B(C6F5)(3)-catalyzed group transfer polymerization of alkyl methacrylates with dimethylphenylsilane through in situ formation of silyl ketene acetal by B(C6F5)(3)-catalyzed 1,4-hydrosilylation of methacrylate monomer
B(C₆F₅)₃-Catalyzed Group Transfer Polymerization of Alkyl Methacrylates with Dimethylphenylsilane through in Situ Formation of Silyl Ketene Acetal by B(C₆F₅)₃-Catalyzed 1,4-Hydrosilylation of Methacrylate Monomer

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The group transfer polymerization (GTP) of alkyl methacrylates has been studied using hydrosilane and tris(pentafluorophenyl)borane (B(C₆F₅)₃) as the new initiation system. For the B(C₆F₅)₃-catalyzed polymerization of methyl methacrylate (MMA) using triethylsilane, tri-n-butylsilane (nBu₃SiH), dimethylphenylsilane (Me₂PhSiH), triphenylsilane, and triisopropylsilane, nBu₃SiH and Me₂PhSiH were suitable for producing well-defined polymers with predicted molar masses and a low polydispersity. The livingness of the GTP of MMA using Me₂PhSiH/B(C₆F₅)₃ was verified by the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurement of the resulting polymers, kinetic analyses, and chain extension experiments. The B(C₆F₅)₃-catalyzed GTP using Me₂PhSiH was also applicable for other alkyl methacrylates, such as the n-propyl, n-hexyl, n-decyl, 2-ethylhexyl, iso-butyl, and cyclohexyl methacrylates. The in situ formation of the silyl ketene acetal by the 1,4-hydrosilylation of MMA was proved by the MALDI-TOF MS and 2H NMR measurements of the polymers obtained from the B(C₆F₅)₃-catalyzed GTPs of MMA with Me₂PhSiH or Me₂PhSiD, which was terminated using CH₃OH or CD₃OD.

Introduction

Group transfer polymerization (GTP) using a silyl ketene acetal (SKA) is categorized as an anionic polymerization method, which has been utilized for polar vinyl monomers, such as alkyl (meth)acrylates and N,N-dialkylacrylamides. In principle, the initiation and propagation reactions during the GTP process are rooted in the Mukaiyama-Michael reaction,¹⁻³ and both a Lewis base and Lewis acid are used as catalysts for the GTP as well as the Mukaiyama-Michael reaction. Although conventional catalysts of Lewis bases, such as nucleophilic anions of SiMe₃F₂⁻,¹⁴⁻⁵ HF₂⁻¹⁴⁻⁶ and CN⁻¹⁴⁻⁶,⁷ and Lewis acids, such as the transition metal compounds of ZnX₂ (X = Cl, Br, and I) ⁶,⁸ were used for the polymerization of (meth)acrylonitrile, they usually needed to be optimized in light of the reactivity of the used monomers. Basically, the controlled GTP of methacrylate monomers had been achieved using conventional nucleophilic anions, while the GTP of acrylate monomers was hardly controlled. On the other hand, organocatalysts have been applied to various GTP systems, resulting in achieving significant improvements of their controlled/living characteristics by the suppression of side reactions, such as transfer reactions to monomers and polymers, due to the low nucleophility of the base organocatalysts and the strong Lewis acidity of the acid ones.⁹ Thus, base organocatalysts, such as N-heterocyclic carbene (NHC),¹⁰⁻¹³ 2,8,9-trisobutyl-2,5,8,9-tetraazaa-1-phosphabicyclo[3.3.3]undecane,¹⁴ 1-tert-butyl-4,4,4-tris(dimethylamino)-2,2-bis[(tris(dimethylamino)-phosphoranylidienamino]-2Λ⁵,4Λ⁵-catenadi(phosphazene),¹⁴⁻¹⁶ and tris(2,4,6-trimethoxyphenyl)phosphine,¹⁷ have been used for the controlled/living GTPs of methyl methacrylate (MMA) and tert-butyl acrylate. In addition, acid organocatalysts, such as triphenylmethyl tetrakis(pentafluorophenyl)borane,¹⁸⁻²¹ (R)-3,3'-bis[3,5-bis(trifluoromethyl)phenyl]-1,1'-binaphthyl-2,2'-disulfonimide,²² trifluromethanesulfonimide,²³⁻²⁶ N-(trimethylsilyl)triflylimide,²⁷,²⁸ and 1-[bis(trifluoromethanesulfonyl)methyl]-2,3,4,5,6-pentafluorobenzene,²⁵,²⁶ were suitable for the controlled/living GTPs of methacrylate, acrylate, and acrylamide monomers, α-methylene-γ-butyrolactone, and γ-methyl-α-methylene-γ-butyrilactone using the appropriate SKAs as initiators. Furthermore, we reported that the acid organocatalysts have been used to synthesize well-defined and structurally defect-free end-functionalized poly(methyl methacrylate)s (PMMA)s and poly(n-butyl acrylate)s in our recent reports.²⁹,³⁰

