Silyl Ketene Acetals/B(C₆F₅)₃ Lewis Pair-Catalyzed Living Group Transfer Polymerization of Renewable Cyclic Acrylic Monomers

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Abstract: This work reveals the silyl ketene acetal (SKA)/B(C₆F₅)₃ Lewis pair-catalyzed room-temperature group transfer polymerization (GTP) of polar acrylic monomers, including methyl linear methacrylate (MMA), and the biorenewable cyclic monomers γ-methyl-α-methylene-γ-butyrolactone (MMBL) and α-methylene-γ-butyrolactone (MBL) as well. The in situ NMR monitored reaction of SKA with B(C₆F₅)₃ indicated the formation of Frustrated Lewis Pairs (FLPs), although it is sluggish for MMA polymerization, such a FLP system exhibits highly activity and living GTP of MMBL and MBL. Detailed investigations, including the characterization of key reaction intermediates, polymerization kinetics and polymer structures have led to a polymerization mechanism, in which the polymerization is initiated with an intermolecular Michael addition of the ester enolate group of SKA to the vinyl group of B(C₆F₅)₃-activated monomer, while the silyl group is transferred to the carbonyl group of the B(C₆F₅)₃-activated monomer to generate the single-monomer-addition species or the active propagating species; the coordinated B(C₆F₅)₃ is released to the incoming monomer, followed by repeated intermolecular Michael additions in the subsequent propagation cycle. Such neutral SKA analogues are the real active species for the polymerization and are retained in the whole process as confirmed by experimental data and the chain-end analysis by matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF MS). Moreover, using this method, we have successfully synthesized well-defined PMMBL-b-PMBL, PMMBL-b-PMBL-b-PMMBL and random copolymers with the predicated molecular weights (Mₙ) and narrow molecular weight distribution (MWD).

Keywords: Frustrated Lewis Pair; group transfer polymerization; silyl ketene acetal; B(C₆F₅)₃

1. Introduction

Lewis pair (LP) polymerization has emerged and attracted intense investigations of the cooperative (or synergistic) catalytic effects of Lewis acid (LA) and Lewis base (LB) pairs on the polymerization of conjugated polar alkenes [1–8], since the seminal works on Frustrated Lewis Pairs (FLPs) by Stephan and Erker in small molecule chemistry [9–12]. For instance, LPs based on strongly acidic, bulky E(C₆F₅)₃ (E = B, Al) LAs and bulky LBs including phosphines and N-heterocyclic carbenes (NHCs) have been employed to initiate rapid addition polymerization of conjugated polar vinyl monomers such as methyl methacrylate (MMA), cyclic and the naturally renewable monomers α-methylene-γ-butyrolactone (MBL), and γ-methyl-α-methylene-γ-butyrolactone (MMBL) [13–15] and monomers bearing the C=C–C=N functionality such as 2-vinylpyridine and 2-isopropenyl-2-oxazoline as well [16,17]. In such polymerizations, the cooperativity of the LA and LB sites of Lewis pairs is essential to achieve an effective polymerization system, which was demonstrated by the borane/phosphine LPs that showed that interacting LPs, and even classical Lewis adducts (CLAs),
can be highly active for the polymerization [18]. This was further nicely demonstrated by Rieger and co-workers, showing the high activity and high degree of control over the polymerization of Michael-type and extended Michael monomer systems by the highly interacting organoaluminum and phosphine LPs [19]. Extending beyond the commonly employed NHC and phosphine LBs, in 2014, Lu and co-workers first reported the N-heterocyclic olefin-based LPs for the polymerization of acrylamides, (meth)acrylates [49,50] and renewable MBL and MMBL [51]. Covalently linked, unimolecular silyl intermediates and perform kinetic and mechanistic studies, thereby providing the much-needed insights into the polymerization mechanism.

