Atom Transfer Radical Polymerization of (Meth)acrylates from Poly(dimethylsiloxane) Macroinitiators

Peter J. Miller† **and Krzysztof Matyjaszewski***

Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

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ABSTRACT: The atom transfer radical polymerization (ATRP) of (meth)acrylates from poly(dimethylsiloxane) (PDMS) macroinitiators is described. Hydrosilylation of commercially available difunctional hydrosilyl terminal PDMS ($M_w/M_n > 1.3$) with allyl- or 3-butenyl 2-bromoisobutyrate resulted in the macroinitiators. Linear semilogarithmic kinetic plots were obtained for the ATRP of acrylates and methacrylates. A nonlinear dependence of molecular weight on conversion was ascribed to a high concentration of low molecular weight chains not readily observed in the size exclusion chromatograph using THF as eluent. Well-defined monofunctional, low-polydispersity PDMS macroinitiators were synthesized by the anionic ring-opening polymerization of hexamethylcyclotrisiloxane. ATRP of acrylates and methacrylates from those compounds showed linear increases in M_n with conversion, demonstrating the effectiveness of ATRP to synthesize a variety of inorganic/organic polymer hybrids. A monofunctional poly(styrene-*b*-dimethylsiloxane) macroinitiator was used to initiate ATRP of *n*-butyl acrylate and methyl methacrylate, resulting in ABC organic/inorganic/organic hybrid triblock copolymers.

Introduction

Of all the inorganic polymers studied, polysiloxanes have been the most widely exploited.[1] Particularly, poly(dimethylsiloxane) (PDMS) is used in materials for its high oxygen permeability and heat transfer properties. However, since PDMS is a fluid at room temperature, the homopolymer lacks dimensional stability. In an effort to produce materials composed of silicones with more desirable mechanical properties, block, graft, and network copolymers containing PDMS segments have been examined. For example, living polystyryllithium was used to initiate ring-opening polymerization of hexamethylcyclotrisiloxane (D_3).[2] This method was only used to synthesize diblock copolymers. Because the resulting lithium silanolate is not sufficiently reactive to initiate polymerization of styrene, coupling techniques were used to make ABA triblock copolymers. Hydrosilylation of vinyl-terminal siloxanes with hydrosilyl functional polystyrenes[3] or coupling of silanolates with chlorosilyl-terminal organic polymers[4−6] were useful in providing the requisite di- and triblock copolymers. Well-defined materials were obtained only in those cases where exact stoichiometry was maintained between the various components of the reactions. Otherwise, extraction or fractionation procedures were necessary to remove unreacted homopolymer from the products.

Free radical polymerizations[7] represent an attractive alternative to ionic polymerizations due to the milder conditions used in the synthesis and a broader spectrum of monomers available to the technique. Block copolymers have been synthesized from PDMS containing terminal azo groups.[8] This led to a mixture of block and homopolymer as a result of initiation by the two different radicals generated upon decomposition of the azo group. In another system, silylpinacolate species embedded in PDMS chains underwent thermal bond homolysis to initiate styrene and methyl methacrylate polymerization.[9,10] In the case of styrene, where coupling was the primary mode of termination, alternating segmental inorganic/organic hybrid polymers were produced. For methacrylate polymerization, ABA triblock copolymers resulted. However, in both cases, the conventional radical processes impeded control over molecular weight and limited manipulation of the relative segment composition.

An improvement to those systems was brought on by the advent of controlled radical polymerization.[11] Hydrosilylation was used to transform hydrosilyl- or vinylsilyl-terminal PDMS into silicones that contained benzyl chloride moieties.[12] The difunctional macroinitiators were used to initiate ATRP of styrene under conditions that provided control over both chain length of the organic segment and overall composition. Well-defined ABA triblock and graft copolymers were synthesized via the ATRP of styrene from the macroinitiators.

The purpose of the current study was to expand the scope of the ATRP method to produce di- and triblock copolymers from PDMS macroinitiators. Polymerizations of acrylates and methacrylates were initiated from mono- and difunctional PDMS containing benzyl chloride or 2-bromoisobutyrate end groups. The synthesis of a variety of block copolymers was examined to demonstrate that hybrids with well-defined architecture and composition could be synthesized for use in potential applications ranging from pressure-sensitive adhesives to biomedical materials.

Experimental Section

Measurements. Size exclusion chromatography (SEC) measurements in THF were conducted 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 weights were calculated with PSS software; calibration was based on low-polydispersity polystyrene standards

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† Current address: Bayer Corporation, 100 Bayer Rd., Pittsburgh, PA 15205.

* To whom correspondence should be addressed.

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for styrene, acrylate, and siloxane polymerizations and poly(methyl methacrylate) (PMMA) standards for copolymers with methyl methacrylate. 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 in deuterated chloroform ($CDCl_3$) on a 300 MHz Bruker spectrometer using Tecmag data acquisition software. All spectra were baseline corrected prior to integration. For samples with aromatic protons, a 4 s relaxation delay was used and 2 s for all other measurements. In determining end group structure and concentration, at least 700 scans were acquired to obtain an acceptable signal-to-noise ratio. Infrared spectra were measured on an ATI Mattson Infinity Series FTIR between salt plates.

Materials. THF and toluene were distilled from purple sodium ketyl solutions. Benzene was distilled from potassium. Styrene (Aldrich) was distilled from calcium hydride. Methyl acrylate, *n*-butyl acrylate, and methyl methacrylate, all from Acros, were all washed three times with 5% aqueous sodium hydroxide and once with water. After drying with magnesium sulfate, the monomers were obtained in pure form by distillation from calcium chloride. Isobornyl acrylate from Aldrich was distilled from diisopropylaluminum. Following purification, all monomers were stored in the freezer. Difunctional hydrosilyl-terminal PDMS was obtained from Gelest; M_n = 4500−33 900, M_w/M_n = 1.2−2.4 (M_n and M_w/M_n values obtained from our SEC). Hexamethylcyclotrisiloxane (D_3) from Aldrich was dissolved in benzene and stirred over calcium hydride overnight at reflux under argon. The solvent was removed by trap-to-trap distillation at reduced pressure. The monomer was then sublimed into another flask and stored at room temperature in the drybox. Triethylamine (TEA) from Acros was stirred over magnesium sulfate and filtered just prior to use. 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.[13] and used to generate 4,4′-di-*n*-nonyl-2,2′-bipyridine (dnNbpy) by a previously reported procedure.[14] Allyl alcohol, 2-bromoisobutyryl bromide, 3-buten-1-ol, *n*-butyllithium (2.5 M solution in hexanes), *sec*-butyllithium (1.3 M solution in hexanes), 2-hydroxyethyl methacrylate (HEMA), chlorotrimethylsilane (TMSCl), diethyl ether, hexanes, 2-methyl-1,4-naphthoquinone (MeNQ), and vinylbenzyl chloride, from Aldrich, were used without further purification. Chlorodimethylsilane, from Aldrich, was distilled from calcium hydride and stored in the drybox. Bis(1,3-divinyl-1,1,3,3-tetramethyldisiloxane)platinum(0) complex in xylene (Karstedt's catalyst), 9.6×10^{-5} mol/mL from Gelest, was used as received.