The challenging tasks in the GTP chemistry are related to the development of versatile catalysts for the random and block copolymerizations of different types of monomers and the use of an
unstable SKA. For the former issue, Taton et al. reported that NHC was efficient for the synthesis of block copolymers composed of methacrylate and acrylate monomers, N,N-dimethylacrylamide, and methacrylonitrile.\textsuperscript{12,13} For the latter issue, we recently reported the polymerization of n-butyl acrylate (nBA) by combining the use of hydroxilane (R\textsubscript{3}SiH) and tris(pentafluorophenyl)borane (B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}) as a novel and very convenient GTP method without the direct use of the unstable SKA, in which the true initiator of (Z)-1-n-butoxy-1-dimethylphenylsiloxy-1-propene in situ formed as fast as a propagation reaction, proceeded through the 1,4-hydroisilylation of nBA with the moisture-stable R\textsubscript{3}SiH of dimethylphenylsilane.\textsuperscript{31} Thus, it is interesting to clarify the limit and scope of this GTP method, such as the applicable monomers and a suitable combination of R\textsubscript{3}SiH with the used monomer. In this study, we now report the GTP of methacrylate monomers, whose reactivity significantly differs from acrylate monomers for the anionic polymerizations involving the GTP using R\textsubscript{3}SiH and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}.

This article describes (1) the GTP of MMA using R\textsubscript{3}SiH and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in terms of the optimization of R\textsubscript{3}SiH, kinetic studies, and molar-mass control, (2) the structural effect of the methacrylate monomers on this GTP characteristics, and (3) the mechanism investigations based on the in situ 1,4-hydroisilylation of MMA with Me\textsubscript{2}PhSiH or Me\textsubscript{2}PhSiD, which was terminated using CH\textsubscript{3}OH or CD\textsubscript{3}OD.

Scheme 1. B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}-catalyzed group transfer polymerizations (GTP) of methacrylate monomers using Me\textsubscript{2}PhSiH.

**Experimental Section Materials.** Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}, >99.5%; water content, <0.001%), n-butyllithium (nBuLi, 1.6 mol L\textsuperscript{-1} in n-hexane), triethylamine (>99.0%), calcium hydride (CaH\textsubscript{2}, >95.0%), methanol (>99.5%), n-hexane (>95.0%), and deuterated chloroform (CDCl\textsubscript{3}, >99.8%) were purchased from Kanto Chemicals Co., Inc. Methyl methacrylate (MMA, >99.8%), n-propyl methacrylate (nPrMA, >98.0%), isobutyl methacrylate (iBuMA, >98.0%), n-hexyl methacrylate (nHMA, >98.0%), 2-ethylhexyl methacrylate (EHMA, >99.0%), cyclohexyl methacrylate (cHMA, >98.0%), n-dodecyl methacrylate (nDMA, >95.0%), tert-butyl methacrylate (tBuMA, >98.0%), allyl methacrylate (AMA, >99.0%), 2-(2-methoxyethoxy)ethyl methacrylate (DEGMA, >97.0%), trans-3-indoleacrylic acid (>98.0%), triethylsilane (Et\textsubscript{3}SiH, >98.0%), tri-n-butylsilane (nBu\textsubscript{3}SiH, >98.0%), trisopropylsilane (iPr\textsubscript{3}SiH, >98.0%), dimethylphenylsilane (Me\textsubscript{2}PhSiH, >97.0%), triphenylsilane (Ph\textsubscript{3}SiH, >96.0%), and methyl isobutyrate (>99.0%) were purchased from Tokyo Kasei Kogyo Co., Ltd. Tris(pentafluorophenyl)borane (B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, >96.0%) was purchased from Wako Pure Chemicals Industries, Ltd., and used after recrystallization in n-hexane at ~30 °C. Dithranol (>90.0%), silver trifluoroacetate (98.0%), sodium trifluoroacetate (98.0%), and deuterated methanol (CD\textsubscript{3}OD, > 99.8%) were purchased from the Sigma-Aldrich Chemicals Co. MMA, nPrMA, tBuMA, nHMA, EHMA, cHMA, nDMA, tBuMA, AMA, DEGMA, CH\textsubscript{2}Cl\textsubscript{2}, Et\textsubscript{3}SiH, (nBu\textsubscript{3}SiH), iPr\textsubscript{3}SiH, Me\textsubscript{2}PhSiH, and methyl isobutyrurate were distilled from CaH\textsubscript{2} and degassed by three freeze-pump-thaw cycles prior to use. Ph\textsubscript{3}SiH was recrystallized from n-hexane prior to use. 1-Methoxy-2-methyl-1-dimethylphenylsiloxyprop-1-ene (SKA\textsubscript{Me2Ph}) and diterodimethylphenylsilane (Me\textsubscript{2}PhSiD) were synthesized according to previously reported procedures.\textsuperscript{29,32} All other chemicals were purchased from available suppliers and used without further purification.