2. Results and Discussion

2.1. Slow MMA Polymerization by R₂SiH/B(C₆F₅)₃ and SKA/B(C₆F₅)₃

Without B(C₆F₅)₃, all six hydroxilanes, including Et₃SiH, Ph₃SiH, 'Bu₃SiH, Me₂C(SiH)₃, Me₃EtSiH, and Me₂PhSiH, showed negligible activity for the polymerization of MMA in

GTP is a successful, commercialized strategy for living polymerization of polar vinyl monomers proceeding through Mukaiyama-Michael reactions [23–25]. Such GTP process could be catalyzed by nucleophilic anionic bases, such as SiMe3F− [23,26,27], HF2− [23,26–28], F− [27–29], CN− [23,27–29], N3− [23,28], oxyanions[30,31], hydrogen bioxyanions [30–32]. Recently, neutral Lewis bases such as NHC [33–38], phosphorus-based nuculeophiles [39,40] and phosphazene superbases [39,41–44] have been demonstrated be efficient catalysts for living GTP of acrylic monomers. On the other hand, Brønsted acids have been employed as activators for GTP as well [45], while GTP of acrylates catalyzed by Lewis acidic catalysts such as zinhal halide [46], mercury iodide [47,48], or organoaluminium [46] requires a much higher catalyst loading (typically 10 mol % based on monomer) to achieve a reasonable degree of polymerization control. Through the oxidative activation of SKAs with a catalytic amount of [Ph₃C][B(C₆F₅)₄] (TTPB) as low as 0.025 mol % (based on monomer), we have successfully achieved high-speed living GTP of polar vinyl monomers catalyzed by the silylium ion R₂Si+, including (meth)acrylates [49,50] and renewable MBL and MMBL [51]. Covalently linked, unimolecular silylene/nucleophile/electrophile bifunctional active species rendered a rate enhancement by a factor of >40 and high stereoselectivity (at low temperature), as compared to the mononuclear SKA system [52]. More recently, a tandem (FLP and LA) activation method was developed for GTP involving the in-situ generation of SKA initiators by 1,4-hydroxilation of a methacrylate monomer. In such a process, the catalysts, such as highly electron deficient silylium cations “R₂Si+” [53] or strong LAs E(C₆F₅)₃ (E = B, Al) [5,6,54,55], play dual role in both hydroxilation (via frustrated Lewis Pair (FLP)-type activation) and activation of monomer (classical LA activation). However, such system was shown to be much less effective for E(C₆F₅)₃ (E = B, Al)-catalyzed GTP at high monomer to initiator ratios [6,53] and ill-controlled for Al(C₆F₅)₃-catalyzed MMA polymerization. In this context, herein we report the SKA/B(C₆F₅)₃ FLP-catalyzed GTP of polar vinyl monomers at room temperature, including MMA, renewable MMBL and MBL. More specifically, a highly interacting 'Bu₅SKA/B(C₆F₅)₃ LP system promotes the living GTP of MMBL and copolymerization of MMBL and MBL to produce well-defined (co)polymers with predicted molecular weights, and narrow molecular weight distributions. More importantly, this SKA/B(C₆F₅)₃ LP system enabled us to isolate key reaction intermediates and perform kinetic and mechanistic studies, thereby providing the much-needed insights into the polymerization mechanism.
CH$_2$Cl$_2$ at room temperature. In the presence of B(C$_6$F$_5$)$_3$, the in-situ generation of SKA initiators from the B(C$_6$F$_5$)$_3$-catalyzed hydrosilylation of the monomer MMA with R$_3$SiH exhibited very low polymerization activity and incomplete monomer conversions for various ratios of [MMA]$_0$/[R$_3$SiH]$_0$/[B(C$_6$F$_5$)$_3$]$_0$ for up to 24 h (runs 1–18, Table S1). On the other hand, the direct use of SKA (Scheme 1) as initiator and B(C$_6$F$_5$)$_3$ as catalyst did not lead to obvious enhancement in MMA polymerization activity compared to R$_3$SiH/B(C$_6$F$_5$)$_3$ systems (runs 19–39, Table S1). The corresponding PMMA polymers all possessed syndio-biased tacticities with a methyl triad distribution of around 70% rr, 28% mr and 2% mm, due to the chain-end control nature of this polymerization system.