Syntheses. *2-Trimethylsilyloxyethyl Methacrylate (HEMA-TMS).* A 1 L three-neck flask was charged with 107 g (0.82 mol) of HEMA, 100 g (0.99 mol) of TEA, and 500 mL of hexanes under argon. The reactor was fitted with a mechanical stirrer and 150 mL pressure equalizing addition funnel which was charged with 107 g (0.99 mol) of TMSCl. The apparatus was cooled to 0 °C in an ice/water bath and the TMSCl added dropwise over a 30 min period. The white mixture was stirred overnight under argon, warming to room temperature over that period. A 200 mL aliquot of hexane was added to the vessel under air, and the mixture was filtered. The solvent was removed from the filtrate by room-temperature distillation at 20 mmHg. The white precipitate was resuspended in 1 L of hexane and stirred for 1 h. The mixture was filtered and the filtrate combined with the original liquid. Distillation was continued until no more bubbling was observed at which time the pressure was reduced to 0.5 mmHg to remove any volatile byproducts. The remaining liquid was vacuum distilled through a 5 in. Vigreux column collecting the product at 45 °C, 1.9×10^{-2} mmHg. The clear colorless liquid was then stored in the freezer when not used for polymerizations. Yield = 120 g (72%). ^{1}H NMR ($CDCl_3$) δ: 6.22 (t, 1H, vinyl CH), 5.78 (q, 1H, vinyl CH), 4.32 (t, 2H, ester CH_2), 3.92 (t, 2H, SiO−CH_2), 2.08 (t, 3H, CH_3), 0.24 (s, 9H, $Si(CH_3)_3$).

Allyl 2-Bromoisobutyrate (AlBr^{i}Bu). Into a 1 L one-neck flask was placed 28 g (0.48 mol) of allyl alcohol and 64 g (0.63 mol) of TEA. The vessel was fitted with a 250 mL pressure equalizing addition funnel which was charged with a solution of 144 g (0.63 mol) of 2-bromoisobutyryl bromide in 250 mL of THF under argon. The reactor was cooled to 0 °C in an ice/water bath and the acid halide solution added at a rate of 2 drops/s. The mixture was stirred overnight, warming to room temperature of its own accord. The reaction mixture was transferred to a l L separatory funnel with 350 mL of diethyl ether. The salts and unreacted acid halide were extracted from the organics by sequential washings with 400 mL of deionized water, 3 × 250 mL of aqueous saturated sodium bicarbonate, and 250 mL of deionized water. The organic phase was isolated and dried over magnesium sulfate. The mixture was filtered, and the solids were washed with ether. The solvent was removed from the filtrate by rotary evaporation and the product isolated as a clear, colorless liquid by distillation at 53−54 °C, 5 mmHg. Yield = 87 g (87%). ^{1}H NMR ($CDCl_3$) δ: 5.90 (m, 1H, vinyl CH), 5.29 (quartet of doublets, 2H, vinyl CH_2), 4.61 (doublet of doublets, 2H, O−CH_2), 1.91 (s, 6H, C(Br)−$(CH_3)_2$) ppm. Elemental analysis for $C_7H_{11}BrO_2$ % found (% expected): C, 40.56 (40.60); H, 5.36 (5.35); Br, 38.55 (38.59).

3-Butenyl 2-Bromoisobutyrate BuBr^{i}Bu. A similar reaction was used for the synthesis of AlBr^{i}Bu except 3-buten-1-ol replaced allyl alcohol. Yield = 27% (colorless liquid). ^{1}H NMR ($CDCl_3$) δ: 5.72 (m, 1H, vinyl CH), 5.00 (triplet of quartets, 2H, vinyl CH_2), 4.25 (t, 2H, O−CH_2), 2.37 (quartet of triplets, 2H, CH−$\mathbf{CH_2}$−CH_2−O), 1.86 (s, 6H, C(Br)−$(CH_3)_2$) ppm. Elemental analysis for $C_8H_{13}BrO_2$ % found (% expected): C, 43.43 (43.46); H, 5.92 (5.93); Br, 36.32 (36.14).

Hydrosilylations. The hydrosilylation of hydrosilyl-terminal PDMS with vinyl benzyl chloride was reported previously.[12]

Hydrosilylations with THF under air were conducted in the same manner whether with AlBr^{i}Bu or BuBr^{i}Bu. A 4.7 g (1.1 mmol) sample of monofunctional hydrosilyl-terminal PDMS (M_n = 4300, M_w/M_n = 1.3), 1.5 g (6.6 mmol) of BuBr^{i}Bu, and 8 mL of THF were placed into a 25 mL round-bottom flask and stirred until a homogeneous solution formed. A 0.11 mL (1.0×10^{-2} mmol) aliquot of Karstedt's catalyst was then injected and the apparatus fit with a reflux condenser and rubber septum. The mixture was heated to solvent reflux overnight. The polymer was precipitated into 350 mL of methanol and stirred vigorously for 20 min. The stirring was stopped, allowing the PDMS phase to settle to the bottom of the beaker, and methanol was then decanted. Another 200 mL of methanol was added; the PDMS was again stirred vigorously for 20 min. After the PDMS was allowed to settle, the methanol was decanted and the silicone transferred to a preweighed vial. The light yellow liquid was dried at 55 °C under vacuum (1 mmHg) overnight. Yield = 3.6 g (77%). ^{1}H NMR ($CDCl_3$) δ: see Figure 6 for labeled peaks. Functionality (determined by the ratio of the integrations of the isobutyrate methyls at 1.93 ppm and the initiator butyl methyl at 0.90 ppm) = 0.54. Hydrosilylations run in toluene under air were the same as that described above, but instead of a reflux condenser, the flask was covered with a rubber septum. The temperature was either room temperature or 70 °C. When an oxygen-free reaction was studied, the solvent was first deoxygenated by bubbling with argon or nitrogen for 15 min at room temperature. With the exception of Karstedt's catalyst, all subsequent solutions were also deoxygenated.

