Group-Transfer Polymerization of *tert*-Butyl Methacrylate and [3-(Methacryloxy)propyl]pentamethyldisiloxane: Synthesis and Characterization of Homopolymers and Random and Block Copolymers

Allen H. Gabor[‡] and Christopher K. Ober*

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

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A synthetic approach for preparing block copolymers consisting of both a [3-(methacryloxy)propyl]pentamethyldisiloxane (SiMA) block and *tert*-butyl methacrylate (*t*-BMA) block using group-transfer polymerization (GTP) was developed. The SiMA polymerizes slowly with oxyanion catalysis but at reasonable rates using bifluoride catalysis. A model reaction eliminated a possible explanation for the slow rate of polymerization of SiMA with oxyanion catalyzed GTP. For high conversion of *t*-BMA to be achieved, additional bifluoride catalyst had to be added to the reactor after the *t*-BMA addition. Often, especially at −44 °C, after the polymerization stalled, additional conversion of the *t*-BMA did not occur until a critical concentration of bifluoride catalyst was established. After this level was reached, the polymerization of *t*-BMA occurred quickly and to high conversion.

1. Introduction

Group-transfer polymerization (GTP) has many attributes which make it excellent for preparing acrylic polymers of controlled architecture, including the ability to control the molecular weight of the chain simply through the ratio of monomer to initiator.[1] However, polymers prepared by GTP do not always have the composition, molecular weight, and polydispersity the polymer chemist was trying to impart to the macromolecules. Determination of the conditions that lead to both complete conversion of monomer and to low polydispersity of the resulting polymer chains need to be found for each specific acrylic or methacrylic monomer.

In this study, the GTP of both [3-(methacryloxy)propyl]pentamethyldisiloxane (SiMA) and *tert*-butyl methacrylate (*t*-BMA) were investigated. GTP requires a catalyst of which oxyanion and bifluoride are the most common.[2] We found that with *t*-BMA and SiMA the choice of catalyst is critical. For example, while oxyanions catalyze the GTP of *t*-BMA, the GTP catalyzed by oxyanions of SiMA occurs at very slow rates. However, the slow polymerization results in low polydispersity polymers and unprecedented time periods of livingness. The GTP of SiMA was not previously reported, although Rannard et al.[3] reported low conversion when polymerizing trimethylsilyl methacrylate by GTP. We attempted to discern the reasons for their low conversion and for our slow rate using oxyanion catalysis by designing a model GTP reaction, which will be discussed in detail in this paper. Using a bifluoride catalyst, the GTP of SiMA is fast and still leads to polymers with narrow polydispersity. However, the GTP of *t*-BMA using bifluoride catalysis results in incomplete conversion of the *t*-BMA if conventional procedures for GTP are followed. The poor GTP of *t*-BMA using bifluoride catalysis was previously reported[4,5] but was puzzling and important enough in our efforts to prepare polymers and block copolymers of these two monomers to warrant further study.

The GTP of *t*-BMA was first studied by Doherty and Müller.[4] GTP requires three components: an acrylic monomer, a catalyst [tris(dimethylamino)sulfonium bifluoride (TASHF2) in Doherty and Müller's case] and an initiator. Doherty and Müller made three main observations: (1) little to no conversion of *t*-BMA resulted if it was added to a reactor that already was charged with TASHF2 and initiator no matter what the temperature of the reactor; (2) below −20 °C, *t*-BMA polymerized to high conversion if it was first mixed in the reactor with either TASHF2 or initiator followed by addition of the third component to the reactor; (3) above −20 °C, to obtain high conversion of the *t*-BMA, several additions of catalyst were needed no matter how the three components were initially added to the reactor. This last observation was confirmed by all other groups who attempted to complete the conversion of *t*-BMA in this manner.[3,5] The low conversion of *t*-BMA using GTP was also reported using oxyanion catalysis.[6] Our own GTP of *t*-BMA do not confirm all of the previous results, and the differences will be discussed in detail in the Results and Discussion.

In this paper, we also report on the synthesis of block copolymers and random copolymers of SiMA and *t*-BMA.

[‡] Current address: Olin Microelectronic Materials, 200 Massasoit Avenue, East Providence, RI 02914-2009.

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Most of these were prepared in pairs of block and random copolymers. Thus, each copolymer has a partner that has approximately the same monomer composition and molecular weight but differs in the placement of the monomeric units along the chain (we refer to these pairs as corresponding copolymers).

The copolymers are designed to be microlithographic resists, capable of being imaged with 193 nm wavelength exposure tools. New polymers need to be developed for 193 nm wavelength resists since conventional aromatic-based photoresists have high absorption at 193 nm wavelength (the resist should not absorb so strongly that the effective dose varies greatly as a function of depth in a resist film).[7,8] A first generation of 193 nm wavelength imagable polymers developed by IBM and MIT Lincoln Laboratory was based on methacrylate type polymers, which have low absorption at 193 nm wavelength. These resists, which use acid-catalyzed deprotection of a *tert*-butyl-protected methacrylic acid component to yield an aqueous base-soluble copolymer, have many of the required properties but lack the reactive ion etch (RIE) resistance necessary for modern semiconductor manufacturing.[9,10] The *t*-BMA and SiMA copolymers we prepared have substantial oxygen RIE resistance while still having low absorption at 193 nm wavelength. The advantages of using block copolymer resists compared to more conventional random copolymer resists were recently reviewed,[11] and the specific lithographic properties of the polymers described in the rest of this paper were reported in detail in reference 12.

2. Experimental Section

2.1. Materials. Methyl methacrylate (MMA), methyl trimethylsilyl dimethylketene acetal (MTSDA), 3-chlorobenzoic acid, tetrabutylammonium hydroxide, CaH_2, $CuCl_2$, and hexamethyldisiloxane were obtained from Aldrich, *t*-BMA was from Scientific Polymer Products, and SiMA was from both Hüls America and Monomer-Polymer Dajac Laboratories. Tris(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF) was obtained from PCR and used as received. The THF, used in the GTP, was reagent grade and was distilled from Na and benzophenone under argon. The acetonitrile was reagent grade and was distilled from phosphorus pentoxide under argon. The MMA and hexamethyldisiloxane were purified by drying over CaH_2 followed by distillation at atmospheric pressure. The *t*-BMA and SiMA were purified by drying over CaH_2,[13] using $CuCl_2$ as an inhibitor,[14] followed by distillation at reduced pressure. MTSDA was purified by distillation at reduced pressure.

2.2. Techniques and Characterization. As GTP reactions are sensitive to water, the polymerizations were done under argon in dry glassware using cannula and syringe techniques and a double-manifold inert-atmosphere system.[15] Unless otherwise indicated, all polymerizations were done at ambient temperature. A Hewlett-Packard 5890A gas chromatograph (GC) was used to monitor the disappearance of monomer for some of the GTPs. Solutions of known concentrations were used to calibrate the GC for both *t*-BMA and SiMA in THF. NMR spectra were obtained using either a Varian XL-200 (200 MHz) or a Varian VNMR-S (400 MHz) NMR spectrometer; unless stated otherwise the solvent was $CDCl_3$. We have measured the T_1 values of protons similar to those of the methyl groups attached to the Si atoms of SiMA and found that they are greater than 2 s.[16] When taking the ^1H NMR spectra of polymers containing SiMA, a delay time of 15 s was used between pulses to obtain proper integration. Number-average molecular weight (M_n) and polydispersity (M_w/M_n) were found by GPC (THF) using PMMA standards, a Waters Associates 510 pump, a 410 refractive index detector and 4.6 × 300 mm Styragel HT3, HT4, HT5, and HT6E columns. A Seiko Instruments TTS220 differential scanning calorimeter was used to measure the glass transition temperatures (T_g's) of the polymers. For P(SiMA) and the block copolymers, the temperature cycle started at -110 °C and increased at 10 °C/min to 160 °C. For P(*t*-BMA) and the random copolymers, the temperature cycle started at 0 °C and increased at 10 °C/min to 160 °C. Each sample was run twice. The T_g's reported were determined using the second run for each sample.

