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$B(C_6F_5)_3$-Catalyzed Group Transfer Polymerization of *n*-Butyl Acrylate with Hydrosilane through In Situ Formation of Initiator by 1,4-Hydrosilylation of *n*-Butyl Acrylate

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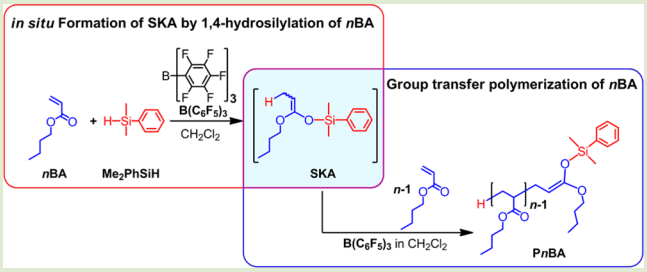
Supporting Information

ABSTRACT: The group transfer polymerization (GTP) of *n*-butyl acrylate (*n*BA) using hydrosilane (R_3SiH) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) has been studied, which did not need to use the initiator of a silyl ketene acetal (SKA) as the starting polymerization component. $B(C_6F_5)_3$ catalyzed the in situ 1,4-hydrosilylation of *n*BA by R_3SiH to generate the corresponding SKA prior to the polymerization of *n*BA, which was confirmed by the ^1H NMR measurement of the model reaction. The formed SKA performed as the initiator for the $B(C_6F_5)_3$-catalyzed GTP of *n*BA leading to well-defined polymers with targeted molar masses and low dispersities.



Silyl ketene acetal (SKA) is widely used as one of the versatile reagents in many organic reactions, such as the Mannich reaction,[1] the Mukaiyama aldol reaction,[2] and the Mukaiyama-Michael reaction,[3] which are important carbon−carbon bond forming reactions. In general, SKAs are synthesized by the reaction of lithium enolates with triorganosilyl chlorides or triflates.[4] Besides, the 1,4-hydrosilylation of an α,β-unsaturated ester using hydrosilane is an alternative method for the synthesis of SKAs.[5]

In polymer chemistry, SKA is mainly utilized as an initiator for the group transfer polymerization (GTP) of acrylic monomers, which proceeds through repetitive iterations of Mukaiyama-Michael reaction.[6] GTP is one of the living anionic polymerizations, in which the initial molar ratio of the monomer-to-SKA is decisive to control the molar mass of the obtained polymer. However, SKA is relatively unstable toward moisture and impurities, which causes the difficulty in producing the targeted molar mass, particularly, a high molar mass. Therefore, it is important to improve the GTP method in terms of the initiating and propagating processes.

Organocatalysts have been found to be more effective for the controlled/living GTPs through fixing the SKA structures in comparison to a conventional Lewis acid and base. For instance, Taton et al. and Waymouth et al. reported that one of the organic Lewis bases, *N*-heterocyclic carbene, was versatile for the GTP of acrylates, methacrylates, *N*,*N*-dimethylacrylamide, and methacrylonitrile.[7] In addition, Chen et al. reported that the Lewis acid of triphenylmethyl salts, such as triphenylmethyl tetrakis(pentafluorophenyl)borate, realized the living GTPs of methacrylates, acrylates, and butyrolactone-based vinylidene monomers.[8] We also reported the Brønsted acid-catalyzed controlled/living GTPs of acrylate and acrylamide using the triisopropylsilyl ketene acetal and silyl ketene amide, respectively.[9,10] However, these well-controlled GTPs still required the use of conventional or originally designed SKAs. Accordingly, of great interest is to develop a GTP method that does not require the use of SKA as the starting polymerization component. Thus, we aimed to design a new GTP method that (1) SKA is in situ generated by the catalytic 1,4-hydrosilylation of an α,β-unsaturated ester as the monomer with a hydrosilane prior to the polymerization, and (2) the same catalyst simultaneously promotes the GTP of the monomer in the presence of the SKA formed in the polymerization system. The key for realizing such a GTP is a dual functional catalyst that promotes both the 1,4-hydrosilylation and the Mukaiyama-Michael reactions. We then focused on the unique catalytic activity of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), a strong organic Lewis acid, which not only catalyzes the 1,4-hydrosilylation of α,β-ketones but also the Mukaiyama-Michael reactions.[11] For the polymer synthesis, Ute et al. reported that $B(C_6F_5)_3$ catalyzed the GTP of ethyl acrylate (EA) to afford the well-defined poly(ethyl acrylate).[12]