When the ligand MeNQ[15] was used, the following procedure was adopted: 5.4 g (0.33 mmol) of monofunctional hydrosilyl-terminal PDMS (M_n = 4300, M_w/M_n = 1.3), 0.4 g (2.0 mmol) of BuBr^{i}Bu, and 15 mL of deoxygenated toluene were placed into a 50 mL round-bottom flask covered with a septum. The solution was deoxygenated by bubbling with argon for 15 min at room temperature. Into a vial, 1.1 mg (6.4×10^{-6} mol) of MeNQ and 10 mL of deoxygenated toluene were placed into a scintillation vial and mixed until a homogeneous yellow solution formed. A 1.0 mL aliquot of this solution was transferred to a 5 mL round-bottom flask, and the solution was deoxygenated for 10 min with argon. To this, 3.7 μL (3.6×10^{-6} mol) of Karstedt's catalyst was added, and the solution was deoxygenated an additional 5 min. The catalyst solution was cannula transferred to the reactor at room temperature under argon, and the flask was placed into a 70 °C oil bath under argon overnight. The yellow/brown homogeneous solution was precipitated into 200 mL of methanol and stirred vigorously for 20 min. The stirring was stopped, allowing the PDMS phase to settle to the bottom of the beaker. The methanol was then decanted and the PDMS stirred vigorously in another 200 mL of methanol for 20 min. After the PDMS was allowed to settle, the methanol was decanted and the silicone dissolved in 10 mL of hexanes and transferred to a preweighed vial. The solvent was removed by rotary evaporation and the liquid dried at 60 °C under vacuum (1 mmHg) overnight. Yield = 5.3 g (98%). ^{1}H NMR ($CDCl_3$) δ: see Figure 6 for labeled peaks. Functionality (determined by the ratio of the integrations of the isobutyrate methyls at 1.93 ppm and the initiator butyl methyl at 0.90 ppm) = 0.95.

Polymerizations. *Monofunctional Hydrosilyl-Terminal PDMS.* In the drybox, 17 g (76 mmol) of D_3, 6.3 mL of THF, and 6.3 mL of toluene were placed into a 50 mL one-neck round-bottom flask and stirred until a clear, colorless solution formed. To this, 0.34 mL (0.85 mmol) of *n*-butyllithium solution was added. After stirring for 6 h at room temperature, the polymerization solution was added dropwise to a solution of 0.92 g (8.4 mmol) of chlorodimethylsilane in 1.0 mL of THF. The heterogeneous white mixture was stirred at room temperature overnight in the drybox. All volatiles, including unreacted D_3, were separated from the polymer by room-temperature vacuum transfer at 1 mmHg. The salt was then removed from the clear, colorless polymer by filtration through a 0.2 μm syringe filter into a preweighed vial. Yield = 13 g (77%). ^{1}H NMR ($CDCl_3$) δ: 4.72 (q, 1H, Si−H), 1.33 (m, 4H, $CH_3-\mathbf{CH_2}-\mathbf{CH_2}$), 0.90 (t, 3H, $\mathbf{CH_3}-CH_2$), 0.57 (m, 2H, CH_2-Si), 0.10 (s, 6H, PDMS methyl) ppm. The functionality determined by comparison of the integrations for the initiator methyl group at 0.90 ppm and the hydrosilyl proton at 4.72 ppm was 0.98.

Hydrosilyl-Terminal Poly(styrene-b-dimethylsiloxane). In the drybox, 1.8 g (17 mmol) of styrene and 8 mL of benzene were placed into a 50 mL round-bottom flask. To this 0.27 mL (0.35 mmol) of a 1.3 M solution of *sec*-butyllithium was added at room temperature. The orange solution was stirred for 60 min. At that time a 0.1 mL aliquot of the reaction was removed and quenched with chlorotrimethylsilane. To the remaining solution, 2.2 g (10 mmol) of D_3 dissolved in 2 mL of THF was injected. The light yellow solution was stirred at room temperature for 2.5 h at which time 0.38 g (3.5 mmol) of chlorodimethylsilane was injected. The heterogeneous white mixture was stirred at room temperature overnight. The flask was removed from the drybox, and all volatiles were removed under room-temperature vacuum (1 mmHg) for 6 h. Benzene was then added to the flask, and the insoluble lithium chloride salt was removed by filtration. The solvent was then removed by rotary evaporation and the white solid dried under room-temperature vacuum (1 mmHg) overnight. ^{1}H NMR ($CDCl_3$) δ: 7.1−6.4 (m, 5H, phenyl), 4.75 (q, 1H, Si−H), 1.95 (m, 1H, *sec*-butyl methine), 1.45 (s, 2H, *sec*-butyl methylene), 1.00 (s, 1H, $CH_2-C\mathbf{H}(PH)-Si$), 0.70 (m, 6H, *sec*-butyl CH_3's), 0.10 (s, 6H, PDMS methyl) ppm. The functionality determined by comparison of the integrations for the initiator methyl groups at 0.70 ppm and the hydrosilyl proton at 4.75 ppm was 0.99.

ATRP. A typical polymerization is as follows: 1.8 g (0.41 mmol) of monofunctional 2-bromoisobutyrate-terminal PDMS ($M_n = 4500$, $M_w/M_n = 1.3$) was placed into a 10 mL Schlenk flask with 4.1 g (41 mmol) of MMA, 20 mg (0.20 mmol) of CuCl, and 4.1 g of toluene. The headspace of the flask was purged with Ar(g), and 170 mg (41 mmol) of dnNbpy was added. The mixture was stirred at room temperature under Ar(g) until a homogeneous maroon solution formed. The solution was deoxygenated by bubbling with argon at room temperature for 15 min. A 0.1 mL aliquot of the reaction mixture was removed, and the flask was placed into a 90 °C oil bath under argon. Periodically, 0.2 mL aliquots of the reaction mixture were removed for kinetic and molecular weight analysis. Upon completion of the reaction, the sample were dissolved directly with the appropriate solvent or analysis by GC or with $CDCl_3$ for conversion measurement by ^{1}H NMR. The same samples were then filtered through a 1 in. column of alumina followed by a 0.2 μm syringe filter before injection onto the SEC. The remaining polymer in the reactor was dissolved in acetone and stirred with a Dowex MSC-2 cation-exchange resin to remove the metal complex. The mixture was then gravity filtered into 1 L of methanol. The precipitated polymer was filtered, redissolved in 80 mL of THF, and precipitated into methanol once more. The filtered product was dried overnight at 60 °C under vacuum.

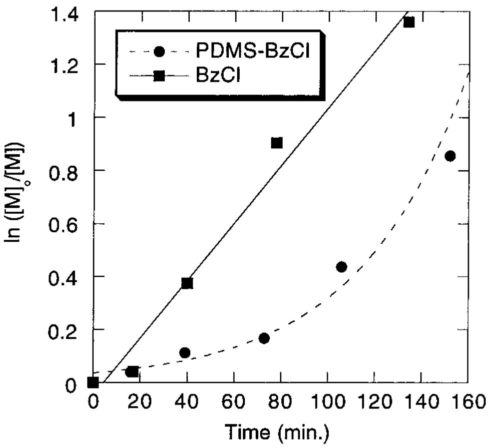
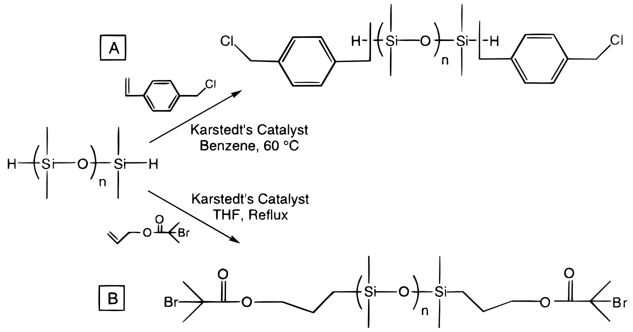


Figure 1. Kinetics of the ATRP of methyl acrylate from (a) benzyl chloride (BzCl, ■) in the presence of PDMS and (b) benzyl chloride-terminal PDMS (PDMS−BzCl, ●). Conditions: $[MA]_0/[R-Cl]_0/[CuCl(dnNbpy)_2]_0 = 58:1:0.25$, 17% (w) PDMS, 90 °C, Ar(g).