2.3. Preparation of Catalysts. Using the purchased TASF, TASHF2 was prepared and recrystallized as described by Sogah et al.[17] ^1H NMR (CD_3CN, 200 MHz, -30 °C) δ 2.81 (s, 18 H, CH_3N), δ 16.34 (t, $J_{HF} = 121.3$ Hz, 1 H, FHF). (Note: The δ value of $+16.34$ ppm for the proton of the bifluoride differs in sign from the value that Sogah et al.[17] reported due to a typing error in their paper. The literature is confusing as Fujiwara and Martin have measured shieldings of -15.8 to -16.8 ppm for the proton of bifluoride, but shieldings increase in sign opposite to the δ scale.[18]) Tetrabutylammonium bis(3-chlorobenzoate) and tetrabutylammonium 3-chlorobenzoate were prepared as described by Dicker et al.[19] Solutions (0.4 M) of all catalysts were prepared in acetonitrile.

2.4. Polymerizations. Numerous polymerizations were done, varying conditions to learn how to improve the rate of polymerization and polydispersity as well as achieve polymers near their theoretical molecular weight based on the ratio of monomer to initiator added to a reactor. Seven polymerization procedures are described below in detail to illustrate some of the different conditions investigated. Shorter descriptions of the synthetic schemes used to prepare the remaining polymers are given in the supporting information for this paper.

2.4.1. Homopolymerization of SiMA with Oxyanion Catalysis [P(SiMA)I]. A 100 mL, three-necked round-bottom flask, with a stir bar, attached to a THF still was fitted with a thermometer and septum. After distilling 20 mL of THF into the reactor, 0.122 mL (0.6 mmol) of MTSDA was added. After 5 min, 0.025 mL of the tetrabutylammonium 3-chlorobenzoate (0.010 mmol) solution was added to the stirred solution. After 5 min, 6.6 mL (21.9 mmol) of SiMA was added, at a rate of 1.3 mL/min using a syringe. No increase in temperature was observed. Samples (~2 mL) were taken and quenched with methanol at 5, 23, 53, 71, 107, and 119 h. GPC (PMMA): M_n (5 h) 2160 g/mol, M_w/M_n 1.14; M_n(23 h) 4640 g/mol, M_w/M_n 1.08; M_n(53 h) 8390 g/mol, M_w/M_n 1.08; M_n(71 h) 9640 g/mol, M_w/M_n 1.07; M_n (107 h) 10 840 g/mol, M_w/M_n 1.07; M_n(119 h) 10 840 g/mol, M_w/M_n 1.08. The theoretical M_n is 10 120 g/mol.

2.4.2. Block Copolymerization of t-BMA and SiMA with Oxyanion Catalysis [P(t-BMA-b-SiMA)I]. A 100 mL, three-necked round-bottom flask, with a stir bar, attached to a THF

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still was fitted with a thermometer and septum. After distilling 15 mL of THF into the reactor, 0.122 mL (0.6 mmol) of MTSDA was added. After 5 min 0.030 mL of the tetrabutylammonium 3-chlorobenzoate (0.012 mmol) solution was added to the stirred solution. After 7 min, 6.9 mL (42.4 mmol) of *t*-BMA was added, at a rate of 2 mL/min using a syringe. After the start of the *t*-BMA addition, the temperature increased 9.2 °C, to 34.4 °C, during a time period of 9 min. Samples (~1 mL) were taken and quenched with methanol at 5, 18, and 26 h. Twenty-six hours after the temperature started to decline, 3.6 mL (11.9 mmol) of SiMA was added within 1 min. No increase in temperature was observed. Samples (~1 mL) were taken and quenched with methanol at 28, 66, 124, and 141 h after adding the SiMA. 189 h after the addition of the *t*-BMA, the polymerization was quenched with 2 mL (49.5 mmol) of methanol. Stirring was continued for 2 days, and then the polymer was precipitated by pouring the solution into a mixture of 80 mL of water and 120 mL of methanol. The polymer was recovered by filtration, dissolved in 20 mL of THF, reprecipitated in a mixture of 80 of mL water and 120 mL of methanol, and then dried in vacuo at ambient temperature, giving a white powder. GPC: P(*t*-BMA) samples: M_n(5 h) 8780 g/mol, M_w/M_n 1.47, M_n(18 h) 8990 g/mol, M_w/M_n 1.47, M_n(26 h) 8850 g/mol, M_w/M_n 1.49. The theoretical M_n for the P(*t*-BMA) block is 10 035 g/mol. P(*t*-BMA-*b*-SiMA) samples: M_n(26 + 28 h) 10 780 g/mol, M_w/M_n 1.38, M_n(26 + 66 h) 12 020 g/mol, M_w/M_n 1.36, M_n(26 + 124 h) 13 140 g/mol, M_w/M_n 1.31, M_n(26 + 148 h) 13 140 g/mol, M_w/M_n 1.31.

2.4.3. Model GTP Reaction of MMA with Hexamethyldisiloxane. A 100 mL, three-necked round-bottom flask, with a stir bar, attached to a THF still was fitted with a thermometer and septum. After distillation of 15 mL of THF into the reactor, 9.7 mL (45.6 mmol) of hexamethyldisiloxane and 0.20 mL (1.0 mmol) of MTSDA were added. After 10 min, 0.05 mL of the tetrabutylammonium bis(3-chlorobenzoate) (0.02 mmol) solution was added to the reactor. After 3 min, 5 mL (46.7 mmol) of MMA was added, at a rate of 1 mL/min using a syringe. After the start of the MMA addition, the temperature increased from 26.2 to 46.2 °C, during 20 min. One hour after the temperature started to decline, a 2 mL sample of the reaction mixture was quenched and precipitated in a mixture of methanol and hexanes. Then, a second 5 mL (46.7 mmol) aliquot of MMA was added, at a rate of 1 mL/min using a syringe. After the start of the second MMA addition the temperature increased from 25.2 to 45.5 °C, during 18 min. During this growth, the polymer, due to its higher molecular weight, precipitated out of the THF−hexamethyldisiloxane mixture. 1.5 h after the temperature started to decline, the polymerization was quenched with 2 mL (49.5 mmol) of methanol. The mixture was stirred for 3.5 h and was then poured into 400 mL of *n*-hexane. The polymer was recovered by filtration, dissolved in 40 mL of THF and precipitated in 450 mL of *n*-hexane. The polymer was dried in vacuo at ambient temperature, giving a white powder. GPC: Sample 1: M_n 5100 g/mol (theory 4778 g/mol), M_w/M_n 1.15. Sample 2: M_n 10 260 g/mol, M_w/M_n 1.11.

2.4.4. Homopolymerization of SiMA with TASHF2 Catalysis [P(SiMA)II]. A 75 mL, three-necked round-bottom flask with a stir bar was fitted with a thermometer, septum, and an addition funnel. The top of the addition funnel had a septum port and a joint used to attach it to a THF still. After distillation of 16 mL of THF into the reactor, 0.122 mL (0.6 mmol) of MTSDA was added. After 10 min, 0.010 mL (4 μmol) of the TASHF2 solution was added to the reactor. After 7 min, 6.6 mL (21.9 mmol) of SiMA was transferred into the addition funnel and then dripped into the round-bottom flask at a rate of 0.5 mL/min. The temperature increased steadily from 22.2 to 34.7 °C during the addition of the SiMA. After the SiMA addition was complete, the temperature slowly cooled to ambient temperature during the next hour. Eight minutes after the addition of SiMA was complete, 0.5 mL of the solution was removed, and a portion was analyzed by GC which showed that 98% of the SiMA was converted. One hour after the addition of the SiMA was complete, 1 mL (25 mmol) of methanol was added to quench the polymerization. After stirring overnight, the polymer was precipitated by pouring the solution into 200 mL of methanol. The precipitates were allowed to settle for 30 min and were collected after decanting off the methanol-based solution. The sticky white polymer was then washed with two 100 mL aliquots of methanol. The polymer was dried in vacuo at ambient temperature to constant weight.