![Scheme 1. Chemical structures of initiators, catalyst and monomers employed in this study.](image)

2.2. Controlled MMBL Polymerization by R$_3$SiH/B(C$_6$F$_5$)$_3$ and SKA/B(C$_6$F$_5$)$_3$

Next, we investigated the effectiveness of the R$_3$SiH/B(C$_6$F$_5$)$_3$ and SKA/B(C$_6$F$_5$)$_3$ systems for renewable monomer MMBL, which is a cyclic analogue of MMA and is readily prepared in a two-step process from the cellulosic biomass-derived levulinic acid. Compared to the MMA polymerization, all R$_3$SiH/B(C$_6$F$_5$)$_3$ and SKA/B(C$_6$F$_5$)$_3$ systems are more effective and controlled for polymerization of MMBL, achieving noticeably better initiation efficiency and narrower molecular weight distribution (Table 1 vs. Table S1). Among the silanes screened, Me$_2$EtSiH and Me$_2$PhSiH achieved quantitative monomer conversion within 30 min ($M_n = 48.1$ kg·mol$^{-1}$, $D = 1.26$, $I^* = 47\%$ for run 1, Table 1; $M_n = 57.4$ kg·mol$^{-1}$, $D = 1.39$, $I^* = 39\%$ for run 2, Table 1). Replacing the Ph group in the R$_3$SiH structure with the electron-withdrawing Cl (i.e., Me$_2$ClSiH) rendered the polymerization reaching completion in 2 h and producing PMMBL with a $M_n$ of 78.6 kg·mol$^{-1}$ and a higher $D$ value of 1.44 (run 3, Table 1). Interestingly, R$_3$SiH with three Et substituents, Et$_3$SiH, when combined with B(C$_6$F$_5$)$_3$, exhibited comparable polymerization activity with that for Me$_2$EtSiH, producing PMMBL with a $M_n$ of 33 kg·mol$^{-1}$ and a $D$ value of 1.27, thus yielding an enhanced initiation efficiency of 68\% (run 4, Table 2). With the increase of steric hindrance of substituents, the corresponding R$_3$SiH exhibited drastically decreased polymerization activity (6 h for Ph$_3$SiH and 24 h for 'Bu$_3$SiH to reach full monomer conversion) and initiation efficiency (21\% for Ph$_3$SiH and 7\% for 'Bu$_3$SiH).
Me2Cl groups with three electron-donating alkyl groups in SKA, we observed a significantly enhanced rate of Me2Cl; the rate of MMBL polymerization was drastically decreased and M molecules with a chlorine atom, the rate of MMBL polymerization was drastically decreased and M.

Since both Me and monomer were premixed, followed by adding initiator to start the polymerization. Carried out in 2.25 mL CH3 with [MMBL]0 = [MBL]0 = 0.936 M. a [MMBL]0, [MBL]0, and D determined by GPC relative to PMMA standards in DMF. a Monomer conversions measured by 1H NMR. a Mw and MWD determined by GPC relative to PMMA standards in DMF. a Initiator efficiency I* (%) = Mw(calcd)/Mw(exptl) × 100, where Mw(calcd) = [MW(MMBL)] × ([MMBL]/[I]0) (conversion) + MW of chain-end groups.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initiator (l)</th>
<th>Monomer (M)</th>
<th>[M][II][B] b</th>
<th>Time (h)</th>
<th>Conv. c (%)</th>
<th>Mw d (kg/mol)</th>
<th>D</th>
<th>I* c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Me2EtSiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>48.1</td>
<td>1.26</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>Me2PhSiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>57.4</td>
<td>1.39</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>Me2C6HsiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>2</td>
<td>100</td>
<td>78.6</td>
<td>1.44</td>
<td>29</td>
</tr>
<tr>
<td>4</td>
<td>Et3SiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>33</td>
<td>1.27</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>Ph2SiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>6</td>
<td>100</td>
<td>105</td>
<td>1.61</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>Bu2SiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>24</td>
<td>100</td>
<td>345</td>
<td>1.51</td>
<td>7</td>
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<tr>
<td>7</td>
<td>Me2PhSKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>45.5</td>
<td>1.33</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>Me2C6HSKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>41.5</td>
<td>1.37</td>
<td>54</td>
</tr>
<tr>
<td>9</td>
<td>Me2EtSiH</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>6</td>
<td>100</td>
<td>85.1</td>
<td>1.82</td>
<td>27</td>
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<tr>
<td>10</td>
<td>Ph3SKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>2</td>
<td>100</td>
<td>68.8</td>
<td>1.37</td>
<td>33</td>
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<tr>
<td>11</td>
<td>Me2SKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>1</td>
<td>100</td>
<td>31.9</td>
<td>1.08</td>
<td>71</td>
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<tr>
<td>12</td>
<td>tBu3SKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>0.5</td>
<td>100</td>
<td>37</td>
<td>1.21</td>
<td>60</td>
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<tr>
<td>13</td>
<td>Bu2SKA</td>
<td>MMBL</td>
<td>200:1:1</td>
<td>1</td>
<td>100</td>
<td>32.2</td>
<td>1.09</td>
<td>70</td>
</tr>
<tr>
<td>14</td>
<td>Bu2SKA</td>
<td>MMBL</td>
<td>100:1:1</td>
<td>0.17</td>
<td>100</td>
<td>13.2</td>
<td>1.08</td>
<td>86</td>
</tr>
<tr>
<td>15</td>
<td>Me2SKA</td>
<td>MBL</td>
<td>200:1:1</td>
<td>24</td>
<td>100</td>
<td>14.6 (58%)</td>
<td>1.20</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>Me2SKA</td>
<td>MBL</td>
<td>100:1:1</td>
<td>0.5</td>
<td>100</td>
<td>12.7</td>
<td>1.12</td>
<td>78</td>
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<tr>
<td>17</td>
<td>tBu2SKA</td>
<td>MBL</td>
<td>200:1:1</td>
<td>24</td>
<td>100</td>
<td>23.4</td>
<td>1.95</td>
<td>81</td>
</tr>
<tr>
<td>18</td>
<td>tBu2SKA</td>
<td>MBL</td>
<td>100:1:1</td>
<td>0.5</td>
<td>100</td>
<td>13.4</td>
<td>1.05</td>
<td>74</td>
</tr>
</tbody>
</table>