Scheme 1



Results and Discussion

Initiation from Small Molecules vs PDMS Macroinitiators. The synthesis of PDMS macroinitiators composed of benzyl chloride termini by hydrosilylation of vinyl benzyl chloride with hydrosilyl-terminal PDMS has been reported previously (Scheme 1A).[12] The ATRP of styrene from mono-[16] and difunctional[12] benzyl chloride-terminal PDMS macroinitiators is also well-documented. However, studies of the ATRP from benzyl chloride alone show that, while it is a kinetically efficient initiator for acrylate polymerization,[17] poor control over molecular weights and polydispersities were observed for methyl methacrylate polymerization.[18] The kinetics of methyl acrylate polymerization from difunctional benzyl chloride terminal PDMS is shown by the circles in Figure 1. The increasing slope of the curve is indicative of slow initiation. To determine whether this was due to relatively slower rates of initiation from the macroinitiator or due to the silicone in the medium, a polymerization was conducted from benzyl chloride in the presence of unfunctionalized PDMS. The squares

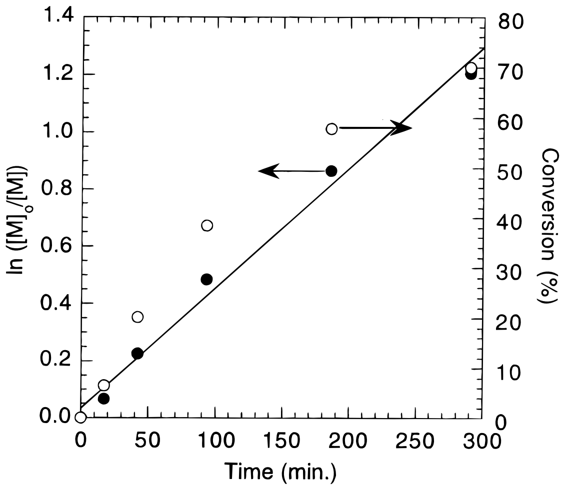


Figure 2. Kinetic plot for the ATRP of MMA from a difunctional 2-bromoisobutyrate terminal PDMS macroinitiator. Conditions: $[MMA]_0/[Br-PDMS-Br]_0/[CuCl(dnNbpy)_2]_0 = 54:1:0.5$, $M_{n,PDMS} = 8200$, 50% *p*-xylene, 90 °C, Ar(g).

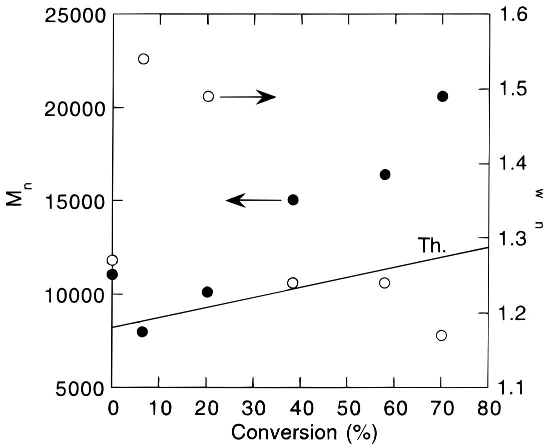


Figure 3. Molecular weight plot for the ATRP of MMA from a difunctional 2-bromoisobutyrate terminal PDMS macroinitiator. Conditions: $[MMA]_0/[Br-PDMS-Br]_0/[CuCl(dnNbpy)_2]_0 = 54:1:0.5$, $M_{n,PDMS} = 8200$, 50% *p*-xylene, 90 °C, Ar(g).

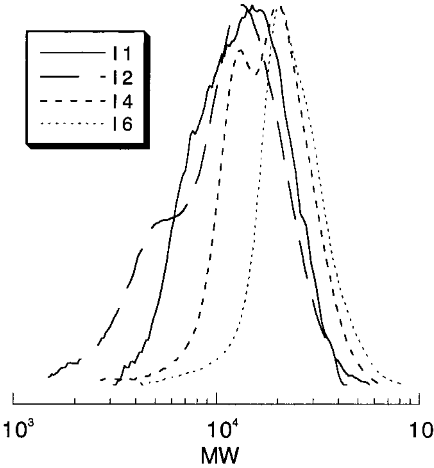


Figure 4. SEC traces for the ATRP of MMA from a difunctional 2-bromoisobutyrate-terminal PDMS macroinitiator. Conditions: $[MMA]_0/[Br-PDMS-Br]_0/[CuCl(dnNbpy)_2]_0 = 54:1:0.5$, $M_{n,PDMS} = 8200$, 50% *p*-xylene, 90 °C, Ar(g). Conversion: (—) 0%, (– –) 6%, (---) 38%, (• • •) 70%.

in Figure 1 show that polymerization in a silicone matrix does not provide an unfavorable relation between the rates of initiation and propagation. Such an observation of slow initiation from the macroinitiator is not without precedent as estimation for the rate constant of addition of styrene to a 1-phenylethyl radical[19] (a small molecule analogue of the repeat unit in polystyrene) was about 10 times larger than the rate constant of propagation[20] of styrene at the same temperature (120 °C).

One other observation from the study was the appearance of the two reaction mixtures. While both were homogeneous at the outset, the reaction with the small molecule initiator phase separated; homogeneity was maintained throughout the polymerization initiated from the macroinitiator. These observations demonstrate that in the latter case a block copolymer was synthesized and shows the compatibilization power these materials have on incompatible systems.