2.4.5. Block Copolymerization of SiMA and t-BMA [P(t-BMA-b-SiMA)II] (No Additional TASHF2 Added during t-BMA Polymerization at -25 °C). A 100 mL, three-necked round-bottom flask, with a stir bar was fitted with a thermometer, septum, and an addition funnel. The top of the addition funnel had a septum port and a joint used to attach it to a THF still. After distillation of 15 mL of THF into the reactor, 0.122 mL (0.6 mmol) of MTSDA was added. After 5 min, 0.0075 mL (3 μmol) of the TASHF2 solution was added to the reactor. After 15 min, 6.6 mL (21.9 mmol) of SiMA was transferred into the addition funnel and then dripped into the round-bottom flask at a rate of 0.5 mL/min. The temperature increased from 23.8 to 26.3 °C during the addition of 6.6 mL of SiMA. Four hours after the start of the SiMA addition, 0.5 mL of the solution was removed and was precipitated into methanol. At 4.5 h after the start of the SiMA addition, an additional 0.0075 mL (3 μmol) of the TASHF2 solution was added to the reactor and the temperature increased 2 °C in the next 10 min. No increase in temperature was observed after an additional 0.0075 mL (3 μmol) of the TASHF2 solution was added 7.5 h after the start of the SiMA addition. A 0.5 mL aliquot of the solution was removed and precipitated into methanol. The reaction vessel was then cooled to -25 °C.[4] Using a syringe, 6.9 mL (42.4 mmol) of *t*-BMA was added to the addition funnel followed by the distillation into the addition funnel of 14 mL of THF. The solution of *t*-BMA and THF was then dripped into the reaction vessel at a rate of 1.5 mL/min. After stirring overnight, the polymerization was quenched with 1 mL (25 mmol) of methanol. Stirring was continued for 3 days, and then the polymer was precipitated by pouring the solution into 400 mL of methanol. The precipitates were allowed to settle for 1 h and were collected after decanting off the methanol-based solution. The white polymer was dissolved in 40 mL of THF, reprecipitated in 400 mL of methanol, and then collected and dried in vacuo at ambient temperature. GPC: P(SiMA) samples: M_n(4 h) 6196 g/mol, M_w/M_n 1.06, M_n(7.5 h) 8010 g/mol, M_w/M_n 1.06. The theoretical M_n, for the P(SiMA) block is 10 120 g/mol.

2.4.6. Block Copolymerization of SiMA and t-BMA [P(t-BMA-b-SiMA)III] (Done at Ambient Temperature with Additional TASHF2 Added during GTP of t-BMA). A 100 mL, three-necked round-bottom flask with a stir bar was fitted with a thermometer, septum, and an addition funnel. The top of the addition funnel had a septum port and a joint used to attach it to a THF still. After distillation of 20 mL of THF into the reactor, 0.163 mL (0.8 mmol) of MTSDA was added. After 5 min, 0.015 mL (6 μmol) of the TASHF2 solution was added to the stirred solution. After 8 min, 8.8 mL (29.1 mmol) of SiMA was placed in the addition funnel and then dripped into the round-bottom flask at a rate of 0.5 mL/min. The temperature increased steadily from 21.3 to 33.9 °C during the addition of the 8.8 mL of SiMA. During the 30 min after the SiMA addition was completed, the temperature cooled to ambient temperature after which 0.5 mL of the solution was removed, and a portion was analyzed by GC which showed that 99% of the SiMA was converted. Using a syringe, 9.15 mL (56.3 mmol) of *t*-BMA was added to the addition funnel followed by the distillation into the addition funnel of 22 mL of THF. After adding 0.015 mL (6 μmol) of the TASHF2 solution to the reaction mixture, 8 mL of the *t*-BMA and THF solution was then dripped into the reaction vessel over the next 4 min, during which the temperature increased 0.2 °C. An additional 0.075 mL (30 μmol) of the TASHF2 solution was added to the reactor, and the temperature went up 1 °C. The remaining of the *t*-BMA and THF solution was added to the reactor over the next 15 min, during which time the temperature increased an additional 3.5 °C. The temperature continued to increase until 6 min after the end of the *t*-BMA addition when the temperature peaked at 5.3 °C above ambient temperature. One and a quarter hours after the end

Table 1. Response in the Temperature of the Reactor and Conversion of *t*-BMA to Additional TASHF2 during the GTP of P(*t*-BMA-*b*-SiMA)III

time additional TASHF2 added (h)	increase in temp of reactor (°C)	conversion (GC) of *t*-BMA (%)[a]
17	1.7	76
17.5	0.7	96
21	0.7	98

[a] For GC analysis, a 0.5 mL sample was removed, from the reactor.

of the *t*-BMA addition a sample (0.5 mL) was removed, and a portion analyzed by GC which showed that 51% of the *t*-BMA was converted. Sixteen hours after the end of the *t*-BMA addition a sample (0.5 mL) was removed, and a portion run through the GC. Analysis of the GC spectrum showed that 76% of the *t*-BMA was converted. Seventeen hours after the end of the *t*-BMA addition, the reactor was cooled to 1 °C. During the next 4 h, three 50 μL (20 μmol) aliquots of the TASHF2 solution were added as shown in Table 1. After the last addition of TASHF2, the polymerization was quenched with 2 mL (50 mmol) of methanol. Stirring was continued for 4 h, and then the polymer was precipitated by pouring the solution into a mixture of 600 mL of methanol and 200 mL of water. The white polymer was recovered by filtration, dissolved in 45 mL of THF, reprecipitated in a mixture of 600 mL of methanol and 200 mL of water, and then dried in vacuo at ambient temperature.

2.4.7. Random Copolymerization of SiMA and t-BMA [P(t-BMA-ran-SiMA)I] (at −44 °C with Additional TASHF2 Added during GTP). A 100 mL, three-necked round-bottom flask with a stir bar was fitted with a thermometer, septum, and an addition funnel. The top of the addition funnel had a septum port and joint used to attach it to a THF still. After distillation of 20 mL of THF into the reactor, 0.124 mL (0.61 mmol) of MTSDA was added. After 3 min, 0.050 mL (20 μmol) of the TASHF2 solution was added to the stirred solution. The reactor was then cooled to −44 °C. After the reactor had reached −44 °C, 1.8 mL (6.0 mmol) of SiMA and 7.0 mL (43 mmol) of *t*-BMA were placed in the addition funnel and then dripped into the round-bottom flask at a rate of 0.5 mL/min. Five minutes after the end of the monomer addition a sample (0.25 mL) was removed, and a portion analyzed by GC which indicated that 26% of the *t*-BMA and 8% of the SiMA were converted. Ten minutes after the end of the *t*-BMA addition, 75 μL (30 μmol) of the TASHF2 solution was added during a 10 min period. The temperature of the reactor did not change until the last 10 μL of the catalyst was added during which it shot up 35 °C to −10 °C. The reactor was allowed to warm to ambient temperature. The polymerization was quenched with 1 mL (25 mmol) of methanol. A portion of the solution was analyzed by GC which indicated that 98% of the *t*-BMA and 100% of the SiMA were converted. Stirring was continued overnight, and then the polymer was precipitated by pouring the solution into a mixture of 325 mL of methanol and 75 mL of water. The polymer was recovered by filtration, dissolved in 20 mL of THF, reprecipitated in a mixture of 325 mL of methanol and 75 mL of water, and then was dried in vacuo at ambient temperature, giving a white powder.

3. Results and Discussion

3.1. Homopolymerizations of SiMA Catalyzed by Oxyanions. One of the hallmarks of GTP is an exothermic reaction occurring when all three components (monomer, catalyst, and initiator) are added to a reactor. However, with SiMA and oxyanion catalysts, such as tetrabutylammonium bis(3-chlorobenzoate) or tetrabutylammonium 3-chlorobenzoate, an increase in temperature was never observed. This observation led us initially to incorrectly conclude that the polymerization was not occurring. Later we realized that polymerization was taking place, but at a slow rate. GTP catalyzed by oxyanions can polymerize bulky silicon-containing methacrylates to high conversion if the polymerization time is extended significantly from that considered “normal” for GTP.