We then designed and demonstrated a new GTP method, that is, the GTP of *n*-butyl acrylate (*n*BA) using hydrosilane (R_3SiH) and $B(C_6F_5)_3$, as shown in Scheme 1. Alkylsilanes and arylsilanes were used to clarify the effect of the hydrosilane

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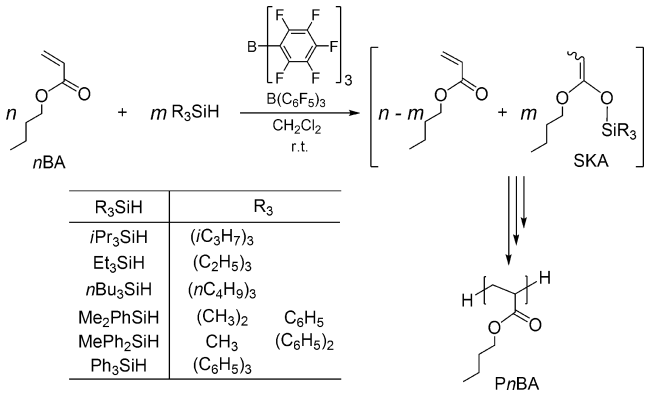
Scheme 1. Group Transfer Polymerization (GTP) of *n*-Butyl Acrylate (*n*BA) Using Hydrosilane (R_3SiH) and Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)



R_3SiH	R_3	
iPr_3SiH	$(iC_3H_7)_3$	
Et_3SiH	$(C_2H_5)_3$	
nBu_3SiH	$(nC_4H_9)_3$	
Me_2PhSiH	$(CH_3)_2$	C_6H_5
$MePh_2SiH$	CH_3	$(C_6H_5)_2$
Ph_3SiH	$(C_6H_5)_3$	

structure on the GTP characteristics. Recently, we demonstrated that the structure of the trialkylsilyl group had rather significant effect on the polymerization control during a Lewis acid-catalyzed GTP process. For instance, the bulky triisopropylsilyl ketene acetals (^{iPr3}SKAs) were most suitable initiators for the pentafluorophenylbis(trifluoromethanesulfonyl)-methane- and *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)-imide-promoted GTPs of methyl acrylate[9] and *n*-butyl acrylate,[13] while the use of less bulky trialkylsilyl ketene acetals, such as 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (^{Me3}SKA) and 1-methoxy-1-triethylsiloxy-2-methyl-1-propene (^{Et3}SKA), led to losing the polymerization control.[9] Based on this background, triisopropylsilane (iPr_3SiH) is therefore considered to be an appropriate hydrosilane because the 1,4-hydrosilylation of *n*BA by iPr_3SiH directly generates a triisopropylsilyl ketene acetal, 1-*n*-butoxy-1-triisopropylsiloxy-2-methyl-1-propene ($^{iPr3}SKA_{nBu}$). The $B(C_6F_5)_3$-catalyzed GTP of *n*BA was carried out using iPr_3SiH under $[nBA]_0/[R_3SiH]_0/[B(C_6F_5)_3]_0$ = 30/1/0.01 (Table 1; run 1). After the reaction

Table 1. Group Transfer Polymerization (GTP) of *n*-Butyl Acrylate (*n*BA) Using Hydrosilane (R_3SiH) and Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)[a]

run	R_3SiH	time (h)	$M_{n,SEC}$[b] (kg mol^{-1})	M_w/M_n[b]
1	iPr_3SiH	4.5		
2	Et_3SiH	0.2	6.5	1.08
3	nBu_3SiH	0.3	5.4	1.06
4	Me_2PhSiH	0.2	4.3	1.06
5	$MePh_2SiH$	2.0	4.4	1.07
6	Ph_3SiH	2.0	4.8	1.09

[a]Ar atmosphere; solvent, CH_2Cl_2; temperature, room temp.; $[nBA]_0$, 1.0 mol L^{-1}; $[nBA]_0/[R_3SiH]_0/[B(C_6F_5)_3]_0$, 30/1/0.01; monomer conv., >99%. [b]Determined by SEC in THF using PMMA standards.

time of 4.5 h, no polymerization occurred and all the monomer remained, indicating that no $^{iPr3}SKA_{nBu}$ was formed in the polymerization system due to the steric bulkiness of the triisopropylsilyl group.