Polymerization from Difunctional Macroinitiators Containing α-Bromoesters Given the results of the study described above, the synthesis of PDMS macroinitiators with more reactive alkyl halide fragments was explored. Since 2-bromoisobutyrates are efficient initiators for polymerizations of styrene, acrylates, and methacrylates, an attachable initiator composed of this species was chosen. Allyl 2-bromoisobutyrate ($AlBr^iBu$) was synthesized by the esterification of allyl alcohol with 2-bromoisobutyryl bromide in a THF/TEA solution. This compound was used in hydrosilylations with difunctional hydrosilyl-terminal PDMS in the presence of Karstedt's catalyst in THF at reflux (Scheme 1B). ATRP of a variety of monomers from macroinitiators of differing molecular weights was then performed. One such example is the polymerization of MMA from a PDMS macroinitiator with $M_n = 8200$ shown in Figures 2–4. A homogeneous catalyst CuBr(dnNbpy)$_2$ was used in the reaction run at 90 °C in 50% xylene. The kinetic plot in Figure 2 was linear, showing that initiation was sufficiently fast relative to propagation and that termination was maintained to low levels. The plot of molecular weight versus conversion (Figure 3) showed an initial decrease followed by a progressive increase. The increase in chain length was also more dramatic than the theoretical molecular weight predicted by the ratio of consumed monomer to the initial concentration of macroinitiator similar to that reported for the ATRP of styrene from benzyl chloride-terminal PDMS macroinitiators.[12] Concomitant with the behavior of M_n, the polydispersity initially showed a dramatic increase followed by a progressive decrease such that, at the conclusion of the reaction, the product polydispersity ($M_w/M_n = 1.17$) was less than the initial value for PDMS, $M_w/M_n = 1.27$. The overlaid SEC traces in Figure 4 illustrate the reason for the molecular weight behavior. At 6% monomer conversion there was a significant low molecular weight distribution which had a smaller chain length than the macroinitiator leading to a decrease in M_n. As the reaction proceeded, the entire trace progressively moved toward lower retention times with the low and high molecular weight fractions eventually coinciding at high conversion leading to the decrease in polydispersity.

One possible explanation for the initial decrease in copolymer M_n was a result of a combination of the broad polydispersity of the macroinitiator and the low refractive index of the PDMS relative to THF, the SEC eluent. Figure 5 shows the SEC trace for a high concentration of the difunctional PDMS sample eluted using differential refractive index (DRI) detection. Since meas-

Table 1. ATRP of Vinyl Monomers from Difunctional PDMS Macroinitiators

init[a]	M_n (M_w/M_n)	monomer	catalyst (equiv)[b]	solvent	T (°C)	conv[c]	M_n (M_w/M_n)
BzCl	4500 (1.2)	styrene	CuCl(dnNbpy)$_2$		130	90	10100 (1.3)
BzCl	9800 (2.4)	styrene	CuCl(dnNbpy)$_2$	xylene	130	70	20600 (1.7)
BzCl	4500 (1.6)	iBnA[d]	CuCl(dnNbpy)$_2$		90	53	12500 (1.6)
BzCl	9800 (2.4)	nBA[e]	CuCl(dnNbpy)$_2$	DMB[f]	100	81	24600 (1.5)
AlBr^{i}Bu	8200 (1.3)	MMA[g]	CuBr(bpy)$_3$	xylene	90	70	20400 (1.2)
AlBr^{i}Bu	33900 (1.8)	MMA	CuBr(bpy)$_3$	xylene	90	34	89600 (1.3)
AlBr^{i}Bu	33900 (1.8)	HEMA−TMS[h]	CuBr(bpy)$_3$	DMB	80	11	62800 (1.6)

[a] Terminal species on difunctional macroinitiators: BzCl = benzyl chloride termini, BuBriBu = 2-bromoisobutyryloxy termini. [b] Molar ratio relative to macroinitiator. [c] Monomer conversion (%). [d] Isobornyl acrylate. [e] *n*-Butyl acrylate. [f] 1,4-Dimethoxybenzene. [g] Methyl methacrylate. [h] 2-(Trimethylsilyloxy)ethyl methacrylate.

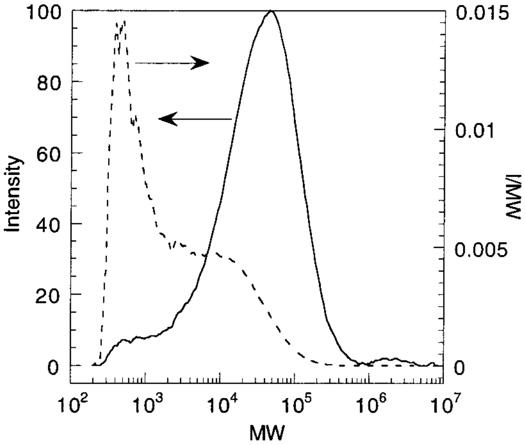
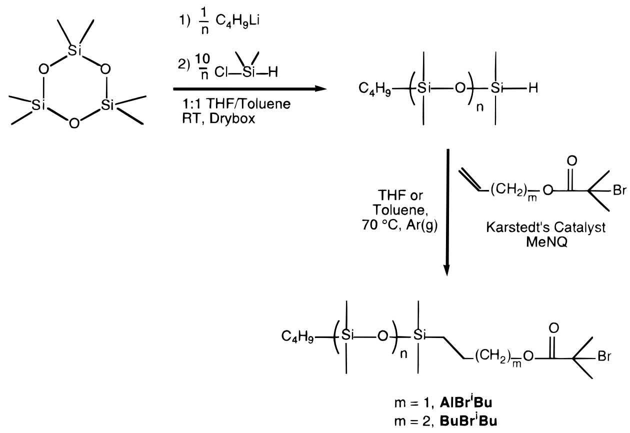


Figure 5. SEC weight (—) and number (---) distributions for a difunctional benzyl chloride-terminal PDMS macroinitiator: SEC eluent = THF, M_n = 43 800, M_w/M_n = 2.05.

urement of peak intensity is proportional to concentration, the trace describes a weight distribution. When each slice is divided by the molecular weight of the polymer at that slice, the result is a curve based on the number of chains in each slice (i.e., a number molecular weight distribution). Such a distribution when plotted for the PDMS in Figure 5 shows that there is a significant fraction of low molecular weight chains in the sample. If each of those chains is completely functionalized, then, when a polymer has a refractive index (relative to THF) sufficiently larger than PDMS, the intensity of the DRI signal coming from that low molecular weight portion of the SEC trace increases dramatically. Furthermore, it is known that the refractive index of a diblock copolymer is the weighted average of the refractive indices of the two constituent blocks.[21] Given this, if each macroinitiator at some period of the reaction adds (essentially) the same length of polymer of higher refractive index, the cumulative refractive index of the blocks derived from the lower molecular weight macroinitiators will be larger than those composed of longer length chains. When measured by DRI, those shorter chains will then give a stronger signal than the larger macromolecules which possess a high weight fraction of silicone leading to the M_n/conversion relationship depicted in Figure 3.

While the polymerization described above gave rather unexpected results, the kinetic and molecular weight plots showed that if the reaction was allowed to proceed for a sufficiently long duration, well-defined inorganic/organic hybrid block copolymers could be synthesized. Since ATRP accommodates a variety of monomers, a broad spectrum of materials can be synthesized from macroinitiators possessing activated alkyl halides capable of undergoing carbon−halogen bond homolysis. Table 1 lists a series copolymers synthesized using this methodology. The data show that with either heterogeneous or homogeneous catalyst systems significant increases in copolymer molecular weight were observed upon addition of the organic blocks. Furthermore, a variety of copolymers were synthesized under controlled conditions based on the decreased polydispersities of the products relative to the initiating macromolecules.