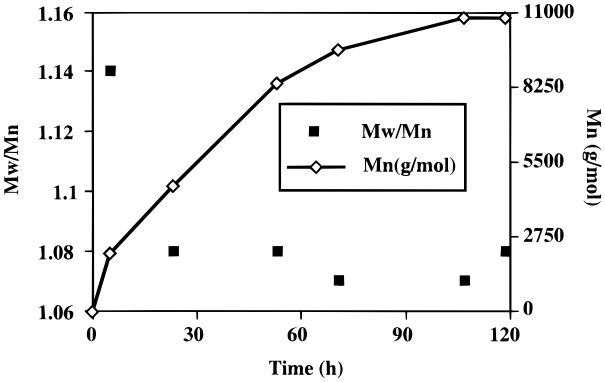

Figure 1. M_w/M_n and M_n vs time for the homopolymerization of SiMA using oxyanion catalyzed GTP [P(SiMA)I, section 2.4.1].

Although the polymerization is slow, the time period that the GTP of SiMA stays living when catalyzed by oxyanions is longer than that usually observed for GTP. Over the period of 120 h, the polymer continued to increase in molecular weight until plateauing near the theoretical molecular weight of 10 120 g/mol (shown in Figure 1 for the polymerization P(SiMA)I and described in section 2.4.1). This time period compares to the typical 1 h polymerization time needed to grow a PMMA chain to 5000 g/mol, with oxyanion catalyzed GTP.[19] The 120 h that P(SiMA)I and the 160 h that P(*t*-BMA-*b*-SiMA)I (section 2.4.2) continued to convert monomer are longer time periods of livingness for GTP than any previously reported. Prior to our work, Dicker et al. reported one of the longer living GTP, where they added MMA onto a growing chain 18 h after the initial monomer addition.[19]

For P(SiMA)I, after the unreacted monomer was separated from the polymer chains by the GPC, the polydispersity of the polymer stayed less than 1.08 for the duration of the polymerization. Also, as described in the synthesis of P(*t*-BMA-*b*-SiMA)I [section 2.4.2], SiMA polymerized slowly but without increasing the polydispersity of the polymer when it was added to a reactor after a block of P(*t*-BMA) was first grown. These results demonstrate that high conversion of these types of silicon-containing methacrylates can be achieved by extending the reaction time from that typically used for GTP catalyzed by oxyanions.

3.2. Model Polymerization. Although previous papers have not reported on the GTP of SiMA, Ranard et al. reported that trimethylsilyl methacrylate could be polymerized only to low conversion using GTP. They suggested that this was due to a competition for the catalyst between the $-OSiMe_3$ of the living end groups of the polymer chains and the $-OSiMe_3$ of the trimethylsilyl methacrylate monomers. The monomers, they proposed, effectively swamp out the catalyst since the number of monomer units is substantially larger than the number of chain ends. However, the presence of impurities or steric hindrance might also play a role in the low degree of polymerization, Rannard et al. ob-

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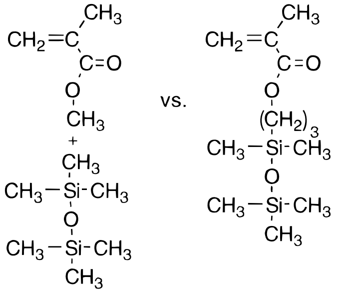

Figure 2. MMA and hexamethyldisiloxane vs SiMA.

Table 2. Yield of Polymers Prepared during This Study

polymer	yield (g)	theoretical yield (g)	% yield adjusted for sampling
P(SiMA)II	4.73	6.01	83
P(SiMA)III	5.15	6.01	88
P(MMA) model polym	9.62[a]	9.36	a
P(*t*-BMA)I	6.16	8.00	85
P(*t*-BMA)II	6.47	8.00	94
P(*t*-BMA)III	5.17	6.50	92
P(*t*-BMA)IV	5.48	7.19	88
P(*t*-BMA-*b*-SiMA)I	6.80	9.30	100
P(*t*-BMA-*b*-SiMA)II	5.20	12.03	45
P(*t*-BMA-*b*-SiMA)IV	14.25	15.98	95
P(*t*-BMA-*b*-SiMA)III	14.38	16.00	95
P(*t*-BMA-*b*-SiMA)V	13.96	16.03	91
P(*t*-BMA-*ran*-SiMA)II	7.45	8.00	96
P(*t*-BMA-*ran*-SiMA)I	7.26	7.75	95

[a] ^{13}C NMR revealed that there was hexamethyldisiloxane impurity present, thus leading to an inaccurate measurement of yield.

Table 3. Number Average Molecular Weight (M_n) and Polydispersity (M_w/M_n) of the P(SiMA) and PMMA Samples Synthesized during This Study Measured by GPC Relative to PMMA Standards

polymer	M_n (g/mol) theory[a]	M_n (g/mol) GPC	M_w/M_n (GPC)
P(SiMA)I	10 120	10 840	1.08
P(SiMA)II	10 120	8 160	1.05
P(SiMA)III	10 120	8 960	1.07
P(MMA) model polym	9 790	10 260	1.11

[a] The "theory" M_n is predicted from the ratio of monomer to initiator added to the reactor. It has been adjusted to take into account the effect of sampling for polymerizations where more than one addition of monomer to the reactor was made.

served for trimethylsilyl methacrylate and the slow rate of polymerization we observed for SiMA. A model polymerization was carried out to elucidate the cause for the slow rate of polymerization of SiMA using oxyanion-catalyzed GTP (section 2.4.3). With a methacrylate containing $-OSiMe_3$ groups it is not possible to separate the effect of the $-OSiMe_3$ group from that of steric hindrance or other possible causes. Therefore, we added an unpolymerizable molecule containing $-OSiMe_3$ groups to the GTP of methyl methacrylate (MMA) to help distinguish between the various effects. Specifically compared were the polymerizations of three different systems: (1) MMA in the presence of hexamethyldisiloxane; (2) MMA in the absence of hexamethyldisiloxane; (3) SiMA. These polymerizations were compared since the silicon atoms of hexamethyldisiloxane are chemically similar to the silicon atoms of SiMA, as shown in Figure 2. If there were differences in the rates of polymerization between MMA alone and MMA with hexamethyldisiloxane they could be attributed to the presence of $-OSiMe_3$ groups. Unlike the GTP of silicon-containing methacrylates, the GTP of MMA is well studied.[17,19] Also, unlike trimethylsilyl methacrylate which can be difficult to handle without some decomposition to methacrylic acid, MMA is easily purified and relatively easy to handle.[13] However, the silicon atoms of trimethylsilyl methacrylate and of hexamethyldisiloxane are chemically different. Thus, while comparison between the GTP of MMA and the GTP of SiMA is possible, a close comparison to the observations of Rannard et al.[3] on the GTP of trimethylsilyl methacrylate is not possible.

The results of the model polymerization demonstrate that the presence of $-OSiMe_3$ groups does not always hinder GTP, even when the molar ratio of methacrylate monomer to $-OSiMe_3$ group is 1:1. The time between the first addition of monomer and the time the maximum temperature is reached, Δt_{max}, is a reproducible measurement which gives an indication of the rate of a GTP reaction. Smaller Δt_{max} values indicate faster rates of polymerization while larger Δt_{max} values indicate slower rates.[19] The Δt_{max} value of 20 min for the first growth of MMA with hexamethyldisiloxane matches the Δt_{max} of 21 ± 2.1 min for the polymerization of MMA without hexamethyldisiloxane reported by Dicker et al.[19] Thus, the kinetics of the GTP of MMA catalyzed by oxyanions both with and without hexamethyldisiloxane are similar. The conversions, as inferred by both GPC and yield, indicate that the MMA was converted to PMMA within 1 h after the first increase in temperature and within 1.5 h after the second increase in temperature. These times are similar to those reported in the literature for the GTP of MMA without hexamethyldisiloxane.[19] Thus, our findings show that GTP can polymerize methacrylates to high conversion at normal rates in the presence of $-OSiMe_3$ groups.