**Measurements.** The \textsuperscript{1}H (400 MHz) and \textsuperscript{13}C NMR (100 MHz) spectra were recorded using a JEOL JNM-A400H or a JEOL-ECS400. The \textsuperscript{2}H NMR (61.4 MHz) spectra were recorded using a JEOL-JNM-A400H. The polymerization solution was prepared in an MBRAUN stainless steel glove-box equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H\textsubscript{2}O, O\textsubscript{2} <1 ppm). The moisture and oxygen contents in the glove-box were monitored by an MB-MO-SE 1 and in MB-OX-SE 1, respectively. Size exclusion chromatography (SEC) measurements of the PMMAs were performed at 40 °C using a Jasco GPC-900 system (Shodex® DU-2130 dual pump, Shodex® RI-71 RI detector, and Shodex® ERC-3125SN degasser) equipped with two Shodex KF-804 L columns (linear, 8 mm × 300 mm) in THF at the flow rate of 1.0 mL min\textsuperscript{-1}. The number average molar mass (\textit{M}\textsubscript{n,SEC}) and dispersity (\textit{M}_{\text{w}}/\textit{M}_{\text{n}}) of the resulting PMMA were determined based on PMMA standards with the \textit{M}_{\text{w}}/\textit{M}_{\text{n}} of 1.25 × 10\textsuperscript{6} g mol\textsuperscript{-1} (1.07), 6.59 × 10\textsuperscript{5} g mol\textsuperscript{-1} (1.02), 3.030 × 10\textsuperscript{5} g mol\textsuperscript{-1} (1.02), 1.388 × 10\textsuperscript{5} g mol\textsuperscript{-1} (1.05), 6.015 × 10\textsuperscript{4} g mol\textsuperscript{-1} (1.03), 3.053 × 10\textsuperscript{4} g mol\textsuperscript{-1} (1.02), and 1.155 × 10\textsuperscript{4} g mol\textsuperscript{-1} (1.04), 4.90 × 10\textsuperscript{3} g mol\textsuperscript{-1} (1.10), 2.87 × 10\textsuperscript{3} g mol\textsuperscript{-1} (1.06), and 1.43 × 10\textsuperscript{3} g mol\textsuperscript{-1} (1.15). The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106-107 W cm\textsuperscript{-2}) operating at 3 Hz was used to produce the laser desorption, and 200-500 shots were summed. The spectra were externally calibrated using narrow-dispersed polystyrene with a linear calibration. Samples for the MALDI-TOF MS
measurements for the PMMAs were prepared by mixing the polymer (1.5 mg mL\(^{-1}\), 10 \(\mu\)L), the matrix (trans-3-indoleacrylic acid, 10 mg mL\(^{-1}\), 90 \(\mu\)L), and the cationizing agent (sodium trifluoroacetate, 10 mg mL\(^{-1}\), 10 \(\mu\)L) in THF.

**Synthesis of 1-methoxy-2-methyl-1-dimethylphenylsiloxyprop-1-ene (SKA\(_{\text{MePh}}\)).** To a solution of disiopropylamine (3.09 mL, 22.0 mmol) in dry THF (50 mL) in a 100-mL cock-attached flask, n-butyllithium (13.8 mL, 22.0 mmol; 1.62 mol L\(^{-1}\) in n-hexane) was dropwise added for several minutes at 0 °C under an argon atmosphere. After stirring for 30 min, methyl isobutyrate (2.27 g, 22.0 mmol) was slowly added. After the reaction mixture was stirred at −78 °C for 30 min, phenylidimethylchlorosilane (3.70 mL, 22.0 mmol) was added. The entire mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure, and the residue was distilled (54 °C, 0.02 mmHg) to give SKA\(_{\text{MePh}}\) as a colorless liquid. Yield, 620 mg (13.1 %). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)), \(\delta\) (ppm) 7.69-7.31 (m, 5H, -C\(_6\)H\(_5\)), 3.41 (s, 3H, -OC\(_3\)H\(_3\)), 1.61-1.47 (s, 6H, -C(CH\(_3\))\(_2\)), 0.63 (s, 6H, -Si(CH\(_3\))\(_2\)C\(_6\)H\(_5\)). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)), \(\delta\) (ppm) 161.1-17.2 (2C, =C(C\(_6\)H\(_5\))), 57.1 (1C, COCH\(_3\)), 91.6 (1C, C=C(CH\(_3\))\(_2\)), 127.45-137.45 (6C, OSi(CH\(_3\))\(_2\)C\(_6\)H\(_5\)), 149.54 (1C, C=COCH\(_3\)).

**B(C\(_6\)F\(_5\))\(_3\)-Catalyzed GTP of MMA using hydrosilane.** A typical procedure is as follows: a stock solution of B(C\(_6\)F\(_5\))\(_3\) (304 \(\mu\)L) under an argon atmosphere at room temperature. This journal is © The Royal Society of Chemistry 2015. J. Name., 2015, 00, 1-3 | 3
good agreement with the exact molar mass of MMA as the

Table 1. B(C6F5)3-catalyzed GTP of MMA using hydrosilane (RSiH) as a potential initiator.

