star, branched, and hyperbranched materials.[26,27]

The applicability of controlled radical polymerization techniques toward the synthesis of star polymers has been demonstrated. For the “arm first” approach, divinylbenzene was used to produce microgels in the radical polymerization of styrene.[28,29] The first report of the “core first” technique described the hexakis(bromomethyl)benzene-initiated ATRP of styrene, methyl acrylate, and methyl methacrylate,[14] but its use was

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rather limited due to poor solubility in the reaction media. Therefore, other hexafunctional initiators were explored such as hexakis(4-(2-bromopropionyloxymethyl)phenoxy)cyclotriphosphazene, **6BrPr**.[30] Initially developed to model the synthesis of organic grafts from functionalized poly(phosphazenes), the initiator has been used for the synthesis of six arm star polystyrenes and acrylates. In one case,[30] a macroinitiator of star poly(methyl acrylate) synthesized from **6BrPr** was used in the ATRP of isobornyl acrylate, thereby yielding a star–block copolymer.

Since reporting the work summarized above, a number of studies have described the use of ATRP in the synthesis of star-branched macromolecules. Pugh et al. used a trifunctional initiator for the synthesis of three-arm polyacrylates for investigations of liquid crystalline polymers.[31] Sawamoto and co-workers also made three-arm star polymers of methyl methacrylate using trifunctional initiators bearing trichloroacetate moieties.[32] In our group, a tetrafunctional inorganic/organic hybrid initiator derived from a cyclotetrasiloxane was used in the ATRP of styrene to produce a four-arm star polymer.[33] Recently, dendrimer techniques have also been used to produce star–block copolymers by ATRP.[27,34]

Three additional contributions have been disclosed. Sawamoto[35] and Gnanou[36] discussed the use of modified calixarenes as initiators for ATRP. Sawamoto studied the synthesis of homo- and block–star (co)polymers from dichloroacetate functionalized calixarenes with four, six, and eight initiating sites per molecule.[35] In the ruthenium/triphenyl phosphine based ATRP of methyl methacrylate and *n*-butyl methacrylate, narrow, monomodal molecular weight distributions were attained for each of the polymers. Upon cleavage of the arms from the core the chain length per arm matched the value predicted by theory. Similarly, Gnanou used an octafunctional calixarene composed of 2-bromopropionate moieties in the copper bromide/bipyridyl promoted ATRP of styrene.[36] Light-scattering experiments demonstrated that star coupling was occurring at relatively low monomer conversions. Under proper conditions, however, post-polymerization cleavage of the core resulted in free polystyrene arms that were one-eighth the molecular weight of the star. In the third study, a multistep dendrimer moiety was used to synthesize hexa- and dodecafunctionalized initiators bearing 2-bromopropionyloxy or 2-bromoisobutyryloxy moieties.[27,37] Star-branched amphiphilic (co)polymers were synthesized by the nickel dibromide/bis(triphenylphosphine) mediated ATRP of methyl methacrylate and 2-hydroxyethyl methacrylate. Standard SEC techniques were used to determine that the polymers had narrow, monomodal molecular weight distributions with ^{1}H NMR used to verify functionality.

The goal of the current study is to demonstrate that initiators for ATRP can be synthesized from a variety of compounds with predetermined functionality using a broad spectrum of reagents. These include heterocyclic inorganic species or inexpensive organic compounds. Compounds with multiple initiating sites per molecule can be manipulated to produce materials with molecular weights that are much larger than those obtained using mono- or difunctional initiators. Polymers with molecular weights exceeding values of $M_n > 500\,000$ and with low polydispersity ($M_w/M_n < 1.2$) have been prepared. Furthermore, kinetic arguments in conjunction with absolute molecular weight determinations have been used in place of core breaking chemistries to verify both the functionality and size of the macromolecules. Confirmation of functionality has also been demonstrated by the synthesis of star–block copolymers from multifunctional polymeric macroinitiators.

Experimental Section

Measurements. Relative size exclusion chromatography (SEC) measurements in THF were carried out using a Waters 510 liquid chromatograph pump equipped with four Polymer Standards Service (PSS) columns (100 Å, 1000 Å, linear, and guard) in series with a Waters 410 differential refractometer. Molecular weight analysis was calculated with PSS software; calibration based on low polydispersity polystyrene standards for styrene and acrylate polymerizations and PMMA standards for reactions with MMA. Triple detection SEC (3D-SEC)[38] was measured in THF using a Spectrasystem P1000 chromatograph pump equipped with PSS (1000 Å, 10^5 Å, and 10^6 Å) and Phenomenex (guard) columns in series with a Wyatt Minidawn light-scattering detector operating at 90° then in parallel with a Waters 410 differential refractometer and a Viscotek T50 intrinsic viscometer. Data acquisition and analysis were performed with PSS software. Calibration of all three detectors was achieved using polystyrene standards of narrow molecular weight distribution and known intrinsic viscosity. Prior to injection, purified polymer samples (see below) were dissolved in 10 mL class A volumetric flasks in THF with *p*-dimethoxybenzene as internal standard. The solution was filtered through a 0.2 μm Teflon syringe filter into a clean vial and stored in the freezer when not in use for injections. Monomer conversion was measured on a Shimadzu GC-14A gas chromatograph equipped with a wide-bore capillary column (DB-Wax, J&W Sci.) or by ^{1}H NMR on a 300 MHz Bruker spectrometer using Tecmag data acquisition software. ^{1}H NMR spectra were run in deuterated chloroform against a TMS reference or a solvent peak of known chemical shift. Broadband decoupled ^{31}P NMR spectra were run on the same instrument at 121 MHz. Spectra were recorded in deuterated chloroform or benzene against an 85% H_3PO_4/D_2O external standard. Electrospray ionization mass spectrometry (ESI MS) was measured in methanol on a Finnigan LCQ in positive ion mode. Infrared spectra were measured on an ATI Mattson Infinity Series FTIR between salt plates.

Materials. THF was distilled from a purple sodium ketyl solution. Styrene was distilled from calcium hydride. Methyl acrylate, *n*-butyl acrylate, *tert*-butyl acrylate, and methyl methacrylate were all washed three times with 5% sodium hydroxide solution and once with water. After drying with magnesium sulfate, the monomers were obtained in pure form by distillation from calcium chloride. Following purification, all monomers were stored in the freezer. Triethylamine was stirred over magnesium sulfate and filtered just prior to use. Hexachlorocyclotriphosphazene was recrystallized from hexane and sublimed prior to use. Ethylene glycol was stirred over magnesium sulfate, filtered and stored over 4 Å molecular sieves. Copper(I) bromide (CuBr) and copper(I) chloride (CuCl) were both stirred in glacial acetic acid overnight, filtered, and washed with absolute ethanol under an argon blanket. The solids were dried under vacuum at 60 °C overnight. 4-Nonylpyridine was synthesized according to the method of Griggs et al.[39] This compound was used to produce 4,4′-di-*n*-nonyl-2,2′-bipyridine (dNbpy) by a previously reported procedure.[17] 2-Bromopropionyl bromide, 2-bromoisobutyryl bromide, 2-bromopropionic acid, 2-bromoisobutyric acid, Dowex 50WX2-100 cation-exchange resin, 4-hydroxybenzaldehyde, sodium hydride, pentaerythritol, 1,1,1-tris(4-hydroxyphenyl)ethane, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), *p*-dimethoxybenzene (*p*-DMB), diphenyl ether (DPE), and 4-vinylbenzyl chloride, all from Aldrich, were used as received. Phosphorus tribromide from Acros was used as received. Tetramethylcyclotetrasiloxane and bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)platinum(0) complex in xylene (Karstedt's catalyst), both from Gelest, were used as received.