Other alkylsilanes, such as triethylsilane (Et_3SiH) and tri-*n*-butylsilane (nBu_3SiH), were also used to examine their suitability, based on the fact that ^{Et3}SKA acted as the efficient initiator for the $B(C_6F_5)_3$-catalyzed GTP of EA.[12] In the case of Et_3SiH (run 2), the polymerization proceeded smoothly and all the monomer was consumed within the polymerization time of 0.2 h. Although the dispersity of the obtained polymer was sufficiently low at the M_w/M_n of 1.08 (Figure S1), the molar mass ($M_{n,SEC}$) of 6.5 kg mol^{-1} estimated by the size exclusion chromatography (SEC) measurement was 1.7 times higher than the calculated one ($M_{n,calcd}$) of 3.8 kg mol^{-1} (calculated from $[nBA]_0/[R_3SiH]_0$ × (MW of *n*BA, 128.17) × conv. + (MW of 2H, 2.02)). In the case of nBu_3SiH (run 3), the polymerization control was slightly improved compared to that using Et_3SiH, that is, the dispersity and molar mass of the obtained polymer using nBu_3SiH were 1.06 and 5.4 kg mol^{-1}, respectively. The insufficient control of the two polymerizations should be attributed to two aspects: (1) the balance of reaction rate of the 1,4-hydrosilylation and the initiation/propagation reaction and (2) occurrence of unexpected termination reaction due to the slightly low stability of the triethylsilyl and tri-*n*-butylsilyl ketene acetal structures. The much faster 1,4-hydrosilylation reaction, than the initiation/propagation reaction, is favorable for controlling the polymerization, such as a low dispersity. However, the occurrence of unexpected termination reactions leads to the higher molar mass than the calculated one.

Arylsilanes, such as dimethylphenylsilane (Me_2PhSiH), diphenylmethylsilane ($MePh_2SiH$), and triphenylsilane (Ph_3SiH), were utilized in order to improve the stability of the trisubstituted silyl group in the SKA and propagating polymer chain end throughout the GTP process. The molar mass and dispersity of the obtained polymers were 4.3 kg mol^{-1} and 1.06 for Me_2PhSiH (run 4), 4.4 kg mol^{-1} and 1.07 for $MePh_2SiH$ (run 5), and 4.8 kg mol^{-1} and 1.09 for Ph_3SiH (run 6; Figure S1), suggesting that the arylsilyl structures improved the polymerization control in the order of Me_2PhSiH > $MePh_2SiH$ > Ph_3SiH. In addition, the polymerization time of 0.2 h for Me_2PhSiH was much shorter than that of 2.0 h for $MePh_2SiH$ and Ph_3SiH. These results definitely supported that Me_2PhSiH was the most suitable hydrosilane for controlling the $B(C_6F_5)_3$-catalyzed GTP of *n*BA.

The well-controlled nature of the $B(C_6F_5)_3$-catalyzed GTP of *n*BA using Me_2PhSiH was demonstrated by analyzing the structure of the obtained polymer. The ^{1}H NMR spectrum of the obtained polymer is shown in Figure S2. The signals at 2.45−2.18 and 2.04−1.21 ppm were assigned to the methine and methylene protons of the polymer main chain, respectively, and those at 4.14−3.93, 1.74−1.51, and 1.51−1.21 ppm and 1.00−0.84 ppm to the methylene and methyl protons of the *n*-butyl side chain, respectively. In addition, the characteristic signal due to the methyl proton of the α-chain end was clearly observed at 1.17−1.06 ppm together with the absence of the phenyl protons due to Me_2PhSiH. These results indicated that the obtained polymer only consisted of *n*BA as the constitutional repeating unit.

For the matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF MS) spectrum, only one population of molecular ion peaks was observed as shown in Figure 1. The distance between two neighboring molecular ion peaks was 128.07 corresponding to the exact mass of *n*BA, 128.08, as the repeating unit. In addition, the *m*/*z* values of the observed molecular ion peaks corresponded to the calculated molar mass of the P*n*BA possessing a hydrogen as the α- and ω-end groups; for example, the observed value of 3227.47 agreed with the calculated value of 3227.10 for the 25-mer structure of $[H\text{-}(nBA)_{25}\text{-}H + Na]^+$. This result strongly suggested that the $B(C_6F_5)_3$-catalyzed GTP of *n*BA using Me_2PhSiH proceeded through a living manner to produce the well-defined P*n*BA.