<table>
<thead>
<tr>
<th>run</th>
<th>R3SiH</th>
<th>Time (h)</th>
<th>Mw,SEC (kg mol−1)</th>
<th>Mw/Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Et3SiH</td>
<td>0.50</td>
<td>5.6</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>nBu3SiH</td>
<td>0.50</td>
<td>3.4</td>
<td>1.11</td>
</tr>
<tr>
<td>3</td>
<td>Me3PhSiH</td>
<td>0.75</td>
<td>3.2</td>
<td>1.09</td>
</tr>
<tr>
<td>4</td>
<td>Ph3SiH</td>
<td>1.65</td>
<td>1.1</td>
<td>1.23</td>
</tr>
<tr>
<td>5</td>
<td>iPr3SiH</td>
<td>115</td>
<td>10.0</td>
<td>1.17</td>
</tr>
</tbody>
</table>

a Solvent, CH2Cl2; temperature, r.t.; Ar atmosphere; [MMA]0, 1.0 mol L−1; [MMA]0/[R3SiH]0/[B(C6F5)3]0, 25/1/0.5; MMA conversion (conv.) determined by 1H NMR in CDCl3, >99 %; Mw,calcd (calculated by [MMA]0/[R3SiH]0 × (conv.) × (M.W. of MMA) + (M.W. of H) × 2), 2.5 kg mol−1. b Determined by SEC in THF using PMMA standards.

The polymerization kinetics was then investigated at room temperature under the initial [MMA]0/[Me3PhSiH]0/[B(C6F5)3]0 of 50/1/0.5, as shown in Figure 2. For the zero-order plot of conv. vs. time (Figure 1a), the conv. increased with the increasing polymerization time and there was no stopping of the polymerization till complete consumption of all the monomer. The first-order plot of ln[1/(1-covn.)] vs. time was found to be linear in the low conv. region and showed a self-acceleration phenomenon repeating in the late polymerization stage probably due to the exothermic and viscous effects of the polymerization system.33 It is worth noting that the induction period time of 6.3 min was observed at the initial polymerization stage in the fitting curve. This induction period could be reasonably assigned to the time required by the 1,4-hydrosilylation of MMA and/or the monomer activation by B(C6F5)3 at the very beginning of the polymerization period because the coordination between B(C6F5)3 and R3SiH and that between B(C6F5)3 and MMA were reported to be the rate-determining steps for the 1,4-hydrosilylation and polymerization processes, respectively.34,35 In addition, the Mw,SEC of the resulting PMMA in Figure 2b linearly increased with the increasing monomer conversion, while the Mw/Mn value showed a decreasing trend. This feature is one of the characteristics for a living polymerization, suggesting that the present polymerization system is certainly the living one. Each measured Mw,SEC was observed to be slightly higher than the calculated value (Mw,calcd) and the initiation efficiency estimated by each Mw,calcd/Mw,SEC was in the range of 78-81% except for the earliest polymerization point in Figure 2. Therefore, the higher Mw,SEC was probably caused by the slightly low initiation efficiency of this polymerization system. Nevertheless, the fact that the initiation efficiency remained unchanged during the entire polymerization course, on the other hand, indicated that the propagating-ends maintained their livingness once they were formed at the very beginning of polymerization period. The detailed reason for the low initiation efficiency was quite complicated because side reactions, such as the 1,2- and 3,4-hydrosilylation of MMA, and three elementary reactions, such as the 1,4-hydrosilylation, initiation, and propagation reactions, could be considered.

The living nature of the GTP of MMA was further verified by the chain extension experiments (Figure 3). Subsequent to the completion for the polymerization of 25 eq. MMA under the condition of [MMA]0/[Me3PhSiH]0/[B(C6F5)3]0 = 25/1/0.5, another 50 eq. MMA was added to examine the propagation of the polymer chain, as to whether or not the polymer chain end kept its living nature. The first-stage polymerization of 25 eq. MMA produced a PMMA with the Mw,SEC of 3.2 kg mol−1 and the Mw/Mn of 1.09. The second-stage polymerization of 50 eq. MMA indicated a complete monomer consumption and afforded the polymer product with the Mw,SEC of 6.8 kg mol−1 and the Mw/Mn of 1.04. The
increase in molar mass was apparently reflected in the SEC profiles as the monomodal SEC trace during the first polymerization stage that was clearly shifted to the high molar-mass region after the completion of the second-stage polymerization, while still maintaining the narrow mono-modal shape. Thus, the chain extension experiments once again implied the living nature of the discussed polymerization system.

**Figure 3.** The SEC traces of the PMMA during first-stage polymerization (solid line) and the PMMA during second-stage polymerization (dashed line).