Syntheses. 1,1,3,3,5,5-Hexakis(4-hydoxymethylphenoxy)-cyclotriphosphazene was synthesized according to the method of Chang.[40]

1,1,3,3,5,5-Hexakis(4-bromomethylphenoxy)cyclotriphosphazene (6BzBr). Into a 500 mL 1-neck round-bottom flask was placed 4.0 g (4.6 mmol) of 1,1,3,3,5,5-hexakis(4-hydoxymethylphenoxy)cyclotriphosphazene with 250 mL of THF under argon. Then, 11 g (32 mmol) of phosphorus tribromide was added dropwise at room temperature and the mixture was stirred overnight. The volume was reduced to 40 mL by rotary evaporation and half of this liquid was precipitated in 1 L of water, collecting a beige precipitate. The material was dissolved in methylene chloride and passed through a silica gel column prepared with the same solvent, collecting the first fraction eluting at $R_f = 0.98$. The solvent was removed, and the white solid was dried under vacuum overnight at 70 °C. Yield = 1.5 g (26%). ^{1}H NMR (CDCl$_3$), δ: 7.26 (d, 2H, **Ar**), 6.92 (d,2H, **Ar**), 4.50 (d, 2H, Ar−**CH$_2$**−Br) ppm. ^{31}P NMR (CDCl$_3$), δ: 6.75 (s) ppm. ESI MS: 1251.5 (parent + H$^+$). Anal. Found (calcd) for $C_{24}H_{18}Br_6N_3O_6P_3$: C, 40.13 (40.32); H, 2.84 (2.90); N, 3.35 (3.36); Br, 38.53 (38.32).

1,1,3,3,5,5-Hexakis(4-(2-bromopropionyloxymethyl)-phenoxy)cyclotriphosphazene (6BrPr). A 3.2 g (3.7 mmol) sample of 1,1,3,3,5,5-hexakis(4-hydoxymethylphenoxy)cyclotriphosphazene was placed into a 250 mL round-bottom flask with 125 mL of THF and 3.4 g (34 mmol) of triethylamine. A solution of 7.1 g (33 mmol) of 2-bromopropionyl bromide and 20 mL of THF was added to a 50 mL pressure equalizing addition funnel fitted to the flask under Ar(g). The reactor was cooled to 0 °C in an ice/water bath, and the acid halide solution was added dropwise. The reaction was stirred overnight and allowed to warm to room temperature of its own accord. The mixture was transferred to a 1 L separatory funnel with 300 mL of diethyl ether and extracted consecutively with 200 mL of H$_2$O, 3 × 200 mL of NaHCO$_3$(aq), and 200 mL of H$_2$O. The organic phase was dried over MgSO$_4$ and filtered and the solvent removed by rotary evaporation. A solution of the compound in 5% THF in CH$_2$Cl$_2$ was run through a silica gel column prepared from the same solvent, collecting the only fraction that eluted. The solvent was removed, and the compound was redissolved in benzene and run through a column of neutral alumina again, collecting the only fraction to elute. The solvent was removed, and the resulting light yellow oil was dried under vacuum at room temperature. Yield (light yellow oil) = 1.0 g (16%). ^{1}H NMR (CDCl$_3$), δ: 7.21 (d, 2H, **Ar**), 6.93 (d, 2H, **Ar**), 5.17 (q, 2H, Ar−**CH$_2$**−O), 4.41 (q, 1H, *C*(*O*)−**CH**−Br), 1.85 (d, 3H, CH(Br)−**CH$_3$**) ppm. ^{31}P NMR (CDCl$_3$), δ: 9.38 (s) ppm. ESI MS: 1705.4 (parent + Na$^+$). Anal. Found (calcd) for $C_{60}H_{60}Br_6N_3O_{12}P_3$: C, 42.81 (42.74); H, 3.59 (3.57); N, 2.50 (2.39); Br, 28.48 (28.53).

1,1,3,3,5,5-Hexakis(4-(2-bromoisobutyryloxymethyl)-phenoxy)cyclotriphosphazene (6Br^{i}Bu). Similar experimental procedures and extraction were used as for **6BrPr** except 2-bromoisobutyryl bromide was used in place of 2-bromopropionyl bromide. Yield (yellow oil) = 100%. ^{1}H NMR (CDCl$_3$), δ: 7.21 (d, 2H, **Ar**), 6.94 (d, 2H, **Ar**), 5.16 (s, 2H, Ar−**CH$_2$**−O), 2.00 (s, 6H, C(Br)−**CH$_3$**) ppm. ^{31}P NMR (CDCl$_3$), δ: 9.27 (s) ppm. ESI MS: 1789.7 (parent + Na$^+$). Anal. Found (calcd) for $C_{66}H_{72}Br_6N_3O_{12}P_3$: C, 44.64 (44.85); H, 4.32 (4.10); N, 2.25 (2.34).

Pentaerythritol Tetrakis(2-bromopropionate) (4BrPr). Identical synthetic procedures and extraction were used as in the synthesis of **6BrPr**. Reagents: 3.1 g (23 mmol) of pentaerythritol, 10 g (99 mmol) of triethylamine, 21 g (99 mmol) of 2-bromopropionyl bromide, and 100 and 40 mL of THF in the reactor and addition funnel, respectively. The product, a white solid, was recrystallized directly from the diethyl ether phase, isolated, and recrystallized again from diethyl ether. Yield = 3.1 g (20%). Mp = 98−99 °C. ^{1}H NMR (CDCl$_3$), δ: 4.17−4.41 (m, 12H, C−**CH$_2$**−O−C(O)−**CH**−Br), 2.62 (s),1.81 (d, 12H, CH(Br)−**CH$_3$**) ppm. The peak at 2.62 ppm is currently unassigned but was weak (1% based on intensity) compared to all other resonances and did not appear to contribute in any deleterious manner to the polymerizations. ESI MS: 698.7 (parent + Na$^+$). Anal. Found (calcd) for $C_{17}H_{24}Br_4O_8$: C, 30.05 (30.20); H, 3.51 (3.58); Br, 47.15 (47.28); O, 18.89 (18.93).

Pentaerythritol Tetrakis(2-bromoisobutyrate) (4Br^{i}Bu). Identical synthetic procedures and extraction were used as in the synthesis of **6BrPr**. Reagents: 3.7 g (27 mmol) of pentaerythritol, 12 g (0.12 mol) of triethylamine, 26 g (0.12 mol) of 2-bromoisobutyryl bromide, 100 and 40 mL of THF in the reactor and addition funnel, respectively. The product, a white solid, was recrystallized directly from the diethyl ether phase, isolated and recrystallized again from diethyl ether. Yield = 8.0 g (41%). Mp = 133−134 °C. ^{1}H NMR (CDCl$_3$), δ: 4.31 (s, 8H, C−**CH$_2$**−O), 1.93 (s, 24H, C(Br)−**CH$_3$**) ppm. ESI MS: 754.7 (parent + Na$^+$). Anal. Found (calcd) for $C_{21}H_{32}Br_4O_8$: C, 34.69 (34.45); H, 4.44 (4.40); Br, 43.51 (43.66); O, 17.34 (17.48).