Scheme 2



Monofunctional Macroinitiators. One strategy that was used to test the above hypothesis was ATRP of (meth)acrylates from well-defined PDMS macroinitiators with narrow molecular weight distributions. The synthesis of monofunctional silicones was achieved by the butyllithium-initiated living anionic ring-opening polymerization of D_3 followed by termination with functional molecules which could be either used directly as initiators for ATRP or transformed by the attachable initiator technique into species that would start the controlled radical polymerization process. For benzyl chloride functional polymers, termination with 2-(*p*-chloromethylphenyl)ethyldimethylchlorosilane yielded a macroinitiator composed of benzyl chloride fragments. ATRP of styrene from a macroinitiator of M_n = 3900, M_w/M_n = 1.14 using a homogeneous CuCl(dnNbpy)$_2$ complex in 50% xylene at 130 °C yielded a diblock copolymer with M_n = 7100, M_w/M_n = 1.19.[16]

The synthesis of 2-bromoisobutyryloxy monofunctional macroinitiators required a two-step process. Attempts to synthesize 3-(2-bromoisobutyryloxy)propyldimethylchlorosilane by the hydrosilylation of allyl 2-bromoisobutyrate with chlorodimethylsilane were unsuccessful due to the high boiling point of the product and the hydrolytic instability of the chlorosilyl group. Therefore, a two-step process of termination/attachable initiator coupling was employed. Scheme 2 illustrates the sequence of reactions used to obtain the products. Living poly(dimethylsiloxane)lithium silanolate was terminated with an excess of chlorodimethylsilane. Following isolation, hydrosilylation of the polymer with

Table 2. Hydrosilylation of Monofunctional Hydrosilyl-Terminal PDMS and Attachable Initiators

PDMS−Si−H M_n (M_w/M_n)	solvent	attachable init	attachable init equiv[a]	Pt(0) (%)[b]	MeNQ (%)[c]	temp (°C)	f[d]
29000 (1.1)	THF	AlBr^{i}Bu	6	1		reflux	0.12
4300 (1.3)	THF	AlBr^{i}Bu	6	1		reflux	0.31
4300 (1.3)	toluene	AlBr^{i}Bu	6	1		70	0.54
4300 (1.3)	THF	BuBr^{i}Bu	6	1		reflux	0.54
3600 (1.4)	toluene	BuBr^{i}Bu	6	1		70	0.88
19000 (1.1)	toluene	BuBr^{i}Bu	12	1		70	0.84
3600 (1.4)	toluene	BuBr^{i}Bu	6	1		RT	0.50
14600 (1.2)	toluene	BuBr^{i}Bu	6	1	2	70	0.80
14600 (1.2)	toluene	BuBr^{i}Bu	6	0.5	1	70	0.88
20160 (1.3)	toluene	BuBr^{i}Bu	6	0.1	0.2	70	0.95
4000 (1.4)	toluene	BuBr^{i}Bu	6	0.1	0.2	70	0.92

[a] Stoichiometry relative to PDMS. [b] Karstedt's catalyst—relative to PDMS. [c] 2-Methyl-1,4-naphthoquinone—relative to PDMS. [d] Functionality—determined by comparison of integrations of isobutyrate methyls at 1.92 ppm versus initiator methyl at 0.90 ppm in the ^{1}H NMR spectrum.

AlBr^{i}Bu mediated by Karstedt's catalyst produced the monofunctional macroinitiator. ^{1}H NMR and FTIR showed that the hydrosilyl group was completely consumed by disappearance of the Si−H peaks at 4.75 ppm and 2134 cm^{-1}, respectively. Quantification of the functionality was made by comparison of the integrations of the isobutyrate methyl protons at 1.93 ppm with the initiator *n*-butyl methyl group at 0.90 ppm in the ^{1}H NMR spectrum. This method proved to be quite accurate as the two species were of similar intensity. The first three entries of Table 2 list the reaction conditions and product functionalities for the hydrosilylation with AlBr^{i}Bu. While conversion to the product was higher in toluene than in THF, high molecular weight shoulders were observed in the SEC traces which resulted in higher molecular weights and polydispersities relative to the hydrosilyl-terminal PDMS starting material. This indicates that some coupling processes may be operating in competition with hydrosilylation.

Since the functionality with AlBr^{i}Bu was not satisfactory (≈50%), 3-butenyl 2-bromoisobutyrate (BuBr^{i}Bu) was used in subsequent hydrosilylations. The latter compound, containing the additional methylene spacer, removes the carbonyl from access to the metal center and reduces the occurrence of double-bond reorganization observed in many hydrosilylation reactions. The final seven entries of Table 2 list the results of those experiments. Under the best conditions for AlBr^{i}Bu, reaction with BuBr^{i}Bu increased the product yield from 54 to 88%. The functionality did not improve to values greater than 90% until the electron-deficient ligand 2-methyl-1,4-naphthoquinone (MeNQ) was added to the catalyst prior to introduction to the polymer/alkene system[15] and the overall concentration of platinum in the reactor was reduced. For higher concentrations of catalyst increasing quantities of a brown/black solid were observed in the flask at the end of the reaction. A homogeneous solution was maintained throughout the reaction with 0.1/0.2% Pt(0)/MeNQ where product functionality was highest. This result corroborates the recent findings by Lewis that the active form of the hydrosilylation catalyst is a nonaggregated platinum species.[22]

It should be noted that when difunctional PDMS prepared by hydrisilylation with BuBr^{i}Bu was used in ATRP, similar results were obtained as in the system using a macroinitiator prepared from AlBr^{i}Bu. For polymerization of *n*-butyl acrylate, while a linear first-order kinetic plot was obtained an initial decrease in M_n with monomer conversion was observed.

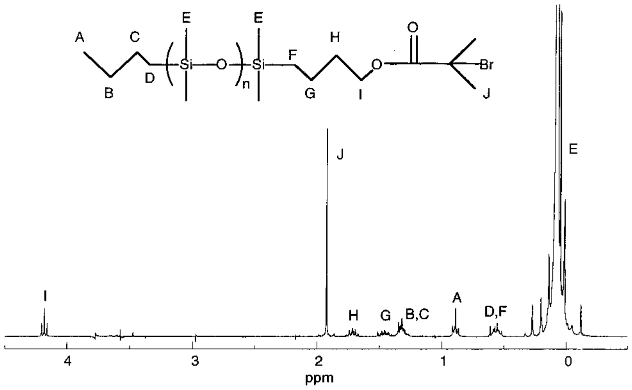


Figure 6. ^{1}H NMR (CDCl$_3$) spectrum of a monofunctional 2-bromoisobutyryloxy terminal PDMS macroinitiator, M_n = 4300, M_w/M_n = 1.3.