The living characteristics of the B(C₆F₅)$_3$-catalyzed GTP using Me₂PhSiH was used to synthesize well-defined PMMAs with targeted molar masses by varying the initial [MMA]/[Me₂PhSiH]₀ ratios of 25, 50, 100, 125, and 125. All the monomers were quantitatively consumed for each polymerization and the SEC trace clearly shifted to the high molar-mass region with the increase in the initial [MMA]/[Me₂PhSiH]₀ ratio, as shown in Figure 4, and all the polymers maintained a narrow polydispersity. The $M_n$ and $M_w$ were 3.2, 5.8, 12.2, 12.5, and 17.6 kg mol$^{-1}$, which was pretty close to the corresponding $M_n$ and $M_w$ of 2.5, 5.0, 10.0, 12.5, and 15.0 kg mol$^{-1}$, respectively, and all their $M_w/M_n$ were narrower than 1.10.

**Figure 4.** The SEC traces of the PMMAs obtained at various [MMA]/[Me₂PhSiH]₀ ratios of (i) 25, (ii) 50, (iii) 100, (iv) 125, and (v) 150.

B(C₆F₅)$_3$-catalyzed GTPs of various methacrylate monomers using Me₂PhSiH. In addition to MMA, this GTP method was applied to other methacrylate monomers, such as the alkyl methacrylates of the n-propyl (PrMA), n-hexyl (nHMA), n-dodecyl (nDMA), 2-ethylhexyl (EHMA), isobutyl (iBuMA), cyclohexyl (cHMA), and tert-butyl (tBuMA) ones and functional methacrylates of the allyl (AMA) and 2-(2-methoxyethoxy)ethyl (DEGMA) ones. The polymerizations were carried out with the initial [monomer]/[B(C₆F₅)$_3$]/[Me₂PhSiH]₀ of 25/1/0.5 and their results are summarized in Table 3. For the GTPs of the alkyl methacrylates, namely, the polymerizations of nPrMA, nHMA, nDMA, EHMA, and iBuMA, which possess primary alkyl substituents, completed within 1 h and the obtained $M_n$ were 4.6, 6.4, 6.4, 5.6, and 4.4 kg mol$^{-1}$ for their corresponding polymer products, which was in approximate agreement with the related $M_n$ of 3.2, 4.3, 6.4, 5.0, and 3.6 kg mol$^{-1}$, respectively. On the contrary, the polymerization of cHMA as a secondary alkyl ester obviously required the long time of 2.7 h, and that of tBuMA as a tertiary alkyl ester hardly proceeded. Figure S2 shows the kinetic studies of the GTPs of MMA, nHMA, EHMA, and cHMA at the [monomer]/[B(C₆F₅)$_3$]/[Me₂PhSiH]₀ ratio of 50/1/0.5 in CH₂Cl₂ at room temperature. Interestingly, MMA, nHMA, and EHMA as primary alkyl esters showed almost the same polymerization behavior and had similar $k_p$ values of ca. 0.05 min$^{-1}$ (Table S1) regardless of the length of the alkyl substituents. In contrast, cHMA apparently had a lower polymerization rate ($k_p = 0.0184$ min$^{-1}$) than the others (Figure S2), which could be due to the increase in the steric hindrance at the secondary CH group. The reason for no polymerization of tBuMA was attributed to the cleavage of the Bu-O bond by the strong acidity of B(C₆F₅)$_3$, which, on the contrary, deactivated B(C₆F₅)$_3$. For the GTPs of the functional methacrylates of AMA and DEGMA, the polymerizations ceased after the polymerization time of 18 h, and the monomer conversions were as low as 6.7% for AMA and 19.8% for DEGMA. We attributed this termination to the possible deactivation of the Lewis acid of B(C₆F₅)$_3$ by the more hydrophilic tert-Bu-O bond by the strong acidity of B(C₆F₅)$_3$, which led to no monomer activation and the stopping of the polymerization after a certain period of polymerization. Therefore, the chemical structure of the substituent had a crucial effect on the polymerization rate and possibility of the GTPs of the methacrylate monomers using B(C₆F₅)$_3$ and Me₂PhSiH.