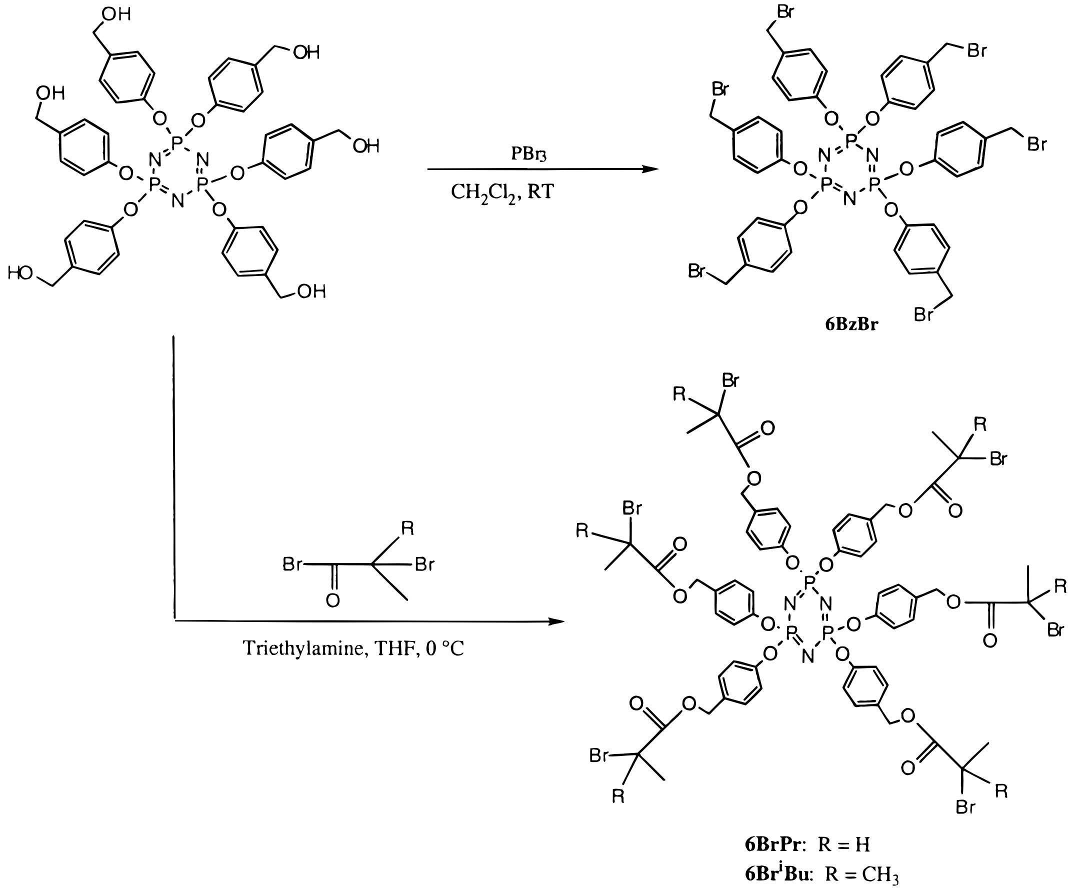
1,3,5,7-Tetrakis(4-chloromethylphenyl)ethyl-1,3,5,7-tetramethylcyclotetrasiloxane (4BzCl). A 5.5 g (36 mmol) sample of *p*-vinylbenzyl chloride and Karstedt's catalyst (0.2 mmol) were combined in a 25 mL round-bottom flask. To this was slowly added 2.0 g (8.2 mmol) of 1,3,5,7-tetramethylcyclotetrasiloxane at room temperature under argon. The temperature was then increased to 40 °C for 1 h. Complete substitution was confirmed by the disappearance of the Si−H stretch at 2200 cm^{-1} in the FTIR spectrum. The excess *p*-vinylbenzyl chloride was removed by high vacuum distillation. Yield = 3.9 g (56%) ^{1}H NMR (CDCl$_3$), δ: 6.89−7.40 (m, 4H, **Ar**), 4.41−4.68 (m, 2H, Cl−**CH$_2$**−Ar), 2.65 (m, 2H, CH$_2$−**CH$_2$**−Ar), 2.19 (m, 1H, Si−**CH**(CH$_3$)−Ar), 1.38 (m, 3H, CH−**CH$_3$**), 0.88 (m, 2H, Si−**CH$_2$**−CH$_2$), 0.15 (m, 3H, Si−**CH$_3$**) ppm. ESI MS: 750.9 (parent). Anal. Found (calcd) for $C_{36}H_{52}Cl_4Si_3O_3$: C, 56.81 (56.46); H, 6.32 (6.16); Cl, 16.52 (16.66).

1,1,1-Tris(4-(2-bromoisobutyryloxy)phenyl)ethane (3Br^{i}Bu). A 500 mL three-neck round-bottom flask was charged with 30 g (0.13 mol) of 2-bromoisobutyryl bromide and 250 mL of THF. The flask was fitted with a pressure-equalizing addition funnel, which itself was charged with a solution of 10 g (33 mmol) of 1,1,1-tris(4-hydroxyphenyl) ethane, 20 g (0.20 mol) of triethylamine, and 200 mL of THF. The reactor was cooled to 0 °C in an ice/water bath and the contents of the addition funnel added dropwise under argon. The reaction was stirred overnight, warming to room temperature of its own accord. The salts were removed by filtration and discarded. The solvent was removed from the filtrate by rotary evaporation. The remaining solid was redissolved in 300 mL of ethyl acetate and extracted with 5% NaOH(aq) followed by water. The organic phase was dried over MgSO$_4$ and the solvent removed. Pure product was obtained as a white solid by recrystallization from a mixture of ethyl acetate/hexanes. Yield = 13 g (55%). Mp = 266−267 °C. ^{1}H NMR (CDCl$_3$), δ: 7.05 (q, 12H, **Ar**), 2.15 (s, 3H, C(Ar)−**CH$_3$**), 2.03 (s, 18H, C(Br)−**CH$_3$**) ppm. ESI MS: 775 (parent + Na$^+$). Anal. Found (calcd) for $C_{32}H_{33}Br_3O_6$: C, 50.95 (51.02); H, 4.34 (4.42).

Ethylene Glycol Bis(2-bromopropionate) (2BrPr). The synthesis of **2BrPr** using a procedure analogous to the synthesis of **6BrPr** has been described previously.[41] An alternative procedure is as follows: 1.1 g (18 mmol) of ethylene glycol, 14 g (91 mmol) of 2-bromopropionic acid, and 0.50 g of Dowex 50WX2-100 cation-exchange resin were placed into a 25 mL 1-neck flask fitted with a Dean−Starke trap. Heat was applied to the vessel under 100 mmHg vacuum to facilitate low-temperature water distillation. The reaction was run until no more water collected in the trap. The resin was separated from the mother liquor by filtration and the product distilled at 93 °C, 7.5 × 10^{-2} mmHg. Yield = 5.7 g (94%). ^{1}H NMR (CDCl$_3$), δ: 4.30−4.40 (m, 6H, C−**CH$_2$**−O−C(O)−**CH**−Br), 1.81 (d, 6H, CH(Br)−**CH$_3$**) ppm. ESI MS: 355.0 (parent + Na$^+$). Anal. Found (calcd) for $C_8H_{12}Br_2O_4$: C, 28.79 (28.94); H, 3.63 (3.64).