The ^{1}H NMR spectrum of the product (M_n = 4380, M_w/M_n = 1.26) of the hydrosilylation of BuBr^{i}Bu with a monofunctional hydrosilyl-terminal PDMS macroinitiator is shown in Figure 6. The primary feature of the spectrum is the connectivity of the attachable initiator. Unlike coupling of hydrosilyl-terminal PDMS with vinylbenzyl chloride,[12] the reaction described here proceeded regioselectively with silicon−carbon bond formation occurring exclusively at the alkene methylene carbon.

The ATRP of *n*-butyl acrylate from monofunctional 2-bromoisobutyrate terminal macroinitiators PDMS was then performed. Figure 7 shows the kinetic plots for polymerizations from low and higher molecular weight silicones. Similar to the reaction from the difunctional initiator (Figure 2), linearity of the plots confirmed conservation of radicals in both of the reactions. From the well-defined monofunctional initiators, however, a continuous increase in molecular weight with conversion was observed. The polydispersities also remained below 1.2 throughout both of the reactions. The overlaid SEC traces for the reaction from the 18 000 MW macroinitiator (circles in Figures 7 and 8) are depicted in Figure 9. The curves show that there was a progressive increase in molecular weight for the entire distribution without the appearance of a high concentration of low molecular weight chains. Because of the well-defined nature of the macroinitiator, none of these low molecular weight species were expected, providing further credence to the hypothesis that the molecular weight/conversion behavior described from the difunctional macroinitiator was due in part to the broad molecular weight distribution of the silicone—a consequence that cannot be avoided due to the step growth method of synthesis. In the SEC traces shown in Figure 9, there was a very broad, weak signal on the low molecular

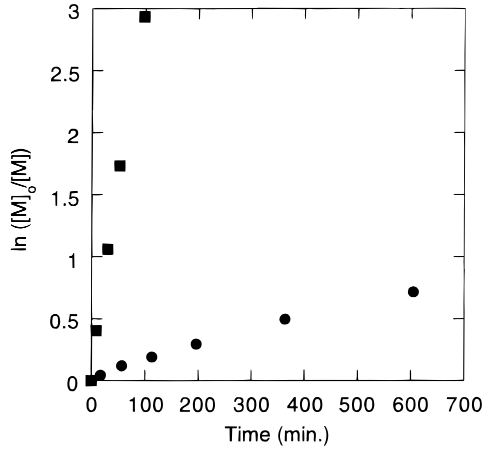


Figure 7. Kinetic plot for the ATRP of *n*-butyl acrylate from two monofunctional 2-bromoisobutyrate-terminal PDMS macroinitiators. Conditions: (●) $M_{n,PDMS} = 18\,900$, $[nBA]_0/[PDMS-Br]_0/[CuBr(dnNbpy)_2]_0 = 312:1:1$, 10% *p*-xylene, 90 °C, N_2 (g); (■) $M_{n,PDMS} = 4380$, $[nBA]_0/[PDMS-Br]_0/[CuBr(dnNbpy)_2]_0 = 78:1:0.5$, 10% *p*-xylene, 90 °C, N_2(g).

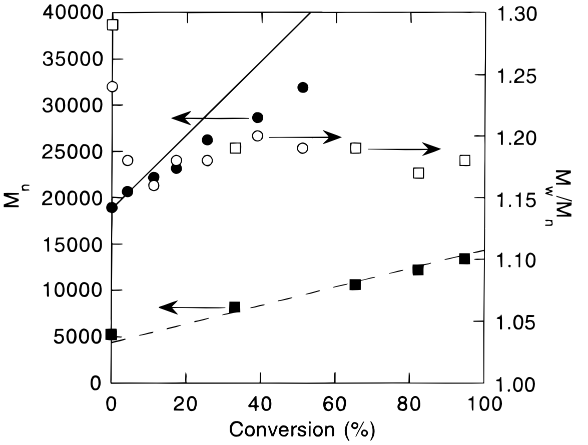


Figure 8. Molecular weight plot for the ATRP of *n*-butyl acrylate from two monofunctional 2-bromoisobutyrate terminal PDMS macroinitiators. Conditions: (●, ○) $M_{n,PDMS} = 18\,900$, $[nBA]_0/[PDMS-Br]_0/[CuBr(dnNbpy)_2]_0 = 312:1:1$, 10% *p*-xylene, 90 °C, N_2(g); (■, □) $M_{n,PDMS} = 4380$, $[nBA]_0/[PDMS-Br]_0/[CuBr(dnNbpy)_2]_0 = 78:1:0.5$, 10% *p*-xylene, 90 °C, N_2(g).

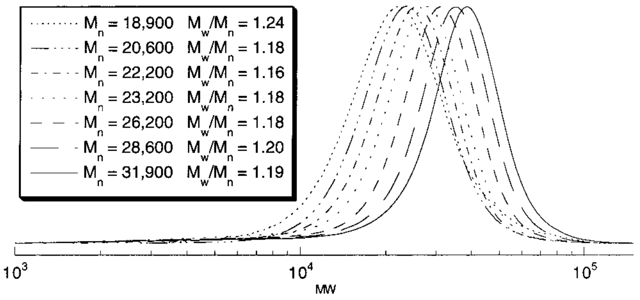


Figure 9. Overlaid SEC traces for the ATRP of *n*-butyl acrylate from a monofunctional 2-bromoisobutyrate-terminal PDMS macroinitiator. $M_{n,PDMS} = 18\,900$, $[nBA]_0/[PDMS-Br]_0/[CuBr(dnNbpy)_2]_0 = 312:1:1$, 10% *p*-xylene, 90 °C, N_2(g).

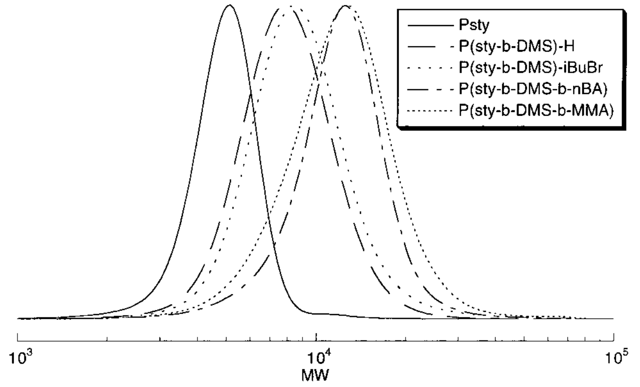


Figure 10. Overlaid SEC traces for the components of the synthesis of monofunctional 2-bromoisobutyrate terminal poly(styrene-*b*-dimethylsiloxane) and the ATRP of *n*-butyl acrylate and methyl methacrylate from that initiator. For synthesis of macroinitiator see Experimental Section. ATRP conditions: *n*-butyl acrylate, $[nBA]_0/[I]_0/[CuBr(dnNbpy)_2]_0 = 78:1:0.5$, 50% *p*-xylene, 90 °C, N_2(g); methyl methacrylate, $[nBA]_0/[I]_0/[CuCl(dnNbpy)_2]_0 = 70:1:0.5$, 50% *p*-xylene, 90 °C, N_2(g). Molecular weight and composition data are listed in Table 3.

weight side of the peak that did not show any change in intensity with conversion. This was most likely due to the 5% of dead silicone chains not properly functionalized in the hydrosilylation reaction. Since the material did not show any change throughout the reaction and the polymer peaks remained symmetrical (no significant termination was observed), that portion of the SEC trace was not integrated in the determination of polymer molecular weight and polydispersity.