We currently do not conclusively understand why the GTP of SiMA catalyzed by oxyanions is slow. The rate was slow even when the more active oxyanion catalyst tetrabutylammonium 3-chlorobenzoate was used [compared to the less active catalyst tetrabutylammonium bis(3-chlorobenzoate) used in the model polymerization[19]]. The model GTP reaction, using MMA and hexamethyldisiloxane, demonstrates that the slow rate is not simply caused by the presence of $-OSiMe_3$ groups. In the literature, it is unclear the effect that other bulky ester groups have on the rate of polymerization of methacrylates. However, reduced catalyst efficiency caused by steric hindrance of the living chain end, by the long and flexible propylpentamethyldisiloxane ester group, seems a likely explanation for the behavior observed with SiMA.

3.3. Homopolymerizations of SiMA Catalyzed by Bifluorides. The slow rate of polymerization of SiMA using oxyanion catalysis was in contrast to the fast polymerization using bifluoride catalysis. For example, the homopolymerization of SiMA to 8110 g/mol in 1 h [P(SiMA)II, section 2.4.4] was at least 50 times faster than that obtained using tetrabutylammonium 3-chlorobenzoate. This increase in the rate of polymerization was expected as Webster et al. reported that the bifluoride catalysts are about 100 times more active than the tetrabutylammonium carboxylates.[2] Using TASHF2, the molecular weights were almost always near the theoretical value, and the polydispersities were always lower than 1.10. Table 3 shows the molecular weight predicted by theory and the molecular weight

Table 4. Number-Average Molecular Weight (M_n) and Polydispersity (M_w/M_n) of the P(*t*-BMA) Synthesized during This Study Measured by GPC Relative to PMMA Standards

polymer	M_n (g/mol) theory[a] M_n	GPC	M_w/M_n (GPC)
P(*t*-BMA)I	20 000	13 800	2.02
P(*t*-BMA)II	20 000	18 110	1.20
P(*t*-BMA)III	20 000	19 690	1.99
P(*t*-BMA)IV	10 000	12 600	1.57

[a] The "theory" M_n is predicted from the ratio of monomer to initiator added to the reactor.

measured by GPC as well as the polydispersity for the P(SiMA) samples prepared for this study (the PMMA model polymerization results are also included). The few times that the molecular weight of P(SiMA) was not near its theoretical value it was low, indicating incomplete conversion of the SiMA added to the reactor. When the initial conversion of the SiMA was incomplete, it could be increased, without increasing the polydispersity of the polymer by adding additional catalyst as described for the synthesis of P(*t*-BMA-*b*-SiMA)II [section 2.4.5].

3.4. GTP of *t*-BMA. With *t*-BMA, the GTP reaction always became deactivated using TASHF2. The low yield of the block copolymer prepared when no additional TASHF2 was added during the *t*-BMA polymerization, and the weight ratio (NMR) of SiMA to *t*-BMA skewed from theoretical, both indicate that there was incomplete conversion of the *t*-BMA added to the reactor during the polymerization of P(*t*-BMA-*b*-SiMA)-II [section 2.4.4]. Also, during the homopolymerizations of *t*-BMA, the highest initial conversion of *t*-BMA was 67%. By initial conversion we mean the amount of *t*-BMA converted without adding more catalyst after the start of the *t*-BMA addition. The time allowed before adding additional catalyst varied depending on whether GC analysis of the samples removed from the reactor indicated the reaction was proceeding. The conversion generally continued to gradually increase for about 20 h after which it plateaued, when the reactor was at ambient temperature. At lower temperatures, the plateauing occurred more quickly, usually within 5 h.

Why does the polymerization stop without converting all of the *t*-BMA? One possibility, which can be discounted, is that the chain ends are dead. A majority of the chain ends are still living as demonstrated by the additional *t*-BMA converted by injecting additional catalyst into the reactor [as described in refs 3−5 and for the synthesis of P(*t*-BMA-*b*-SiMA)III [section 2.4.6] and P(*t*-BMA-ran-SiMA)I [section 2.4.7]]. Thus, deactivation of the catalyst seems to be the likely reason for the incomplete conversion of *t*-BMA. Table 4 shows the molecular weight predicted by theory and the molecular weight measured by GPC as well as the polydispersity for the P(*t*-BMA) samples prepared for this study.

As mentioned in the Introduction, observations of the problematic nature of the GTP of *t*-BMA were made by previous researchers.[3−6] While clearly there are difficulties with the GTP of *t*-BMA using bifluoride catalysis, we were not able to confirm all of the previous results of other researchers. Our results indicate that the GTP of *t*-BMA is even more complicated than previously thought. Of all the prior research, we found the paper by Doherty and Müller[4] to be the most detailed and helpful. However, we did have slightly different observations which lead us to different conclusions. For example, Doherty and Müller proposed that a side reaction between a stoichiometric amount of catalyst and silyl ketene acetal end groups of the polymer chains was the cause of the deactivation of the catalyst above −20 °C and that this reaction did not occur below −20 °C. Two of our observations do not corroborate their proposal: (1) The amount of catalyst necessary to achieve high conversion of the *t*-BMA is larger than is considered normal for GTP even when the polymerizations were done at −44 °C (for example, P(*t*-BMA-*ran*-SiMA)I [section 2.4.7]). For all the temperatures investigated, to obtain a final conversion of the *t*-BMA greater than 90%, 8−12.4 mol % of TASHF2 relative to MTSDA needed to be added to the reactor compared to the 0.1−1 mol % normally used for GTP;[2] (2) For many of the GTPs, the conversion was not observed to increase further (for most of the polymers, initially there was a finite amount of conversion), until a threshold value of catalyst was added after which the conversion of *t*-BMA shot up within a minute to greater than 90%. Such behavior was always observed at −44 °C but was more erratic at higher temperatures. The first observation indicates that even below −20 °C there are side reactions, which deactivate the TASHF2. The second observation cannot be explained by a stoichiometric reaction of TASHF2 with the silyl ketene acetal chain ends as such a reaction would not stop until enough catalyst was added to react with all the chain ends (the most TASHF2 we added was 12.4 mol % relative to the initiator). A more likely side reaction might be due to an impurity (which is difficult to remove from *t*-BMA) reacting with the TASHF2.[20] In this scenario, after enough TASHF2 is added to effectively remove any impurities, the next aliquot of TASHF2 then catalyzes the GTP of *t*-BMA to high conversion.

The observation of Doherty and Müller[4] that little to no conversion of the *t*-BMA resulted if it was added to a reactor that was already charged with the TASHF2 and initiator was also not confirmed by us. However, the initial conversions of *t*-BMA we observed varied widely (0−82%), and there did seem to be a greater tendency for no initial conversion to occur when the *t*-BMA was added in such a manner (three out of seven polymerizations). Two of the three GTPs that did not initially polymerize the *t*-BMA were at ambient temperature and the third was done at −44 °C. At ambient temperature the lack of conversion was apparent by the absence of an observable increase in temperature after the addition of *t*-BMA to the reactor was started. In these two cases the polymerizations were started by temporarily stopping the *t*-BMA addition and injecting TASHF2 into the reactor through a septum port until an increase in temperature was observed and then resuming the addition of *t*-BMA. This method is described in detail for P(*t*-BMA-*b*-SiMA)III [section 2.4.5]. For three of the *t*-BMA homopolymerizations (P(*t*-BMA)II−IV) a small amount (0.5% relative to the initiator) of TASHF2 was added to the *t*-BMA in the addition funnel and then this mixture was added to the reactor containing both MTSDA and TASHF2. During these polymerizations there was always initial conver-

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(20) Sogah, D. Y. Personal Communication.

(21) Gabor, A. H. Ph.D. Thesis, Cornell University, 1996.

sion of the *t*-BMA, which ranged from 21 to 67%. Thus, four out of seven GTPs without a cofeed of TASHF2 had initial conversion and three out of three GTPs with a cofeed of TASHF2 had initial conversion.