Ethylene Glycol Bis(2-bromoisobutyrate) (2Br^{i}Bu). A 5.6 g (91 mmol) sample of ethylene glycol, 32 g (0.20 mol) of 2-bromopropionic acid and 2.7 g of Dowex 50WX2-100 cation-exchange resin were placed into a 100 mL 1-neck flask fitted with a Dean−Starke trap. Heat was applied to the vessel under 100 mmHg vacuum to facilitate low-temperature water distillation. The reaction was run until no more water was

Scheme 1. Diagram for the Syntheses of the Hexafunctional Initiators 6BzBr, 6BrPr, and 6Br^{i}Bu from Hexakis(4-hydroxymethylphenoxy)Cyclotriphosphazene



collected in the trap. The resin was separated from the mother liquor by filtration. The mother liquor was dissolved in diethyl ether and extracted three times with saturated sodium bicarbonate solutions. The organic phase was dried with $MgSO_4$ and the solvent removed by rotary evaporation. The product was distilled at 85 °C, 2.3×10^{-2} mmHg. Upon sitting at room temperature, the clear colorless liquid crystallized to a white solid. Yield = 9.2 g (28%). Mp = 48−50 °C. ^{1}H NMR ($CDCl_3$), δ: 4.38 (s, 4H, C−$\mathbf{CH_2}$−O), 1.88 (2, 12H, C(Br)−$\mathbf{CH_3}$) ppm. ESI MS: 383.0 (parent + Na^+). Anal. Found (calcd) for $C_{10}H_{16}Br_2O_4$: C, 33.48 (33.36); H, 4.44 (4.48).

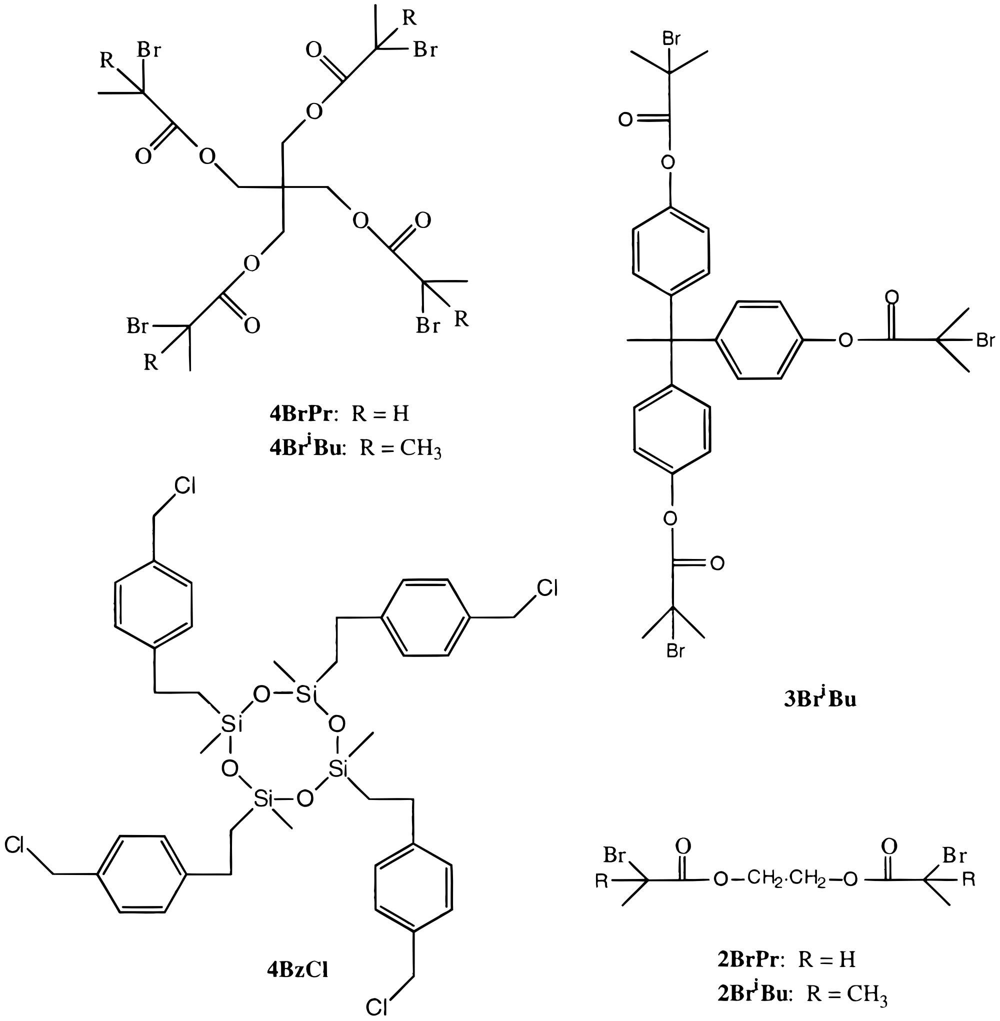
Polymerizations. A typical polymerization is as follows: 40 mg (5.9×10^{-5} mol) of **4BrPr** and 3.0 g (23 mmol) of *n*-butyl acrylate were placed into a 10 mL round-bottom flask. Then, 17 mg (0.12 mmol) of CuBr and 4.0 g (31 mmol) of *n*-butyl acrylate were placed into a 25 mL Schlenk flask. Both flasks were covered with rubber septa and purged with argon. A 0.10 g (0.24 mmol) sample of dNbpy was added to the Schlenk flask. Both homogeneous solutions were sparged with argon at room temperature for 15 min followed by cannula transfer of the initiator solution to the Schlenk flask. The homogeneous maroon solution was stirred an additional 5 min at room temperature. Approximately 0.2 mL of solution was removed, and the flask was placed into a 90 °C oil bath under argon. Periodically, additional 0.2 mL aliquots were removed for analysis. Upon completion of the reaction, the mixture was dissolved in approximately 100 mL of acetone and stirred with 3−5 g of Dowex MSC-2 cation-exchange resin for 30−60 min to remove the copper. The mixture was then gravity filtered into 1.4 L of 10% H_2O/methanol. A 2 mL aliquot of brine was added to the flask to promote sedimentation of the poly(butyl acrylate). The methanol phase was decanted, the polymer dissolved in 80 mL of THF and the precipitation repeated. The product was dried overnight at 60 °C under vacuum.