Table 2. B(C6F5)3-catalyzed copolymerization of MMBL and MBL by tBu2SKA/B(C6F5)3 system a.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M1/M2</th>
<th>Conv. b (%)</th>
<th>Mw c (kg/mol)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 d</td>
<td>100 MMBL + 100 MBL</td>
<td>MBL:100</td>
<td>28.3</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>100 MMBL/100 MBL</td>
<td>MBL:100</td>
<td>25.7</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>100 MMBL/100 MBL/100 MMBL</td>
<td>MBL:100</td>
<td>37.1</td>
<td>1.06</td>
</tr>
</tbody>
</table>

a Carried out in 2.25 mL CH3Cl2 at room temperature, where [MMBL]0 = [MBL]0 = 0.936 M and addition method: catalyst and monomer were premixed, followed by adding initiator to start the polymerization. b Monomer conversions measured by 1H NMR. c Mw and MWD determined by GPC relative to PMMA standards in DMF. d MBL and MMBL was added at the same time.

When switching to the SKA/B(C6F5)3 system, both Me2PhSKA/B(C6F5)3 and Me2EtSiHSKA/B(C6F5)3 system achieved quantitative monomer conversion in 30 min and similar initiation efficiency (50% vs. 54%) under our current standard polymerization conditions ([MMBL]0/[SKA]0/[B(C6F5)]3 = 200:1:1, 0.25 mL MMBL, 2.25 mL CH3Cl2, RT). Replacing the phenyl group with a chlorine atom, the rate of MMBL polymerization was drastically decreased and quantitative monomer conversion was obtained in 6 h for Me2ClSKA/B(C6F5)3 system, producing PMMMB with a Mw of 85.1 kg·mol⁻¹, a broader D value of 1.82 (Table 1, run 9), and thus giving a lower I*% of 27. The combination of Ph3SKA with B(C6F5)3 produced a polymerization system that is comparable with that of Me2ClSKA/B(C6F5)3 (run 10 vs. 9, Table 1). Interestingly, by replacing the three Ph groups with three electron-donating alkyl groups in SKA, we observed a significantly enhanced initiation efficiency I* (%) (71 for Me2SKA, run 11; 61 for tBu3SKA, run 12; 70 for tBu2SKA, run 13).