Regardless of how the TASHF2 was initially added to the reactor, there was never complete conversion of the *t*-BMA unless additional TASHF2 was added. Initial *t*-BMA conversions as high as 82% were observed. Many factors were investigated to try to determine what conditions lead to the highest initial conversion of the *t*-BMA. These conditions included the reactor temperature and the initial concentration of TASHF2 relative to both *t*-BMA or MTSDA, but no trends were found with these variables if all the polymerizations were used. However, if the three polymerizations which initially had no conversion were not considered, then there was a correlation between the initial conversion and the reactor temperature. The correlation indicates that the higher the reactor temperature the larger the initial conversion of *t*-BMA. This result, along with the finding that the polymerizations tend to stay active longer at ambient temperature than at lower temperatures is not currently well understood and will be the subject of future investigations.

The question remains, How best can *t*-BMA be polymerized using GTP? The answer largely depends on what polymer properties are important, as currently a method does not exist to consistently obtain low polydispersity P(*t*-BMA) of near theoretical molecular weight with GTP. If low polydispersity is critical, then it is best to not inject additional TASHF2 into the reactor after the *t*-BMA addition, e.g., P(*t*-BMA-*b*-SiMA)II [section 2.4.5]. However, to obtain polymers near theoretical molecular weight, additional catalyst should be added to the reactor until conversion is determined to be complete. Another method that shows promise is using oxyanion catalysis. For example, during the GTP of P(*t*-BMA-*b*-SiMA)I [section 2.4.2], the *t*-BMA block polymerized to within 88% of its theoretical molecular weight within 5 h. This is a much higher conversion of *t*-BMA than was reported by previous researchers using oxyanion-catalyzed GTP.[6] After the *t*-BMA block grew, a SiMA block was added without injecting additional catalyst, indicating that the oxyanion catalyst was not poisoned during the polymerization of the *t*-BMA.

3.5. Block and Random Copolymer Synthesis. A family of block and corresponding random copolymers with different monomeric ratios was prepared using GTP. As shown in Figure 3, when the GTP of *t*-BMA became deactivated during the synthesis of P(*t*-BMA-*b*-SiMA)III, IV, and V, additional catalyst was added to reactivate the polymerization. The random copolymers were synthesized using GTP by simultaneously adding *t*-BMA and SiMA. When additional TASHF2 was added for the GTPs, the block and random copolymers were polymerized to near their expected monomeric composition (to be discussed in more detail in section 3.6). Table 5 shows the molecular weights predicted based on the ratio of monomer to initiator and the molecular weights measured by GPC. When the additional TASHF2 was added to the reactor, the molecular weights were within 30% of their theoretical values. Also, with the exception of P(*t*-BMA-*b*-SiMA)II for which no additional TASHF2 was added, high yields of the copolymers were obtained as shown in Table 2.

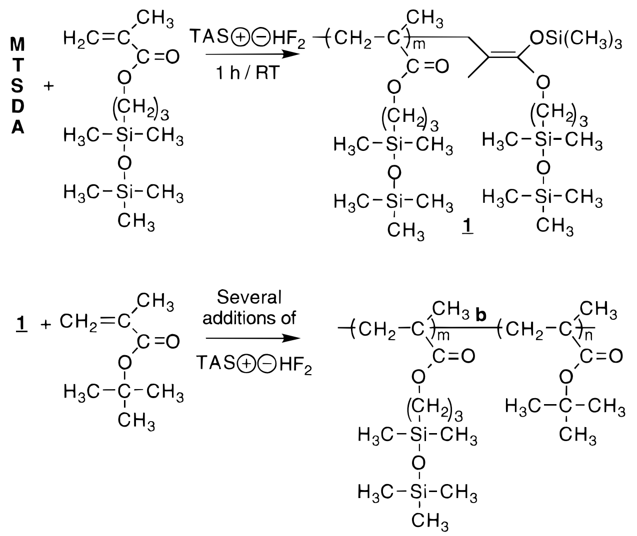

Figure 3. Synthetic scheme used to prepare P(*t*-BMA-*b*-SiMA)III, IV, and V. MTSDA is the initiator methyl trimethylsilyl dimethylketene acetal.

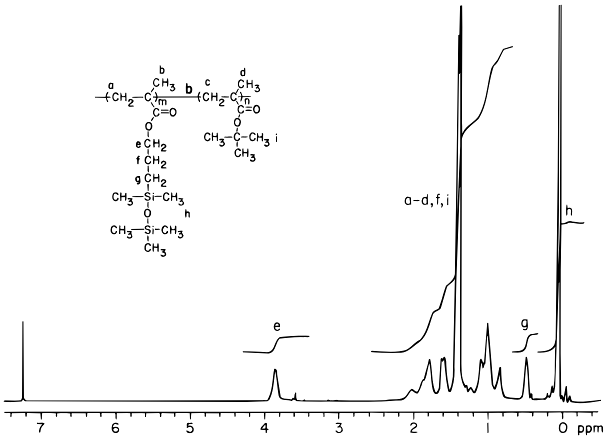

Figure 4. ^{1}H NMR spectrum of P(*t*-BMA-*b*-SiMA)III.

Table 5. Number-Average Molecular Weight (M_n) and Polydispersity (M_w/M_n) of the Block and Random Copolymers Synthesized during This Study Measured by GPC Relative to PMMA Standards

polymer	M_n (g/mol) theory[a]	 GPC	M_w/M_n (GPC)
P(*t*-BMA-*b*-SiMA)I	17 080	13 140	1.31
P(*t*-BMA-*b*-SiMA)II	20 530	14 860	1.09
P(*t*-BMA-*b*-SiMA)III	20 170	15 230	1.34
P(*t*-BMA-*b*-SiMA)IV	15 240	14 010	1.26
P(*t*-BMA-*b*-SiMA)V	13 160	10 030	1.64
P(*t*-BMA-*ran*-SiMA)I	12 700	16 560	1.63
P(*t*-BMA-*ran*-SiMA)II	20 010	21 310	1.67

[a] The "theory" M_n is predicted from the ratio of monomer to initiator added to the reactor. It was adjusted to take into account the effect of sampling for polymerizations where more than one addition of monomer to the reactor was made.

3.6. NMR Characterization of Composition and Tacticity of Polymers. The ^{1}H NMR spectrum of P(*t*-BMA-*b*-SiMA)III is shown in Figure 4. The copolymers were analyzed by ^{1}H NMR to determine the molar ratio of the two monomeric units, and these results are shown in Table 6 (how the ^{1}H NMR spectra were interpreted is detailed in the supporting information). If additional TASHF2 was added to the reactor to increase the conversion of the *t*-BMA, the composition of the copolymers was usually within 3% of theory. This is compared to P(*t*-BMA-*b*-SiMA)II which had no additional TASHF2

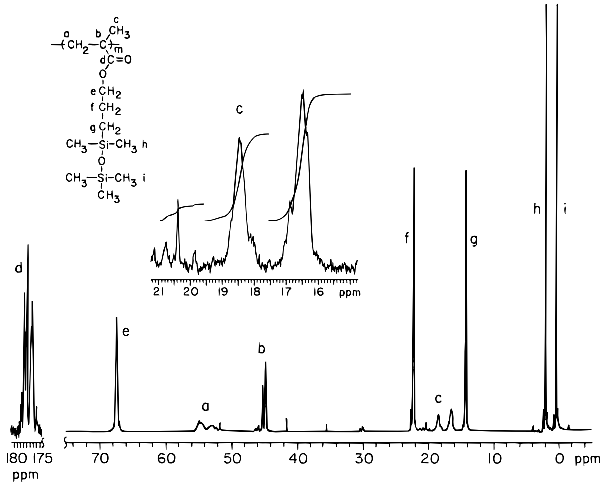

Figure 5. ^{13}C NMR spectrum of P(SiMA)II.

Table 6. Composition of Polymers Based on Analysis of NMR Spectra

polymer	*t*-BMA/SiMA theory,[a] wt ratio	*t*-BMA/SiMA NMR, wt ratio	wt % SiMA (NMR)
P(*t*-BMA-*b*-SiMA)I	1.59	1.96	33.8
P(*t*-BMA-*b*-SiMA)II	1.05	0.76	56.8
P(*t*-BMA-*b*-SiMA)III	1.01	1.05	48.8
P(*t*-BMA-*b*-SiMA)IV	2.05	1.98	33.6
P(*t*-BMA-*b*-SiMA)V	3.92	3.92	20.3
P(*t*-BMA-*ran*-SiMA)I	3.73	3.78	20.9
P(*t*-BMA-*ran*-SiMA)II	1.00	1.11	47.4

[a] The theoretical weight ratio of the block copolymers is adjusted for samples taken during the growth of the first block.