Results and Discussion

Initiator Syntheses. One of the goals of the current work was to demonstrate that inorganic compounds could be modified to produce multifunctional hybrid initiators. Heterocycles such as cyclotriphosphazenes and cyclosiloxanes containing reactive pendant groups were reacted with compounds containing activated alkyl halides capable of undergoing bond homolysis in the presence of copper(I) complexes. Scheme 1 illustrates how the cyclotriphosphazene containing six hydroxy substituents,[40] was used in one-step reactions to synthesize hexafunctional initiators bearing primary, secondary, or tertiary alkyl halides. In the case of the benzyl bromide, **6BzBr**, the hydroxide was brominated using phosphorus tribromide. Alternatively, esterification with either 2-bromopropionyl bromide or 2-bromoisobutyryl bromide yielded the respective initiators, **6BrPr** and **6Br^{i}Bu**.

For heterocycles based on silicones, hydrosilylation chemistry was used to produce an inorganic/organic hybrid initiator. The tetrafunctional compound, **4BzCl**, was obtained by hydrosilylation of 1,3,5,7-tetramethylcyclotetrasiloxane with 4-vinylbenzyl chloride (Figure 1) in an adaptation of a procedure used to prepare poly(dimethylsiloxane) macroinitiators.[42] The functionalization reaction was monitored by FTIR spectroscopy for complete disappearance of the Si−H stretching peak at 2200 cm^{-1}.

The versatility of the hydroxyl group toward transformation reactions was further exploited in the esterification of a number of organic polyols. Figure 1 shows a series of di-, tri-, and tetrafunctional initiators pro-



4BrPr: R = H
4Br^{i}Bu: R = CH$_3$

3Br^{i}Bu

4BzCl

2BrPr: R = H
2Br^{i}Bu: R = CH$_3$

Figure 1. Structures of di-, tri-, and tetrafunctional initiators used in the current study.

duced from compounds bearing multiple hydroxyl units. All of the precursors were commercially available and initiators were obtained after only one reaction—esterification with an α-bromo acid halide.[41] This procedure was used to synthesize initiators composed of either 2-bromopropionyloxy (**4BrPr**, **2BrPr**) or 2-bromoisobutyryloxy (**4Br^{i}Bu**, **3Br^{i}Bu**, **2Br^{i}Bu**) species. However, a milder procedure was also adopted for the difunctional initiators **2BrPr** and **2Br^{i}Bu**. Under conditions which would facilitate removal of water, namely, elevated temperatures and reduced pressures, the initiators were obtained by reaction of ethylene glycol with the appropriate α-bromocarboxylic acid in the presence of a cation-exchange resin. This process did not require dry solvents—reactions were performed in bulk—and products could be obtained with relative ease.

Polymerizations. For each of the initiators studied conditions were developed which provided linear first-order kinetic plots typical of a controlled/"living" polymerization. Such is the case in Figure 2 for the ATRP of styrene from the hexafunctional initiator **6BzBr** composed of benzyl bromide moieties. The linear relation between the logarithm of monomer conversion and time indicates conservation of radicals throughout the reaction. The SEC traces shown in Figure 3 display narrow, monomodal peaks. A small shoulder on the high molecular portion of the peak, indicative of chain coupling, does not appear until 74% conversion which further supports the limited contribution of termination.

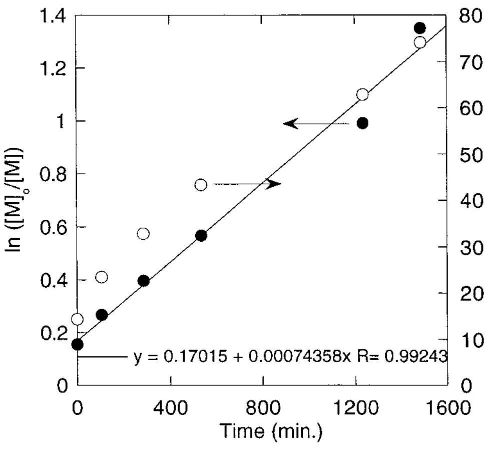


Figure 2. Kinetic plot for the ATRP of styrene initiated by **6BzBr**. $[M]_0/[I]_0/[CuBr(dNbpy)_2]_0$ = 576:1:2, 105 °C, 50% diphenyl ether.

However, the molecular weight/conversion plot shown in Figure 4 illustrates marked deviations from the relation $M_{n,theo} = (([M]/[I]_0) \times MW_{mon}) + MW_{init}$. For a controlled/"living" polymerization the observed molecular weight should coincide with the theoretical relation, and such a discrepancy would indicate a transfer reaction to some low molecular weight species. Increased polydispersities and unsymmetrical SEC traces would also be observed. Here, the molecular weight

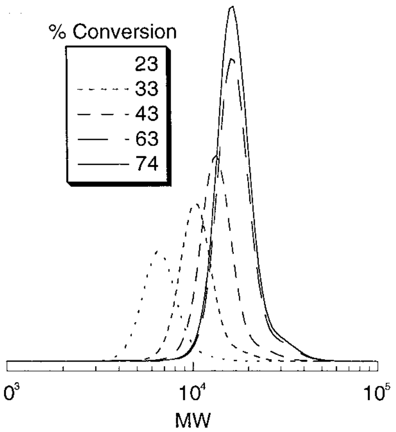


Figure 3. SEC chromatograms of the ATRP of styrene initiated by **6BzBr**. $[M]_0/[I]_0/[CuBr(dNbpy)_2]_0 = 576:1:2$, 105 °C, 50% diphenyl ether.

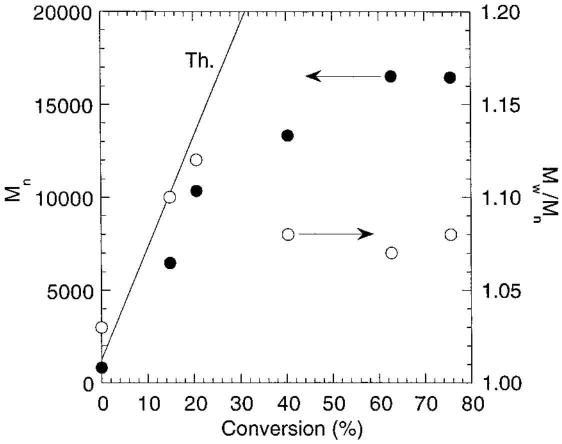


Figure 4. Evolution of molecular weight with conversion for the ATRP of styrene initiated by **6BzBr**. $[M]_0/[I]_0/[CuBr(dNbpy)_2]_0 = 576:1:2$, 105 °C, 50% diphenyl ether.

distributions remain very low, $M_w/M_n < 1.1$, and the SEC chromatograms in Figure 3 demonstrate that there are no low molecular weight tails indicative of transfer processes. Thus, the deviation from theory may be due to the lower hydrodynamic volumes of star-branched polymers relative to linear analogues of the same molecular weight.[27,35,36]

During the optimization of the $CuBr(dNbpy)_2$-catalyzed ATRP of styrene from **6BzBr** at 90 °C, experiments run with higher concentrations of catalyst relative to initiator or lower monomer-to-initiator ratios resulted in unsymmetrical SEC chromatograms composed of pronounced high molecular weight shoulders. When carried to high conversion, the reactions gelled. Star coupling was also reported by Gnanou and coworkers for the ATRP of styrene from an octafunctional initiator.[36] Taken together, the results confirm that a low radical concentration is paramount to the synthesis of well-defined materials by ATRP. When the active species concentration was too high, radical coupling[43] resulted leading to aggregates of stars and high molecular weight shoulders on the SEC traces. Sufficiently low active species concentrations yielded materials with monomodal, narrow molecular weight distributions even at high monomer conversions. Results showed that catalyst concentrations in the range of 30−50% of the *alkyl halide* concentration were best. A similar conclusion was reached in the synthesis of polymer brushes by ATRP.[44]