ABC Triblock Copolymers. The synthesis of poly(styrene-*b*-dimethylsiloxane) diblock copolymers by anionic polymerization is well-known. However, ABA or ABC triblock copolymers where the silicone is designated as the B segment is generally not possible because the lithium silanolate does not possess sufficient nucleophilicity to initiate polymerization of styrene or (meth)acrylates. Therefore, some other transformation technique, such as that described above, is necessary.

The strategy toward the synthesis of monofunctional 2-bromoisobutyrate terminal inorganic/organic diblock copolymer macroinitiators is illustrated in Scheme 3. Living polystyryllithium was used to initiate the anionic ring-opening polymerization of D_3 in a benzene/THF solution at room temperature. Five equivalents of chlorodimethylsilane was injected into the reactor, yielding the hydrosilyl-terminal diblock copolymer. After purification, integration of the ^{1}H NMR spectrum revealed a functionality of 0.99 The SEC traces of the trimethylsilyl-terminal polystyrene and hydrosilyl-terminal poly(styrene-*b*-dimethylsiloxane), shown in Figure 10, were both symmetrical with molecular weight increasing from $M_n = 4600$ to $M_n = 7760$. The optimum hydrosilylation technique described above was then used to attach 3-butenyl 2-bromoisobutyrate to the silicone chain end. The functionality of the purified macroinitiator, determined by ^{1}H NMR, was 0.8, but the reliability of that value was suspect due to overlap of the polystyrene backbone resonances with the initiator *sec*-butyl methyl protons. The entire SEC trace shifted to slightly higher molecular weight, $M_n = 7900$, indicating efficient addition of the 2-bromoisobutyrate fragment.

Two atom transfer radical polymerizations were conducted from the same poly(styrene-*b*-dimethylsiloxane) macroinitiator. In one reaction *n*-butyl acrylate was polymerized in the presence of a $CuBr(dnNbpy)_2$ catalyst at 90 °C in 50% *p*-xylene. The molecular weight of the purified polymer (Figure 10) increased to $M_n = 10\,200$; the polydispersity was less than 1.2. The relative composition of the styrene, silicone, and acrylate phases was 1.99:1.34:1.00 (Table 3). The product was a rubbery solid after isolation by precipitation into methanol.

Scheme 3

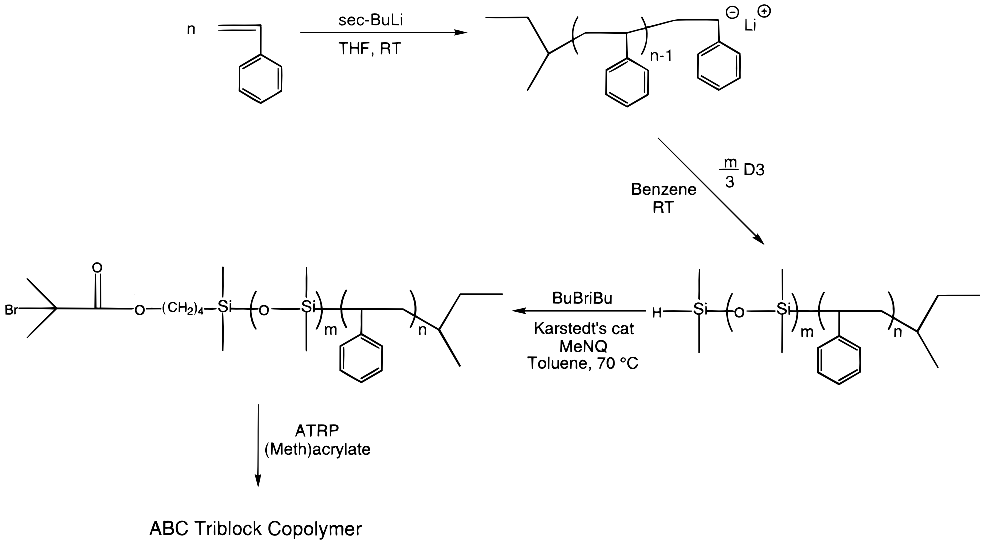


Table 3. Molecular Weight and Composition Data of the Components Used in the Synthesis of Inorganic/Organic ABC Triblock Copolymers

material	M_n^{a}	$M_\mathrm{w}/M_\mathrm{n}^{a}$	molar ratio^{b}
Psty	4600	1.09	
P(sty-*b*-DMS)-H^{c}	7760	1.15	
P(sty-*b*-DMS)-^{i}BuBr^{d}	7900	1.17	
P(sty-*b*-DMS-nBA)	10200	1.18	1.99:1.34:1.00
P(sty-*b*-DMS-MMA)	10100	1.21	1.98:1.38:1.00

^{a} Calculated relative to linear polystyrene standards. ^{b} Determined by ^{1}H NMR. ^{c} Hydrosilyl-terminal poly(styrene-*b*-dimethylsiloxane). ^{d} 2-Bromoisobutyrate-terminal poly(styrene-*b*-dimethylsiloxane).

Methyl methacrylate was the monomer polymerized in the second experiment. As in the MMA polymerization from the difunctional bromine terminal macroinitiator, the mixed halogen system mediated by CuCl(dnNbpy)$_2$ was used to provide controlled polymerization.[18] As in the acrylate polymerization, the SEC trace shown in Figure 10 demonstrated a clean, efficient shift of the entire macroinitiator distribution; molecular weight increased from $M_\mathrm{n} = 7900$ to $M_\mathrm{n} = 10\,100$, and polydispersity was 1.2. The relative composition of styrene, silicone, and methacrylate was 1.98:1.38:1.00. Following precipitation into methanol, the product was isolated as a white powder.

Conclusions

The use of end group functionalization chemistries in conjunction with controlled radical polymerization techniques has allowed for the synthesis of copolymers with a broad spectrum of compositional and architecture complexity. In the case of the inorganic/organic hybrid polymeric materials described here, the results demonstrate that new modes of polymerization can be utilized to produce a family of novel macromolecules from common, well-established components. Furthermore, the control over chain length and relative composition should serve as a useful tool in the determination of structure/property relationships for these and many other copolymers. Such information will be valuable for the material scientist in determining which material best suits his or her application.

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