Mechanism of B(C₆F₅)$_3$-catalyzed group transfer polymerization of MMA using Me₂PhSiH. In order to provide a more profound insight into this polymerization system, the polymerization mechanism was studied based on the $^1$H NMR measurement of a polymerization system, control experiments of GTP using Me₂PhSiH and an SKA, and the deuteration experiments of the polymer chain-ends. The $^1$H NMR spectra of (a) MMA, (b) Me₂PhSiH, (c) a mixture of MMA, Me₂PhSiH, and B(C₆F₅)$_3$ at a molar ratio of 1/1/0.5, and (d) 1-methoxy-2-methyl-1-dimethylphenylsiloxyprop-1-ene (SKA-Me₂Ph) prepared by the reaction of methyl isobutyrate with lithium disopropylamide (LDA) in CDCl₃ are shown in Figure 5 in order to compare each
other to ascertain the in situ formation of \( \text{SKA}_{\text{Me2Ph}} \) as the true initiator. In the spectrum of the mixture (Figure 5c), the characteristic proton signals completely disappeared at 6.13 and 5.58, 3.68, and 1.98 ppm due to CH\(_2\)=C(CH\(_3\))CO\(_2\)C\(_6\)H\(_5\), and the chemical shift was observed because the interaction between Me2PhSiH and B(C\(_6\)F\(_5\))\(_3\) was very weak. Nonetheless, based on the facts that mixing Me2PhSiH, B(C\(_6\)F\(_5\))\(_3\), and MMA in CDCl\(_3\) produced SKA\(_{\text{Me2Ph}}\), while mixing Me2PhSiH and MMA in CDCl\(_3\) did not, it is rather clear that B(C\(_6\)F\(_5\))\(_3\) catalyzed the in situ 1,4-hydrosilylation of MMA with Me2PhSiH.

### Table 3. B(C\(_6\)F\(_5\))\(_3\)-catalyzed GTPs of various methacrylate monomers using Me\(_2\)PhSiH as the initiator

<table>
<thead>
<tr>
<th>run</th>
<th>Monomer (M)</th>
<th>time (h)</th>
<th>conv. (^b) (%)</th>
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<tr>
<td>6</td>
<td>nPrMA</td>
<td>1</td>
<td>&gt;99</td>
</tr>
<tr>
<td>7</td>
<td>nHMA</td>
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<tr>
<td>9</td>
<td>EHMA</td>
<td>1</td>
<td>&gt;99</td>
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<tr>
<td>10</td>
<td>tBuMA</td>
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<td>11</td>
<td>cHMA</td>
<td>2.7</td>
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<tr>
<td>12</td>
<td>tBuMA</td>
<td>72</td>
<td>-</td>
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<tr>
<td>13</td>
<td>AMA</td>
<td>18</td>
<td>6.7</td>
</tr>
<tr>
<td>14</td>
<td>DEGMA</td>
<td>18</td>
<td>20</td>
</tr>
</tbody>
</table>

\(^a\)Ar atmosphere; temperature, r.t.; [monomer]\(_0\), 1.0 mol L\(^{-1}\) in CH\(_2\)Cl\(_2\); [N in CDCl\(_3\)]. \(^b\)M\(_{\text{calcd.}}\) = [M]\(_0\)/[Me\(_2\)PhSiH]\(_0\) \times (\text{conv.}) \times (\text{M.W. of monomer}) standards. (\(\_\) stands for no data)

### Table 4. Control B(C\(_6\)F\(_5\))\(_3\)-catalyzed polymerizations of MMA using Me\(_2\)PhSiH and SKA\(_{\text{Me2Ph}}\)

<table>
<thead>
<tr>
<th>run</th>
<th>[Me(_2)PhSiH](_0)/[B(C(_6)F(_5))(_3)](_0)</th>
<th>conv. (^b) (%)</th>
<th>(M_n/\text{SEC}) (^c) (kg mol(^{-1}))</th>
<th>(M_n/M_h) (^c)</th>
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<tr>
<td>15</td>
<td>0/0.5</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>1/0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>1/0</td>
<td>&gt;99</td>
<td>3.1</td>
<td>1.08</td>
</tr>
<tr>
<td>18</td>
<td>[SKA(_{\text{Me2Ph}})](_0)/[B(C(_6)F(_5))(_3)](_0)</td>
<td>0/0.5</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>1/0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>1/0</td>
<td>&gt;99</td>
<td>3.3</td>
<td>1.08</td>
</tr>
</tbody>
</table>

\(^a\)Ar atmosphere; temperature, r.t.; [MMA]\(_0\), 1.0 mol L\(^{-1}\) in CH\(_2\)Cl\(_2\); [MMA]\(_0\)/[Me\(_2\)PhSiH or SKA\(_{\text{Me2Ph}}\)]\(_0\), 25. \(^b\) Determined by \(^1\)H NMR in CDCl\(_3\). \(^c\) Determined by SEC in THF using PMMA standards.