The rather unique effect of temperature in styrene polymerization was also encountered. The tetrafunctional inorganic/organic hybrid initiator, **4BzCl**,[33] listed in entry 11 of Table 1, utilizes benzyl chloride fragments as the initiating species in ATRP. Higher temperatures ($T = 130$ °C) were required to achieve appreciable rates of polymerization. However, this made a competing reaction, thermal initiation,[43] more significant as Figure 5 illustrates. The low molecular weight shoulder observed with increasing monomer conversion indicates the presence of linear chain contaminants. When initiated by benzyl bromide or 2-bromopropionate fragments,[36] the low molecular weight material was not observed on the SEC chromatograms. The lower reaction temperatures (∼100 °C) provided sufficiently fast rates of polymerization and reduced the proportion of thermally initiated monofunctional chains to undetectable levels.

It was stated earlier that star polymers could be synthesized from a broad spectrum of initiators with varying functionality. The data listed in Table 1 further emphasizes this point. Entries 1−8 describe polymerizations of styrene (Sty), methyl acrylate (MA), *n*-butyl acrylate (^{n}BA), *tert*-butyl acrylate (^{t}BA), and methyl methacrylate (MMA) initiated from the hexafunctional inorganic/organic hybrid initiators **6BzBr**, **6BrPr**, and **6Br^{i}Bu**. In these systems monomodal molecular weight distributions were observed with polydispersities $M_w/M_n < 1.2$. Not until high conversions were shoulders indicative of chain coupling observed on the SEC chromatograms.

ATRP from the tetra- and hexafunctional initiators listed in Table 1 were all very similar in their behavior (see Supporting Information). The kinetic plots were linear, indicating conservation of radicals throughout the reaction. However, the molecular weight plots showed marked decreases of measured molecular weight vs that predicted by theory. Concurrently, polydispersity decreased progressively with monomer conversion. These points provide an important distinction from analogous monofunctional initiators due to the multiplicity of alkyl halide moieties per molecule. When a termination event occurs for a macromolecule propagating in only one direction, that chain ceases to participate in the ATRP process. Conversely, if termination occurs in a polymer with multiple active sites that initiator molecule is not “dead”—the other active sites continue to propagate and grow toward high molecular weight material. If such termination were significant, it would be evident in the kinetic plot, where a decrease in the slope of the curve would be observed.

The polymerizations listed in Table 1 show the variations in reactions and conditions used in the polymerizations. Many of the monomers reported thus far, such as styrene, acrylates, and methacrylates, polymerized under conditions typical for ATRP. Furthermore, reactions were run both with substituted bipyridines or with linear amines. In such cases, temperature could also be varied; faster rates of polymerization can be achieved with linear amines than with bipyridines at a given temperature.[45] Finally, when the glass transition of the polymer was lower than the reaction temperature, the reactions were run at or near bulk conditions. A low concentration of solvent was used to serve as an internal standard for measurement of monomer conversion. For the high T_g styrene and

Table 1. Conditions and Results for the ATRP of Styrene, Acrylates, and Methacrylates from a Series of Multifunctional Initiators

entry[a]	initiator	monomer	catalyst[b]	stoichiometry[c]	solvent (conc)	T (°C)	conv (%)	M_n, theor[d]	M_n[e]	M_w/M_n[e]
1	6BzBr	styrene	A	576:1:2	DPE (50%)	105	64	38 000	14 000	1.07
2	6BzBr	MA	A	1394:1:3	bulk	90	84	101 000	53 000	1.17
3	6BzBr	MA	A	11 116:1:12	bulk	90	57	545 000	269 000	1.19
4	6BrPr	MA	A	1394:1:2	bulk	90	54	120 000	20 000	1.14
5	6BrPr	^{n}BA	A	1395:1:3	bulk	90	65	127 000	52 000	1.16
6	6BrPr	^{t}BA	B	1395:1:3	DMB (5%)	70	46	82 000	57 000	1.16
7	6Br^{i}Bu	^{n}BA	B	1560:1:2	DMB (10%)	70	42	84 000	54 000	1.15
8	6Br^{i}Bu	MMA	C	3000:1:3	DPE (50%)	90	38	114 000	81 000	1.12
9	4BrPr	^{n}BA	A	930:1:2	bulk	90	82	98 000	85 000	1.12
10	4Br^{i}Bu	^{n}BA	B	1040:1:1.3	DMB (10%)	70	58	77 000	70 000	1.08
11	4BzCl	styrene	C	384:1:4	bulk	130	72	29 000	13 000	1.16
12	3Br^{i}Bu	^{n}BA	B	300:1:1	DMB (11%)	70	80	31 000	30 000	1.11
13	2BrPr	^{n}BA	A	465:1:1	bulk	90	88	52 000	46 000	1.19
14	2Br^{i}Bu	^{n}BA	B	780:1:2	DMB (10%)	75	78	78 000	63 000	1.16

[a] Kinetic and molecular weight plots for entries 1−14 listed in Supporting Information Figures A−N respectively. [b] A = CuBr(dNbpy)$_2$, B = CuBr(PMDETA), C = CuCl(dNbpy)$_2$, [c] [M]$_0$/[I]$_0$/[catalyst]$_0$. [d] Theoretical molecular weight calculated by $M_n = (\Delta[M]/[I]_0)(MW_M)$. [e] SEC using differential refractive index detection vs linear polystyrene standards.

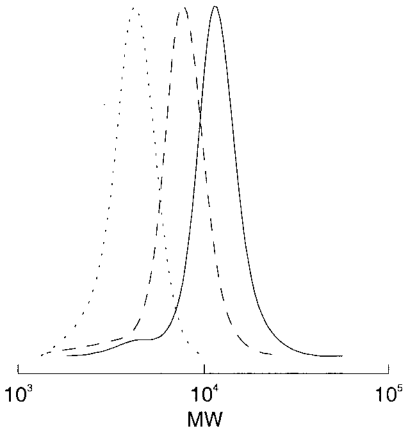


Figure 5. SEC chromatograms for the ATRP of styrene initiated by a modified tetrafunctional cyclotetrasiloxane, **4BzCl**. Key: (- - -) 19% conversion, $M_n = 3400$, $M_w/M_n = 1.06$; (− − −) 44% conversion, $M_n = 6900$, $M_w/M_n = 1.10$; (—) 72% conversion, $M_n = 12\,600$, $M_w/M_n = 1.11$.