Since both Me2SKA/B(C6F5)3 and tBu2SKA/B(C6F5)3 system exhibited the highest initiation efficiency for the polymerization of MMBL (around 70%) under our current condition, therefore, we employed both systems to examine their efficacies for polymerization of the homologues of MMBL, MBL or tulipalin A, which is a natural substance found in tulips and the MBL ring is an integral building block of many natural products. For polymerization with a 200:1:1 [MBL]:[Me2SKA]:[B(C6F5)3] ratio, it took 24 h for both Me2SKA/B(C6F5)3 and tBu2SKA/B(C6F5)3 system to reach complete monomer
consumption. However, it should be noted that PMBL produced by $^{^6}$MeSKA/($C_6F_5)_3B$ system exhibited a bimodal MWD. For polymerization with 100:1:1 [MBL]/[SKA]/[($C_6F_5)_3B$] ratio, only 30 min is needed to achieve quantitative monomer conversion for both systems, affording PMBL with predicted $M_n$ and small $D$ values ($^{^6}$MeSKA: $M_n = 12.7$ kg·mol$^{-1}$, $D = 1.12$, $I^* = 78\%$, Run 16; $^{^i}$BuSKA: $M_n = 13.4$ kg·mol$^{-1}$, $D = 1.05$, $I^* = 74\%$, Run 18, Table 1). These results indicated $^{^i}$BuSKA/($C_6F_5)_3B$ system exhibited better control on the polymerization than that for $^{^6}$MeSKA/($C_6F_5)_3B$ system.

In fact, the MMBL polymerization by $^{^i}$BuSKA/($C_6F_5)_3B$ system is living and controlled, and near quantitative monomer conversion was achieved for polymerization with varied [MMBL]/[BuSKA] ratio from 100 to 800. GPC traces of PMMMBL produced by $^{^i}$BuSKA/($C_6F_5)_3B$ system also exhibited the gradual shift to the high-molar-mass region with an increase in the [M]/[I] ratio from 100 to 800 and maintained a narrow and unimodal MWD (Figure 1). Although increasing the catalyst loading of ($C_6F_5)_3B$ would enhance the polymerization rate, the polymer MW is dependent on the concentration of initiator $^{^i}$BuSKA and independent on the concentration of catalyst ($C_6F_5)_3B$ (vide infra), which is evidenced by the linear increase of the $M_n$ values of PMMMBL produced by $^{^i}$BuSKA/($C_6F_5)_3B$ system with an increase in the [MMBL]/[BuSKA] ratio from 100 to 800 (Figure 2, $R^2 = 0.994$), while $D$ values remained in the very narrow range of 1.08 to 1.13 (Figure 2). It is noted that $M_n$ value of PMMMBL obtained for polymerization with different [MMBL]/[($C_6F_5)_3B$] ratio maintained around 60 kg·mol$^{-1}$ (Figure S21), which revealed that the concentration of ($C_6F_5)_3B$ has an effect the polymerization rate, but not on both polymer MW and MWD. Therefore, ($C_6F_5)_3B$ is not the initiator but the catalyst for the activation of monomers. In addition to the aforementioned linearly increased polymer MW with the increase of varied monomer to initiator ratio, the living characteristics of MMBL polymerization by $^{^i}$BuSKA/($C_6F_5)_3B$ was also confirmed by a plot of the PMMMBL $M_n$ vs monomer conversion at a fixed [MMBL]/[BuSKA]/[($C_6F_5)_3B$] ratio of 400:1:1, which clearly show a straight line ($R^2 = 0.999$) with very narrow $D$ value in the range of 1.08–1.2 (Figure 3).

$\textbf{Figure 1.}$ GPC traces of PMMMBL samples produced by $^{^i}$BuSKA/($C_6F_5)_3B$ with various [MMBL]/[BuSKA] ratios at RT. Conditions: [MMBL]$_0$/[BuSKA]$_0$/[($C_6F_5)_3B$]$_0$ = 400:4:1, 400:2:1, 400:1:1, 400:0.5:1, [MMBL]$_0 = 0.936$ M.
with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}·MMBL probably due to high reactivity of dimeric SKA analogue for reaction of SKA with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}·MMBL. Similar FLP was generated in the reaction of MeSKA with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in 1:1 ratio and observed the formation of FLP, which is evidenced by the fact that there is no obvious interaction observed in the reaction of MeSKA with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (Figures S11 and S12).