For the control experiments of the GTPs using Me\(_2\)PhSiH or a SKA (Table 4 and Figure S3), the polymerizations of 25 equivalents of MMA were carried out at room temperature in CH\(_2\)Cl\(_2\) at the [Me\(_2\)PhSiH]\(_0\)/[B(C\(_6\)F\(_5\))\(_3\)]\(_0\) ratios of 0/0.5 (run 15), 1/0 (run 16), and 1/0.5 (run 17) and the [SKA\(_{\text{Me2Ph}}\)]\(_0\)/[B(C\(_6\)F\(_5\))\(_3\)]\(_0\) ratio of 0/0.5 (run 18), 1/0 (run 19), and 1/0.5 (run 20). In the cases of the [Me\(_2\)PhSiH]\(_0\)/[B(C\(_6\)F\(_5\))\(_3\)]\(_0\) of 0/0.5 and the [SKA\(_{\text{Me2Ph}}\)]\(_0\)/[B(C\(_6\)F\(_5\))\(_3\)]\(_0\) of 0/0.5, the polymerizations in absence of Me\(_2\)PhSiH as a precursor of the initiator and SKA\(_{\text{Me2Ph}}\) as a true initiator did not produce any oligomeric and polymeric products.
suggesting that Me₂PhSiH indeed played the role of a potential initiator during the polymerization process and B(C₆F₅)₃ could not initiate the polymerization without Me₂PhSiH. In the cases of the [Me₂PhSiH]₀/[B(C₆F₅)₃]₀ of 1/0 and the [SKA]₀/[B(C₆F₅)₃]₀ of 1/0, the polymerizations without B(C₆F₅)₃ also did not produce any oligomeric or polymeric products, suggesting that B(C₆F₅)₃ undoubtedly acted as the catalyst during the polymerization course. In the cases of the [Me₂PhSiH]₀/[B(C₆F₅)₃]₀ of 1/0.5 and the [SKA]₀/[B(C₆F₅)₃]₀ of 1/0.5, the polymerizations afforded the targeted polymers as expected. These control experiments led to the conclusion that B(C₆F₅)₃ played the role of a potential initiator during the polymerization course and B(C₆F₅)₃ could not act as the catalyst during the polymerization course. In the cases that at a terminating-end, such as the α,ω-hydro, α,ω-dideutero, α-deutero,ω-hydro, and α,ω-dihydro poly(methyl methacrylate)s (H-PMMA-H, H-PMMA-D, D-PMMA-H, and D-PMMA-D, respectively) by B(C₆F₅)₃-catalyzed GTP of MMA using Me₂PhSiH or Me₂PhSiD as the potential initiator and CH₃OH or CD₃OD as the quenching agent.

**Scheme 2.** Synthesis of the α,ω-dihydro, α-hydro,α-deutero,α-hydro, and α,ω-dideutero poly(methyl methacrylate)s (H-PMMA-H, H-PMMA-D, D-PMMA-H, and D-PMMA-D, respectively) by B(C₆F₅)₃-catalyzed GTP of MMA using Me₂PhSiH or Me₂PhSiD as the potential initiator and CH₃OH or CD₃OD as the quenching agent.

**Table 5.** B(C₆F₅)₃-catalyzed GTP of MMA using Me₂PhSiH or Me₂PhSiD as a potential initiator and CH₃OH or CD₃OD as a terminator

<table>
<thead>
<tr>
<th>run</th>
<th>Initiation</th>
<th>Termination</th>
<th>Mₙ,SEC (kg mol⁻¹)</th>
<th>Mₙ/Mₚ</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Me₂PhSiH</td>
<td>CH₃OH</td>
<td>3.1</td>
<td>1.08</td>
<td>H-PMMA-H</td>
</tr>
<tr>
<td>21</td>
<td>Me₂PhSiH</td>
<td>CD₃OD</td>
<td>2.9</td>
<td>1.09</td>
<td>H-PMMA-D</td>
</tr>
<tr>
<td>22</td>
<td>Me₂PhSiD</td>
<td>CH₃OH</td>
<td>3.2</td>
<td>1.09</td>
<td>D-PMMA-H</td>
</tr>
<tr>
<td>23</td>
<td>Me₂PhSiD</td>
<td>CD₃OD</td>
<td>3.4</td>
<td>1.09</td>
<td>D-PMMA-D</td>
</tr>
</tbody>
</table>

* Ar atmosphere; [MMA]₀, 1.0 mol L⁻¹ in CH₂Cl₂; polymerization time, 1 h; temperature, r.t.; [MMA]₀/[dimethylphenylsilane]₀/[B(C₆F₅)₃]₀ 25/1/0.5; conv. determined by ¹H NMR in CDCl₃, > 99%; Mₙ,calcd., 2.5 kg mol⁻¹.  

The deuterium atom for H-PMMA-D, D-PMMA-D, and D-PMMA-D was further confirmed by ²H NMR measurements in CHCl₃ at room temperature, as shown in Figure 7. There are no deuterium signals in the ²H NMR spectrum of H-PMMA-H, as shown in Figure 7a, because no deuterated compounds were used. For the PMMA of run 21, the deuterium signal from the methine group at the terminating-end was observed at 2.38 ppm, while that due to the methyl deuterium at the initiating-end was not observed at 1.20 ppm, as shown in Figure 7b. For the PMMA of run 22, the observed deuterium signal was just the opposite to those of run 21, i.e., the deuterium signal from the methyl at the initiating-end was observed at 1.20 ppm, while that due to the methine deuterium at the terminating-end was not observed at 2.38 ppm. These results were perfectly consistent with the designed structures of H-PMMA-D and D-PMMA-H when using the dimethylphenylsilane/methanol combinations of Me₂PhSiH/CH₃OH, Me₂PhSiH/CD₃OD, Me₂PhSiD/CH₃OH, and Me₂PhSiD/CD₃OD led to the targeted polymer products of H-PMMA-H, H-PMMA-D, D-PMMA-H, and D-PMMA-D, as designed and desired.
PMMA prepared by the B(C₆F₅)₃-catalyzed GTP using Me₂PhSiH or Me₂PhSiD. In addition, the perfect deuteration at the terminating-end using CD₃OD indicated that only the propagation reaction and no side reactions, such as chain transfer and backbiting reactions, occurred during the entire polymerization.