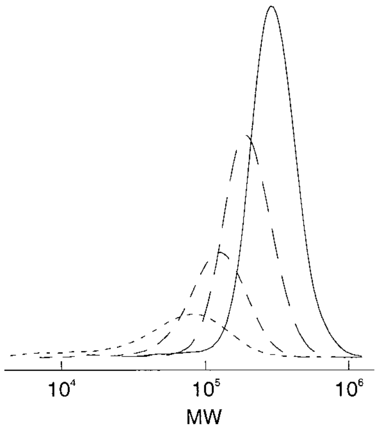


Figure 6. SEC chromatograms of the ATRP of methyl acrylate initiated by the hexafunctional initiator **6BzBr** measured vs linear polystyrene standards. Key: (- - -) 7% conversion, $M_n = 32\,910$, $M_w/M_n = 2.43$; (− − −) 17% conversion, M_n = 94,820, $M_w/M_n = 1.36$; (— —) 36% conversion, $M_n = 178\,200$, $M_w/M_n = 1.19$; (—) 57% conversion, $M_n = 269\,300$, $M_w/M_n = 1.19$. For experimental conditions, see entry 3, Table 1.

methacrylate polymerizations, solvent was used to ensure that the reaction did not solidify at high conversion.

High Molecular Weight Poly(methyl acrylate). Entry 3 of Table 1 describes the polymerization of methyl acrylate from **6BzBr** using the homogeneous catalyst CuBr(dNbpy)$_2$ at a monomer to initiator concentration of 11 000:1, corresponding to a molecular weight of 1 million at quantitative conversion. A high concentration of catalyst relative initiator was used to ensure there was sufficient activator and deactivator to provide control for a system which was very dilute in alkyl halide. The SEC traces in Figure 6 show a decrease in polydispersity with conversion concomitant with the formation of symmetrical peaks demonstrating the effectiveness of ATRP to produce high molecular weight materials with precision. The low molecular weight shoulder present in the SEC trace of the sample at 7% monomer conversion is ascribed to slow initiation of the benzyl bromide moieties. Once initiated, all arms grow and the differences in chain length become less significant compared to the polymer molar mass as the reaction progresses. The number-average molecular weight for the last sample at 54% monomer conversion was $M_n = 269\,000$ as measured by SEC calibrated relative to linear polystyrene standards. When the absolute number-average molecular weight of the purified polymer was measured on a 3D-SEC system, the value of $M_n = 557\,000$ was in good agreement with the theoretical prediction of 545 000. This result confirms that the reaction proceeded in a controlled fashion and shows that differences in hydrodynamic volume between the star-branched polymers and linear analogues can become significant as molecular weight increases.

Polymer Functionality and Absolute Molecular Weight. It was necessary to verify that each of the alkyl halide fragments of the initiators was participating in the ATRP process. Other authors[35,36] have addressed this analytically by cleaving the cores of star polymers from the initiators to determine the chain length of arms predicted by the ratio of star (absolute) molecular weight divided by the functionality. An alternative method, shown below, utilizes a kinetic approach.

In ATRP the rate of polymerization, R_p, obeys the expression shown in eq 1 where k_p is the propagation rate constant, K is the equilibrium constant of exchange between active and dormant species and [M], [I], [Mt^{n}X] and [Mt^{n+1}X$_2$] are the concentrations of monomer, initiator, activator, and deactivator, respectively.[17,46,47] Equation 1 shows that rate has a first-order dependence on both monomer and initiator concentrations. For multifunctional initiators the expression has to be modified to account for the number of alkyl halide

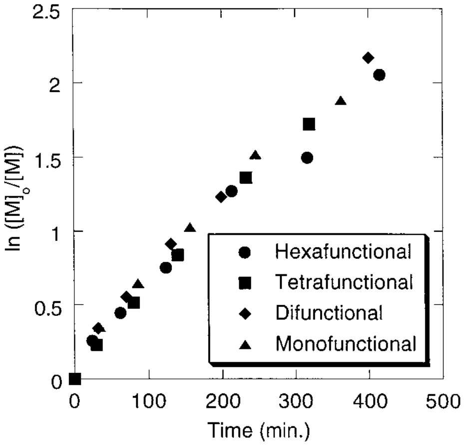


Figure 7. First-order kinetic plots for the ATRP of *n*-butyl acrylate initiated by mono-, di-, tetra-, and hexafunctional initiators containing 2-bromopropionyloxy species. $[M]_0/[R-Br]_0/[CuBr(dNbpy)_2]_0 = 232:1:0.5$, 90 °C, bulk.

moieties on each initiating molecule.

$$R_p = k_p K[M][I]_o \frac{[Mt^n X]}{[Mt^{n+1} X_2]} \qquad (1)$$

Therefore, a more general form of the rate expression is given in eq 2 where the initiator concentration has been multiplied by the number of alkyl halide species per molecule, *f*. Equation 2

$$R_p = k_p K f[M][I]_o \frac{[Mt^n X]}{[Mt^{n+1} X_2]} \qquad (2)$$

then serves as a method for verifying the functionality of an initiator bearing multiple alkyl halide sites. Regardless of the functionality of the initiators examined, two reactions that have the same concentration of alkyl halide fragments (benzyl halides, α-halo esters, etc.) will consume monomer at the same rate since the product of *f**[I] is constant. Figure 7 shows the kinetic plot of such an experiment performed using the hexa- (**6BrPr**), tetra- (**4BrPr**), di- (**2BrPr**), and monofunctional (methyl 2-bromopropionate) initiators in the ATRP of *n*-butyl acrylate where the ratio of monomer to 2-bromopropionate species was 232:1. Since identical concentrations of catalysts were used, the same amounts of deactivating persistent radicals ($CuBr_2$) species should be produced due to identical concentrations of growing radicals (identical rates).[46,47] The rates of polymerization were the same for all of the initiators indicating that each active species was participating in the polymerization. Since the ratio of monomer to alkyl halide was held constant but the concentration of initiator was changed, then, by eq 2, the initiators must have different functionalities. Furthermore, the results in Figure 7 also verify that the inorganic core of the initiator does not interfere with the kinetics of the ATRP process.

Equation 2 is a kinetic expression and as such does not give any information on the molecular weight behavior of the polymers. In fact, when the concentration of active species is held constant among initiators of varying functionality, the monomer-to-initiator ratio for those compounds differs. Figure 8 shows the corresponding molecular weights, measured against a linear polystyrene calibration curve, for the polymerizations depicted in Figure 7. The poly(*n*-butyl acrylate) synthesized from the mono- and difunctional initiators yielded linear molecular weight/conversion behavior as expected for macromolecules free of branches. However, the higher molecular weight polyacrylate derived from the difunctional initiator did not show agreement with the polystyrene calibration standards indicating that the poly(*n*-butyl acrylate) has a lower hydrodynamic volume than polystyrene of an identical molecular weight (see Table 2, vide infra). The star polymers, however, show a behavior similar to the polystyrene star displayed in Figure 4—marked deviations of measured molecular weight from that predicted by theory. The effect of branching becomes significant between the tetra- and hexafunctional initiators where the differences in molecular weight between those two reactions are small.

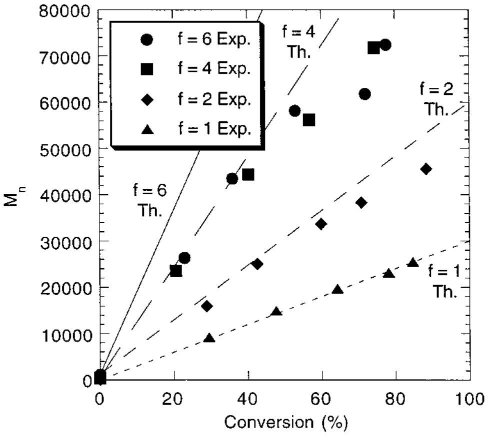


Figure 8. Molecular weight vs conversion plot for the ATRP of *n*-butyl acrylate initiated by mono-, di-, tetra-, and hexafunctional initiators containing 2-bromopropionyloxy species. $[M]_0/[R-Br]_0/[CuBr(dNbpy)_2]_0 = 232:1:0.5$, 90 °C, bulk.