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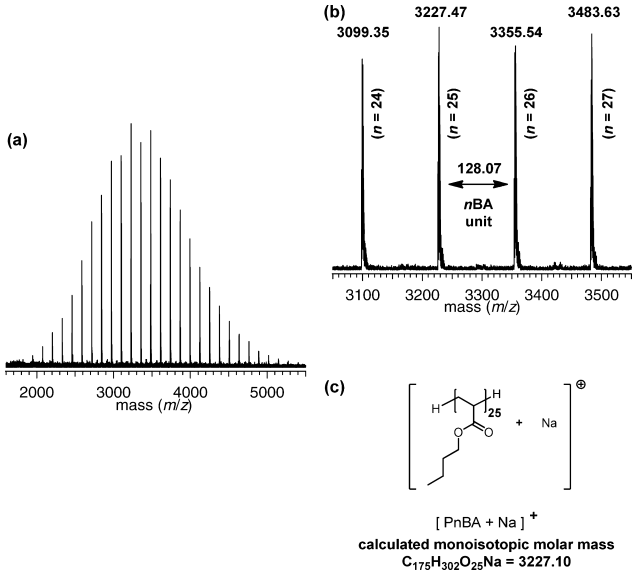


Figure 1. MALDI-TOF MS spectrum in reflector mode of the obtained P*n*BA ($[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0/[\text{B}(\text{C}_6\text{F}_5)_3]_0$, 25/1/0.01; conversion, >99%; $M_{n,SEC}$, 4.0 kg mol^{-1}; M_w/M_n, 1.06).

The stabilizing property of the dimethylphenylsilyl group toward the SKA and the propagationg polymer chain-end was confirmed by the chain extension experiment. After the first GTP with the $[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0$ of 25, the second GTP was carried out by adding another 75 equiv of *n*BA. The SEC trace apparently shifted to the higher molar mass region from 3.4 to 14.7 kg mol^{-1}, which sufficiently agreed with the $M_{n,calcd}$s of 3.2 and 13.0 kg mol^{-1}, respectively. In addition, the low dispersity (M_w/M_n) of 1.08 for the first GTP remained as 1.04 for the second GTP, as shown in Figure 2a.

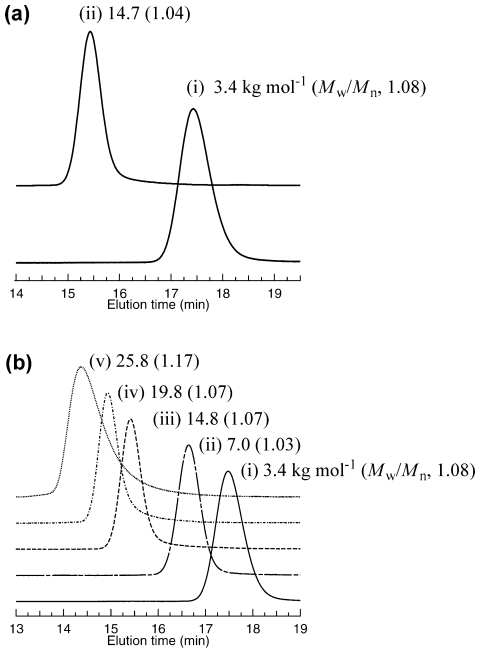
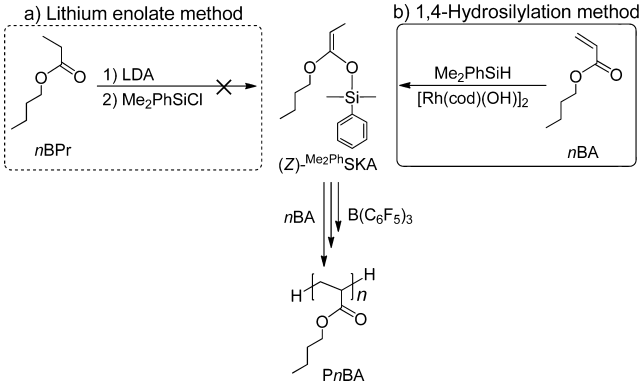


Figure 2. SEC traces of (a) the P*n*BAs obtained from (i) the first polymerization and (ii) the second polymerization in the chain extension experiment and (b) the P*n*BAs obtained at different $[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0$ ratios of (i) 25, (ii) 50, (iii) 100, (iv) 150, and (v) 200.