We also prepared B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}·MMA (Figures S7 and S8) and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}·MMBL (Figures S9 and S10) adduct for the study of their reaction with SKA, respectively. The reaction of MeSKA with B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}·MMA at room temperature in C\textsubscript{6}D\textsubscript{6} generated major products of dimeric SKA analogue Me\textsubscript{3}SiO(OMe)C≡C(Me)CH\textsubscript{2}CMMe\textsubscript{2}C(OMe)=O··IB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} as two isomers (Z/E) in a 3:2 ratio due to the cis-trans isomerism of MMA (Scheme 2), which could readily derived from the analysis of \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectra (Figures S15 and S17). The characteristic proton signals at 0.18 ppm for major isomer and 0.16 ppm for minor isomer attributed to the trimethyl substituents of silyl group in the dimeric SKA analogue is the result of the high field shift from the original 0.18 ppm for neutral MeSKA,
which is different from that for Me$_3$Si$^+$ generated by vinylogous hydride abstraction of MeSKA with Ph$_3$C$^+$, exhibiting signal at 0.65 ppm [49]. This result suggests that the silyl group in the dimeric SKA analogue was neutral rather than Me$_3$Si$^+$. In combination with the fact that $^{19}$F NMR spectrum exhibiting similar signals [δ -129.03 (br, 6F, o-F), −142.24 (br, 3F, p-F), −160.09 (s, 6F, m-F))] (Figure S16) with that for B(C$_6$F$_5$)$_3$·MMA adduct (Figure S8), we proposed the structure for corresponding dimeric SKA analogues as shown in Scheme 2. Similarly, the reaction of $^1$BuSKA with B(C$_6$F$_5$)$_3$·MMA cleanly afforded the single-monomer-addition product (Scheme 2), as revealed by the $^1$H-, $^{19}$F- and $^{13}$C-NMR spectra (Figure 4a,b, and Figure S20). However, we did not observe the formation of such dimeric SKA analogue for reaction of SKA with B(C$_5$F$_3$)$_3$·MMBL probably due to high reactivity of MMBL.

Scheme 2. Generation of first-monomer-addition intermediate or active propagating species (A or B denotes Z/E isomers).

Figure 4. (a) $^1$H- and (b) $^{19}$F-NMR spectra of $^1$Bu$_3$SiO(OMe)C=C(Me)CH$_2$CMe$_2$C(OMe)=O···B(C$_5$F$_3$)$_3$. 

![Scheme 2](image2.png)

![Figure 4](image1.png)
2.4. Kinetics and Mechanism of Polymerization

To continue the investigation of the mechanistic aspects of the polymerization, we next examined the kinetics of the MMBL polymerization by the $[^i\text{Bu}]\text{SKA}/[\text{B(C}_6\text{F}_5)_3]$. The kinetic experiments employed $[\text{MMBL}]_0/[[^i\text{Bu}]\text{SKA}]_0/[\text{B(C}_6\text{F}_5)_3]_0$ with varied ratio of 400:1:0.5, 400:1:1, 400:1:2, 400:1:4 and a fixed $[\text{MMBL}]_0/[[^i\text{Bu}]\text{SKA}]_0$ ratio of 400. As can be seen from the representative kinetic plots of $\ln([\text{MMBL}]_0/[^i\text{Bu}]\text{SKA})$ vs. time, the polymerization clearly showed a first-order dependence on $[\text{MMBL}]$ for all ratios investigated (Figure 5). Furthermore, a double logarithm plot (insert) of the apparent rate constants ($k_{app}$) obtained from the slopes of the best-fit lines to the plots of $\ln([\text{MMBL}]_0/[^i\text{Bu}]\text{SKA})$ vs. time as a function of $\ln[\text{B(C}_6\text{F}_5)_3]$ was fit to a straight line ($R^2 = 0.960$) with a slop of 2.07. Therefore, the kinetic order with respect to the $[\text{B(C}_6\text{F}_5)_3]$ catalyst concentration; these kinetics results suggest a bimolecular propagation.

![Figure 5](image_url)

**Figure 5.** First-order kinetic plots for MMBL polymerization by $[^i\text{Bu}]\text{SKA}/[\text{B(C}_6\text{F}_5)_3]$ in CH$_2$Cl$_2$ at RT: $[\text{MMBL}]_0 = 0.936$ M; $[^i\text{Bu}]\text{SKA}]_0 = 2.34$ mM; $[\text{B(C}_6\text{F}_5)_3]_0 = 9.36$ mM (Δ), 4.68 mM (▲), 2.34 mM (□), 1.17 mM (■). Inset: plot of $\ln(k_{app})$ vs. $\ln[\text{B(C}_6\text{F}_5)_3]$. In the second set of kinetic experiments, with a fixed $[\text{MMBL}]_0/[\text{B(C}_6\text{F}_5)_3]_0$ ratio of 400, the kinetic experiments was carried out with varied $[\text{MMBL}]_0/[\text{B(C}_6\text{F}_5)_3]_0/[[^i\text{Bu}]\text{SKA}]_0$ ratio of 400:1:0.5, 400:1:1, 400:1:2, 400:1:4. The same first-order dependence was observed for all ratios investigated in this study (Figure 6). A double logarithm plot (insert) of the apparent rate constants ($k_{app}$), obtained from the slopes of the best-fit lines to the plots of $\ln([\text{MMBL}]_0/[\text{MMBL}])$ vs. time, as function of $\ln[^i\text{Bu}]\text{SKA}$ was fit to a straight line ($R^2 = 0.960$) with a slop of 1.132, revealing that the propagation is first-order in the concentration of $[^i\text{Bu}]\text{SKA}$. Overall, the polymerization by the $[^i\text{Bu}]\text{SKA}/[\text{B(C}_6\text{F}_5)_3]$ systems follows a bimolecular, activated monomer propagation mechanism.