Table 2. Relative and Absolute Molecular Weight Data for Samples of Poly(*n*-butyl acrylate) Synthesized from Di-, Tetra-, and Hexafunctional Initiators

	M_n			
functionality[a]	theor	SEC[b]	3D-SEC	$[\eta]$[c]
2	40 000	32 100	35 200	2.3
2	80 000	62 600	80 500	4.5
4	40 000	33 800	45 100	1.6
4	80 000	58 000	75 500	2.6
6	40 000	27 100	43 600	1.0
6	80 000	50 000	81 500	2.3

[a] Number of initiating sites per molecule. [b] Measured by SEC vs linear polystyrene standards. [c] In dL/g, determined by the area under curve of $[\eta] \times$ MW vs elution volume trace.

The polydispersities (Figure 9) of the polymer samples measured in the above study remained low ($M_w/M_n < 1.2$) indicating control during each of the reactions. The linear semilogarithmic plot and low polydispersities show again that control over radical concentration is important in producing well-defined materials. Here, $[^nBA]_0/[R-Br]_0/[CuBr(dNbpy)_2]_0 = 232:1:0.5$ at 90 °C provided fast rates and good control over the polymerization regardless of the functionality of the initiator.

To address the differences between observed and theoretical molecular weights as well as the poor relative size resolution between the tetra- and hexafunctional poly(*n*-butyl acrylate) stars described above, 3D-SEC was used to determine absolute molar masses. Poly(*n*-butyl acrylate) samples of predetermined theoretical molecular weights of M_n = 40 000 and M_n = 80 000 were synthesized from 2-bromoisobutyrate-functionalized initiators containing two (**2Br^{i}Bu**), four

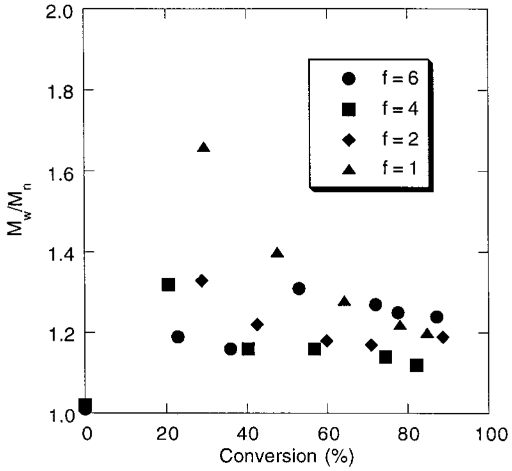


Figure 9. Polydispersity vs conversion plot for the ATRP of butyl acrylate initiated by mono-, di-, tetra-, and hexafunctional initiators containing 2-bromopropionyloxy species. $[M]_0/[R-Br]_0/[CuBr(dNbpy)_2]_0 = 232:1:0.5$, 90 °C, bulk.

(**4Br^{i}Bu**), and six (**6Br^{i}Bu**) initiating sites per molecule. The relative and absolute measurements of molecular weight are compared in Table 2. The results show that as the functionality of the initiator increased, the molecular weight measured vs linear polystyrene standards deviated more from the theoretical value. This correlated with the decrease in intrinsic viscosity measured using the on-line viscometer and corresponded with the trend expected between linear and star polymers with increasing arm number. Finally, the absolute molecular weights measured with the 3D-SEC system agreed well with the theoretical values. The discrepancy between the relative and 3D-SEC results for the $M_{n,th} = 80\,000$ linear polymer may have been due to possible chain transfer to polymer known to exist in the free radical polymerization of *n*-butyl acrylate.[48] However, since ATRP from each initiator was performed under similar conditions, the trend in the data in Table 2 remained valid. The larger deviation of the true molecular weight for the MW = 40 000 samples was due primarily to the operation of the light-scattering detector near its lower detection limit. Nevertheless, the table demonstrated that the polymerizations were indeed controlled/"living".

Star–Block Copolymers. An advantage of the ATRP process is the preservation of chain end functionality. The alkyl halide species can be transformed into other functionalities or used to initiate ATRP of other monomers to make block copolymers.[13,49–54] Since star polymers synthesized by ATRP also exhibit conservation of active species, star–block copolymers have been synthesized by polymerization of another monomer from a preformed polymeric macroinitiator.[30,35] In one such case, a hexafunctional star poly(methyl acrylate) initiated by **6BzBr** was used as a macroinitiator for the copper bromide/dinonyl bipyridine mediated polymerization of isobornyl acrylate. SEC traces for the polymerizations of the homocopolymers and block copolymers are shown in Figure 10. In each case the chromatograms shift cleanly to higher molecular weight. Since the methyl acrylate polymerization was purposely stopped at ~50% conversion, termination was minimal as shown by the absence of a high molecular weight shoulder in the chromatograms. This way a star–block copolymer composed of a soft, low T_g segment in the core and a hard, high T_g shell was synthesized. Combinations such as these are useful for the design of materials in thermoplastic elastomeric applications.

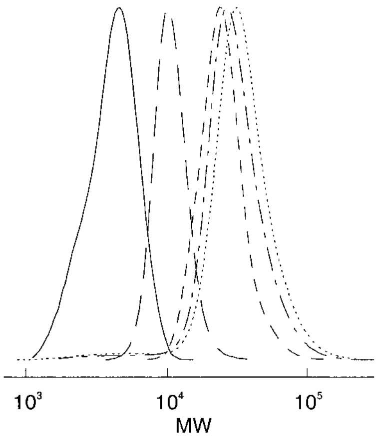


Figure 10. SEC chromatograms for the homo- and subsequent copolymerization of methyl acrylate and isobornyl acrylate initiated by **6BzBr** and catalyzed by a CuBr/dNbpy complex at 90 °C. Key: (—) MA, $M_n = 3000$, $M_w/M_n = 1.18$; (— —) MA, $M_n = 9000$, $M_w/M_n = 1.08$; (– – –) MA, $M_n = 20\,000$, $M_w/M_n = 1.14$; (– -) ^{i}BnA, $M_n = 44\,000$, $M_w/M_n = 1.29$; (- - -) ^{i}BnA, $M_n = 48{,}000$, $M_w/M_n = 1.37$.

Conclusion

A variety of organic and inorganic/organic hybrid multifunctional initiators can be modified to produce initiators for star polymers by a controlled/"living" polymerization method. The use of a free radical technique to produce polymers with these branched architectures allows for the synthesis of materials with a broad spectrum of compositions. The technique should be amenable to the synthesis of star–block and star–random copolymers for use in surfactant, viscosity modification, or adhesives technologies. More complex materials such as those described here will be a goal of future publications from this laboratory.

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Supporting Information Available: Kinetic and molecular weight/polydispersity plots (Figures A–N) for the entries in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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