The living characteristics of the GTP of *n*BA using Me_2PhSiH and $\text{B}(\text{C}_6\text{F}_5)_3$ were applied to the synthesis of the well-defined P*n*BAs with the targeted molar masses by varying the initial molar ratio of *n*BA and Me_2PhSiH ($[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0$) of 25, 50, 100, 150, and 200. The SEC trace of the resulting P*n*BAs shifted to the higher molar mass region with the increasing $[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0$ ratio. The $M_{n,SEC}$s of 3.4, 7.0, 14.8, 19.8, and 25.8 kg mol^{-1} for the P*n*BAs obtained under the conditions of $[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0$ = 25, 50, 100, 150, and 200 fairly agreed with their $M_{n,calcd}$s of 3.2, 6.4, 12.8, 19.2, and 25.6 kg mol^{-1}, respectively, and their M_w/M_ns were as low as 1.03−1.08.

1-*n*-Butoxy-1-dimethylphenylsiloxy-1-propene ($^{\text{Me2Ph}}$SKA) was typically synthesized as a GTP initiator to discuss the polymerization mechanism of the $\text{B}(\text{C}_6\text{F}_5)_3$-catalyzed GTP using hydrosilanes. There are two methods, a) the lithium enolate method, and b) the 1,4-hydrosilylation method, to prepare $^{\text{Me2Ph}}$SKA, as shown in Scheme 2. We first carried out

Scheme 2. Synthesis of (*Z*)-$^{\text{Me2Ph}}$SKA by (a) Lithium Enolate Method and (b) 1,4-Hydrosilylation Method, and the GTP of *n*BA using (*Z*)-$^{\text{Me2Ph}}$SKA and $\text{B}(\text{C}_6\text{F}_5)_3$



the synthesis of $^{\text{Me2Ph}}$SKA by the lithium enolate method in which *n*-butyl propionate (*n*BPr) was treated with lithium diisopropylamide (LDA) and subsequently reacted with chlorodimethylphenylsilane (Me_2PhSiCl). However, no $^{\text{Me2Ph}}$SKA was obtained because the lithium enolate of *n*BPr was very unstable for the reaction with Me_2PhSiCl. Thus, we synthesized $^{\text{Me2Ph}}$SKA by the 1,4-hydrosilylation method in which *n*BA was reacted with Me_2PhSiH using the hydroxy(cyclooctadiene)-rhodium(I) dimer ($[\text{Rh}(\text{cod})(\text{OH})]_2$).[14] Fortunately, $^{\text{Me2Ph}}$SKA was obtained as a colorless liquid in the yield of 41%, and the (*Z*)-configuration of $^{\text{Me2Ph}}$SKA ((*Z*)-$^{\text{Me2Ph}}$SKA) was determined by the ^{1}H and ^{13}C NMR spectra and NOE spectrum, as shown in Figures 3c, S3, and S4, respectively.

The polymerization of *n*BA using (*Z*)-$^{\text{Me2Ph}}$SKA and $\text{B}(\text{C}_6\text{F}_5)_3$ with the $[n\text{BA}]_0/[(Z)\text{-}^{\text{Me2Ph}}\text{SKA}]_0/[\text{B}(\text{C}_6\text{F}_5)_3]_0$ of 50/1/0.01 was carried out to verify the initiating performance of (*Z*)-$^{\text{Me2Ph}}$SKA. The GTP of *n*BA proceeded smoothly and all of the monomer was consumed within 15 min. Although the $M_{n,SEC}$ of the obtained P*n*BA was 8.7 kg mol^{-1}, which was slightly higher than the $M_{n,calcd}$ of 7.1 kg mol^{-1}, the M_w/M_n estimated from the monomodal SEC trace was as narrow as 1.12. These results strongly indicated that $^{\text{Me2Ph}}$SKA was able to initiate the $\text{B}(\text{C}_6\text{F}_5)_3$-catalyzed GTP of *n*BA.