Table 7. Relative Triad Intensities (*I*) as Well as Probabilities of Meso and Racemic Placement following Each Other for the Homopolymers Prepared for This Study

polymer	I_{rr}	I_{mr}	I_{mm}	*P*(m/r)	*P*(r/m)	*P*(m/r) + *P*(r/m)
P(*t*-BMA)II	50	41	9	0.70	0.29	0.99
P(SiMA)II	54	37	9	0.67	0.26	0.93

added and deviated from the theoretical weight ratio of *t*-BMA to SiMA by 28%.

^{13}C NMR analysis was performed to determine tacticity of the homopolymers. The ^{13}C NMR spectrum of P(SiMA) is shown in Figure 5. From the integrated peaks of the carbon of the methyl group in the 15−21 ppm region, the tacticity of the polymer was determined. The rr, mr, and mm triads were assigned for both P(*t*-BMA) and P(SiMA) based on those known for PMMA.[22] As reported in Table 7, the triads are predominately syndiotactic and heterotactic which is common for polymers prepared using GTP.[17,19] The probability of a racemic placement following a meso placement of a monomer [P(m/r)] and the probability of a meso placement following a racemic placement of a monomer [P(r/m)] sum to one, within experimental error, for both homopolymers (see ref 21 for details). This indicates that the polymers follow Bernoullian probability.[17,23]

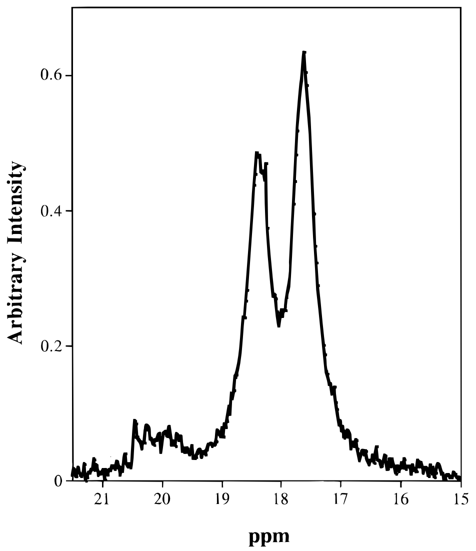

Figure 6. Methyl (CH_3) region of ^{13}C NMR spectrum of P(*t*-BMA)II.

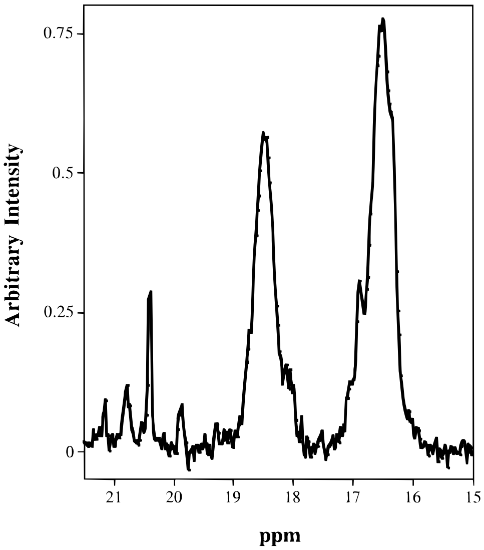

Figure 7. Methyl (CH_3) region of ^{13}C NMR spectrum of P(SiMA)II.

3.7. Confirmation of Structure of Polymers by NMR. ^{13}C NMR analysis was employed to confirm the chain structure of both the random and block copolymers (described in detail in ref 21). For the ^{13}C NMR analysis, the methyl (CH_3) regions of the NMR spectra of both P(*t*-BMA)II and P(SiMA)II were used (Figures 6 and 7, respectively). These spectra were digitized, and their integrated area normalized. The NMR spectrum of a block copolymer does not differ significantly from the spectra of the parent homopolymers combined.[24] If a copolymer consists of two distinct blocks, the sum of the two homopolymer spectra, each properly weighted to adjust for the monomeric composition of the copolymer, should overlap the NMR spectrum of the block copolymer. However, the spectrum of a random copolymer will not match the sum of the two homopolymer spectra since it will not only have tacticity effects, but also monomer sequence effects. The methyl (CH_3) regions of the NMR spectra for both P(*t*-BMA-*b*-SiMA)III and P(*t*-BMA-*ran*-SiMA)II are shown in Figures 8 and 9 respectively. The sum of the two homopolymer spectra properly weighted are also shown in these

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[22] Johnson, L. F.; Heatley, F.; Bovey, F. A. *Macromolecules* **1970**, *3*, 175.

[23] Bovey, F. A. In *High Resolution NMR of Macromolecules*; Academic Press: New York, 1972; p 154.

[24] Bovey, F. A. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 1, p 367.

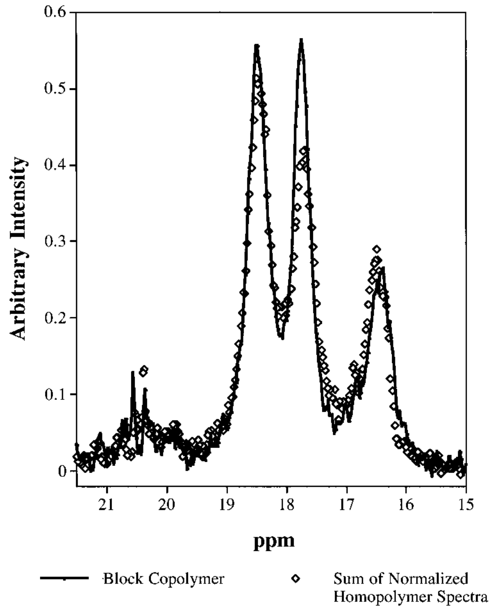

Figure 8. Methyl (CH_3) region of ^{13}C NMR spectrum of P(*t*-BMA-*b*-SiMA)III. The sum of the normalized homopolymer spectrum matches well the block copolymer spectrum indicating that it is a block copolymer.

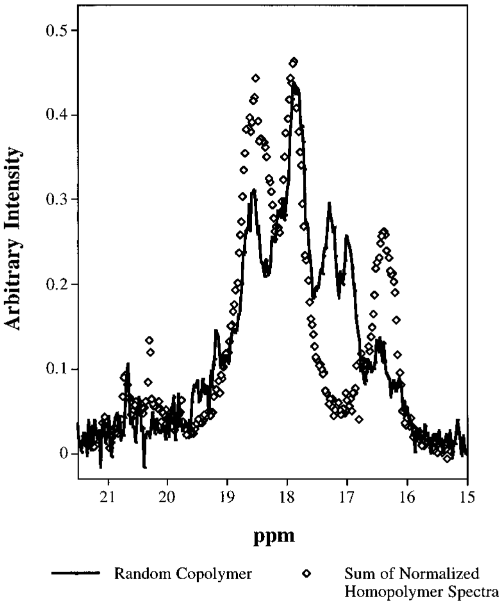

Figure 9. Methyl (CH_3) region of ^{13}C NMR spectrum of P(*t*-BMA-*ran*-SiMA)II. The sum of the normalized homopolymer spectrum does not match well the random copolymer spectrum indicating that it is a random copolymer.

Table 8. Theoretical and Experimental Number-Average Sequence Length for P(*t*-BMA-*ran*-SiMA)II

	theoretical	experimental
n_{SiMA}	1.47	2.3–4.5
$n_{t\text{-BMA}}$	3.12	*a*

[a] No characteristic peak exists for the *t*-BMA which would allow the experimental number-average sequence length to be calculated.

figures. The weighting given to each homopolymer spectrum was determined by the molar ratios of SiMA to *t*-BMA in the copolymers. The homopolymer spectra were shifted as much as 0.10 ppm for the block copolymer and as much as 0.25 ppm for the random copolymer to obtain the best fit for each copolymer spectrum. ("Best fit" means trying to match the summation of the two homopolymer spectra to the experimental spectrum of the copolymers. This was done for both the block and the random copolymer even though for the random copolymer the summation should not be the same as the experimental spectrum. In this way the test is more stringent for the random copolymers than the block copolymers.) This shifting is acceptable as the different samples for NMR were of different concentration, and it is known that there are concentration effects on chemical shifts.[25]

Analysis of the spectra in this way confirms the structure of the copolymers. The sum matches well the block copolymer spectrum confirming the structure of the block copolymer (Figure 8). However, the sum does not match the spectrum of the random copolymer (Figure 9), indicating that SiMA and *t*-BMA are mixed in a random fashion along the polymer chain.