Based on the mechanistic study of the 1,4-hydrosilylation of an α-unsaturated ketone and the normally accepted mechanism of the Lewis acid-catalyzed GTP, we now proposed a plausible mechanism for the B(C₆F₅)₃-catalyzed GTP of MMA using a hydrosilane, as shown in Scheme 3. Four elementary reactions are involved during the entire polymerization including (A) activation of the hydrosilane, (B) 1,4-hydrosilylation of MMA to produce the true initiator of SKA Me₂Ph and release of the catalyst, (C) monomer activation by B(C₆F₅)₃, and (D) initiation and propagation reactions. We assumed step A, which was reported by Pries et al. Step B proceeded very fast and was completed prior to step D as confirmed by the ¹H NMR measurements in Figure 5. Step C seems to be the rate-determining step because steps A, B, and D

Figure 6. Normal and expanded MALDI-TOF MS spectra in reflector mode of (a) H-PMMA-H (run 17), (b) H-PMMA-D (run 21), (c) D-PMMA-H (run 22), and (d) D-PMMA-D (run 23).

Figure 7. ¹H NMR spectra of (a) H-PMMA-H (run 17), (b) H-PMMA-D (run 21), (c) D-PMMA-H (run 22), and (d) D-PMMA-D (run 23) in CHCl₃.
were quite fast.\textsuperscript{35} The coordination of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} to the carbonyl group of MMA was not clearly observed by comparing the \textsuperscript{1}H NMR spectra of MMA and the mixture of MMA and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in CDCl\textsubscript{3} because no obvious change in the chemical shift was seen due to the activation of MMA by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}. This seems once again to support that step C was relatively slower than the other steps. Step D was widely accepted for the Lewis acid-catalyzed GTP. Therefore, we definitely proposed the new GTP mechanism through the \textit{in situ} formation of silyl ketene acetal by the 1,4-hydrosilylation of methacrylate monomers.

\textbf{Scheme 3.} A proposed mechanism for the B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}-catalyzed GTP of MMA using Me\textsubscript{2}PhSiH.

\begin{center}
\includegraphics[width=0.8\textwidth]{Scheme3.png}
\end{center}

\section*{Conclusion}

We established the convenient GTP methodology of MMA using Me\textsubscript{2}PhSiH and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}, in which the direct use of typically employed silyl ketene acetal was avoided. The bulkiness of the used hydrosilane was found to have a significant effect on the polymerization control and moderately bulky hydrosilanes, such as Me\textsubscript{2}PhSiH and nBu\textsubscript{3}SiH, were suitable for the molar-mass control. The B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}-catalyzed GTP of MMA using Me\textsubscript{2}PhSiH was proven to proceed in a living fashion based on the compositional analyses, kinetic studies, and chain extension experiments, which could be applied to produce PMMAs with the targeted molar masses. In addition, this polymerization method could be applied to primary alkyl methacrylate monomers, while the polymerization rates of the secondary alkyl methacrylates were obviously slower than those of the primary alkyl methacrylates and no polymerization proceeded for the tertiary butyl methacrylate. In addition, B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} played the important role as a dual catalyst for both the 1,4-hydrosilylation and propagation reactions, suggesting that B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} and hydrosilane are dispensable for the present controlled/living GTP system. Finally, the mechanism for the polymerization coupled with the hydrosilylation and Mukaiyama-Michael reactions has been intensively investigated in order to provide a profound insight into the new GTP methodology.

\section*{Acknowledgment.}

This work was financially supported by the MEXT (Japan) program “Strategic Molecular and Materials Chemistry through Innovative Coupling Reactions” of Hokkaido University and the MEXT Grant-in-Aid for Scientific Research on Innovative Areas “Advanced Molecular Transformation by Organocatalysts”. S. Kikuchi and K. Takada were partially funded by the JSPS Fellowship for young Scientists.

\section*{Notes and references}

\begin{enumerate}
\end{enumerate}
B(C₆F₅)₃-Catalyzed Group Transfer Polymerization of Alkyl Methacrylates with Dimethylphenylsilane through in Situ Formation of Silyl Ketene Acetal by B(C₆F₅)₃-Catalyzed 1,4-Hydrosilylation of Methacrylate Monomer

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The B(C₆F₅)₃-catalyzed group transfer polymerization (GTP) of alkyl methacrylates using hydrosilane and its polymerization mechanism have been studied in this study.