Finally, we confirmed the in situ formation of $^{\text{Me2Ph}}$SKA in the polymerization system. The model reaction was carried out under the condition with the $[n\text{BA}]_0/[\text{Me}_2\text{PhSiH}]_0/[\text{B}-$

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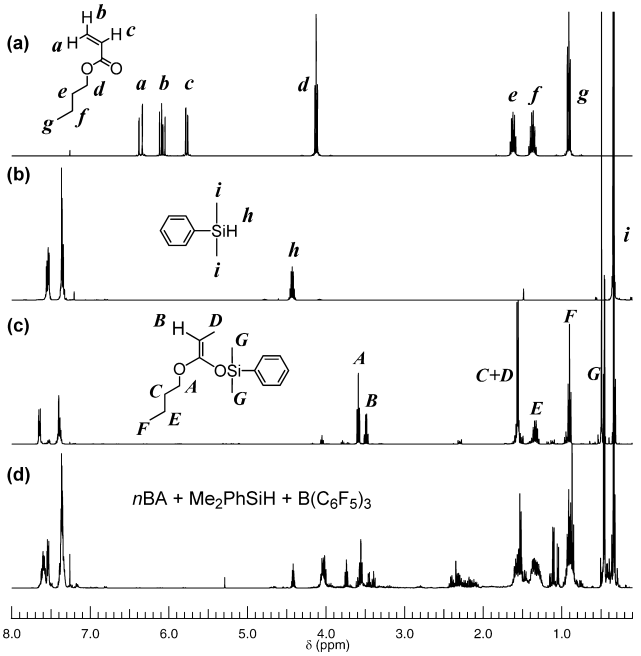

Figure 3. ^{1}H NMR spectra of (a) *n*BA, (b) Me_2PhSiH, (c) (*Z*)-^{Me2Ph}SKA, and (d) the mixture of *n*BA, Me_2PhSiH, and $B(C_6F_5)_3$ ($[nBA]_0/[Me_2PhSiH]_0/[B(C_6F_5)_3]_0$ = 1/1/0.01) measured in $CDCl_3$ at room temperature.

$(C_6F_5)_3]_0$ of 1/1/0.01 in $CDCl_3$. In order to estimate the structures of the reaction products, the ^{1}H NMR spectra of *n*BA and Me_2PhSiH are shown in Figure 3a and b, respectively. In the ^{1}H NMR spectrum of the reaction mixture (Figure 3d), the characteristic signals completely disappeared at 6.36, 6.08, and 5.77 ppm due to the *E*-vinyl (*a*), *Z*-vinyl (*b*), and methine (*c*) protons of *n*BA, respectively, and those decreased greatly at 4.49 and 0.40 ppm due to the hydro (*h*) and methyl (*i*) protons of Me_2PhSiH, respectively, whereas the characteristic signals appeared at 3.59 and 3.49 ppm due to the vinyl (*A*) and methylene (*B*) protons of ^{Me2Ph}SKA, respectively. Me_2PhSiH was not fully consumed because the $B(C_6F_5)_3$-catalyzed oligomerization of *n*BA was fast, resulting in an imbalanced consumption between *n*BA and Me_2PhSiH. However, these results definitely supported the fact that the 1,4-hydrosilylation of *n*BA by Me_2PhSiH was catalyzed by $B(C_6F_5)_3$ to produce ^{Me2Ph}SKA. Thus, for the polymerization of *n*BA using $Me_2PhSiH/B(C_6F_5)_3$, $B(C_6F_5)_3$ catalyzed the in situ 1,4-hydrosilylation of *n*BA by Me_2PhSiH leading to ^{Me2Ph}SKA that acted as the initiator for controlled/living GTP of *n*BA to produce the polymer with a very low dispersity, meaning that the rate of 1,4-hydrosilylation was extremely faster than that of polymerization.

In summary, we have established a new methodology for the GTP proceeding in a controlled/living fashion without using a relatively unstable silyl ketene acetal as the initiator, which is the first known report in the GTP chemistry to the best of our knowledge. For the GTP of acrylate monomers, there is difference in the initiator structure between the present new method with in situ forming of the dimethylphenylsilyl ketene acetal and the conventional method using the triisopropylsily ketene acetal. It is important to clarify this characteristic to utilize GTP as a commercially available method for producing acrylic polymers. Thus, we have also focused on expanding this methodology to synthesize methacrylate and acrylamide polymers.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section and additional data (SEC data and NMR spectra). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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