The degree of randomness can be assessed by comparing the theoretical number average sequence length (n) of each monomer to that determined from the integrated area of characteristic peaks. The theoretical number average sequence length is given by eq 1, where

$$n_{\text{theory}} = 1/(1 - P) \qquad (1)$$

P is the mole fraction of SiMA units.[26] The experimental number average sequence length for SiMA is given by eq 2.[26] The origin of equation 2 is described in ref 21.

$$n_{\text{SiMA}} = \frac{N_{\text{SiMA-SiMA-SiMA}} + N_{\text{SiMA-SiMA-}t\text{-BMA}} + N_{t\text{-BMA-SiMA-}t\text{-BMA}}}{N_{t\text{-BMA-SiMA-}t\text{-BMA}} + 0.5N_{\text{SiMA-SiMA-}t\text{-BMA}}} \qquad (2)$$

where $N_{\text{SiMA-SiMA-SiMA}}$ = the number of SiMA–SiMA–SiMA compositional triads, $N_{\text{SiMA-SiMA-}t\text{-BMA}}$ = the number of SiMA–SiMA–*t*-BMA compositional triads, and $N_{t\text{-BMA-SiMA-}t\text{-BMA}}$ = the number of *t*-BMA–SiMA–*t*-BMA compositional triads.

The methods used to determine the number of the different compositional triads are described in the supporting information. The random copolymer has a number-average sequence length for SiMA which differs from that predicted for a perfectly random copolymer [of P(*t*-BMA-*ran*-SiMA)II's composition] by theory. However, the values given in Table 8 are most likely an overestimate as discussed in the supporting information. Most likely the simultaneous cofeed of SiMA and *t*-BMA to the reactor results in a random copolymer that has only a slight gradient in monomeric composition along the polymer chain. Thus, the random and block copolymers prepared by GTP are structurally different.

3.8. Thermal Properties of Polymers. The glass transition temperatures of many of the polymers prepared during this study are reported in Table 9. Strong microphase separation of the block copolymers would be indicated by two distinct T_g's, one for each mi-

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(25) Levy, G. C.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance for Organic Chemists*; John Wiley & Sons, Inc.: New York, 1972; p 115.

(26) Randall, J. C. *Polymer Sequence Determination: Carbon-13 NMR Method*; Academic Press: New York, 1977.

Table 9. Glass Transition Temperature (T_g), wt % SiMA, and M_n (GPC) for the Polymers Prepared for This Study

	T_g (°C)		transition	wt % SiMA	GPC Mn
polymer	midpoint.	onset	width (°C)^a	(NMR)	(g/mol)
P(SiMA)III	−44	−53	17	100.0	8 960
P(*t*-BMA)I	112	107	12	0.0	13 800
P(*t*-BMA-*b*-SiMA)I	61	42	45	33.8	13 140
P(*t*-BMA-*b*-SiMA)II	48	41	39	56.8	14 860
P(*t*-BMA-*b*-SiMA)III	31	−37	136	48.8	15 230
P(*t*-BMA-*b*-SiMA)IV	74	45	46	33.6	14 010
P(*t*-BMA-*b*-SiMA)V	75	40	56	20.3	10 030
P(*t*-BMA-*ran*-SiMA)I	84	50	43	20.9	16 560
P(*t*-BMA-*ran*-SiMA)III^b	68	52	30	34.2	13 020
P(*t*-BMA-*ran*-SiMA)II	50	22	44	47.4	21 310

^{a} The transition width is the temperature difference between the onset of the T_g and the end of transition. ^{b} Prepared by free radical polymerization as described in ref 12.

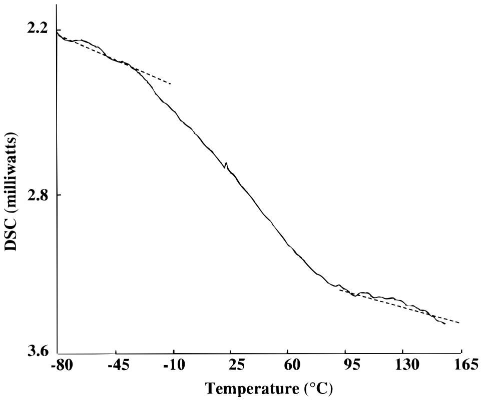

Figure 10. DSC curve for P(*t*-BMA-*b*-SiMA)III (8.5 mg). The copolymer is weakly microphase separated, leading to a very broad transition approximately between the T_g's of the two parent homopolymers.

crophase.[27] The block copolymers prepared are not in the strong segregation regime. We believe that most of our block copolymers are in the weak segregation regime. This conclusion is not surprising as the number of repeating units for the polymer chains is low due to the relatively high molar mass of the two monomers. The theoretical number of repeat units varies from 80 to 110 for the block copolymers of this study. In the weak segregation regime, the interface between the two phases approaches the width of the phases and the mole fraction of one block across the interface varies sinusoidally.[28] When this happens, one can view the microphase-separated material as having many phases of different compositions. Such a material will show thermal transitions at all the temperatures between the transitions of the phase that has the highest concentration of block A and the phase that has the highest concentration of block B. Because the block copolymers are weakly segregated, there is not a contradiction in the polymers consisting of two distinct blocks (as demonstrated by NMR analysis in section 3.7) and having one broad T_g.

The DSC for P(*t*-BMA-*b*-SiMA)III is shown in Figure 10. P(*t*-BMA-*b*-SiMA)III is a fairly symmetric block copolymer (a volume ratio of the two blocks around one) and exhibits the widest transition region (136 °C), indicating that of these weakly phase-separated block copolymers, it has the strongest phase separation. It starts and ends its transition region near the T_g's of P(SiMA) and P(*t*-BMA). The asymmetric block copolymers have narrower transition widths, indicating a greater degree of mixing of the two blocks. This is expected as it is known that asymmetric block copolymers require a larger enthalpic driving force than symmetric block copolymers to achieve the same degree of phase separation.[29] As the component of SiMA is increased from 20.9 to 47.4 wt %, the T_g's for the random copolymers decrease from 84 to 50 °C. The thermal properties of the block copolymers did not have many clear trends because the T_g's were affected by both monomeric composition and the degree of phase separation. However, the temperature at which the transition region ended (the high-temperature side of the transition region) varied less than 20 °C over the entire composition range studied for the block copolymers (20.3−56.8 wt % SiMA). If the composition range were narrowed to approximately that of the random copolymers (20.3−48.8%), the end of the transition region varied only 12 °C, from 87 to 99 °C. This is probably an additional indication that the block copolymers are weakly phase separated and therefore have a P(*t*-BMA) rich phase. Higher molecular weight block copolymers would have a larger driving force for microphase separation and would exhibit even greater differences in thermal properties compared to corresponding random copolymers.

4. Conclusions

With the GTP procedures presented here, SiMA- and *t*-BMA-based copolymers and their derivatives can be prepared to take advantage of the improved properties of controlled architecture polymers. The GTP of SiMA can be catalyzed by both oxyanion and bifluoride catalysts. However, the bifluoride catalyst leads to much faster rates of polymerization while still achieving polymers of low polydispersity and near theoretical molecular weight. The block and random copolymers prepared were shown to have the targeted structures by analysis of their ^{13}C NMR spectra. The absence of two distinct T_g's for the block copolymers is caused by their being weakly phase separated and is not an indication of the block copolymers being tapered.

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Supporting Information Available: Experimental data (8 pages). Ordering information is given on any current masthead page.

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