On the basis of the above kinetic results, coupled with mechanistic insights obtained through monitoring the polymerization and characterization of the reaction intermediates (vide supra), we propose the following initiation and propagation mechanism for polymerization of polar vinyl monomers by the SKA/[$\text{B(C}_6\text{F}_5)_3$ LP system taking MMBL as example (Scheme 3). In this mechanism, the reaction was initiated with the intermolecular Michael addition of the ester enolate groups of the SKA to the vinyl group of $\text{B(C}_6\text{F}_5)_3$-activated monomer, meanwhile the Si-O bond of SKA was cleaved and the silyl group was transferred to the carbonyl group of the $\text{B(C}_6\text{F}_5)_3$-activated...
monomer to generate the single-monomer-addition species or the active propagating species. In the propagation cycle, the $\mathrm{B(C_6F_5)_3}$ catalyst is released from the propagating chain to the incoming monomer, followed by the subsequent intermolecular Michael addition to generate the polymeric SKA intermediate (Scheme 3). Our kinetic studies indicated that the polymerization is first-order dependent on both monomer and $\mathrm{iBuSKA}$ initiator concentration, but second-order dependent on $\mathrm{B(C_6F_5)_3}$ catalyst concentrations, which revealed that the rate ($k_2$) of the intermolecular Michael addition of the SKA or its homologues to the $\mathrm{B(C_6F_5)_3}$-activated monomer is comparable with that ($k_1$) for the release of the catalyst $\mathrm{B(C_6F_5)_3}$ from the ester group of the growing polymer chain to the incoming monomer for monomer activation ($k_1 \approx k_2$).

The low MW PMMBL produced by the $\mathrm{iBuSKA/B(C_6F_5)_3}$ system was analyzed by matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF MS). As can be seen from Figure 7, The MS spectrum consisted of two series of molecular mass ions. A plot (Figure 8a) of $m/z$ values for the major series vs the number of MMBL repeat units ($n$) yielded a straight line with a slope of 112 (mass of MMBL) and an intercept of 323 corresponding to the sum of end groups: MeOC(=O)C(Me)$_2$/Si(iBu)$_3$ + Na$^+$. This analysis yielded a polymer chain structure of MeOC(=O)C(Me)$_2$-(MMBL)$_n$-Si(iBu)$_3$, with both the initiating (the ester enolate group) and termination (the silyl group) chain ends being derived from $\mathrm{iBuSKA}$. Furthermore, a linear plot of $m/z$ values for the minor series in the MS spectrum vs the MMBL repeat units ($n$) gave the same slope but a different intercept of 125 (Figure 8b), which corresponds to the sum of end groups: MeOC(=O)C(Me)$_2$-(MMBL)$_n$-H + Na$^+$. Formation of such enolate/H chain end is presumably a result of desilylation during the preparation of the MALDI-TOF sample.
Figure 7. MALDI-TOF mass spectrum of the low-MW PMMBL sample produced by $^{i}{\text{BuSKA}}/B(C_6F_5)_3$ in $\text{CH}_2\text{Cl}_2$ at RT.
2.5. Random and Block Copolymerizations of MMBL with MBL

The living features of polymerization of MMBL and MBL by \(^{1}\text{BuSKA}/[\text{B}(\text{C}_6\text{F}_5)_3]\) system, as demonstrated by the above described experiments, also enabled the synthesis of well-defined copolymers. As shown in Table 2, when both monomers were added simultaneously, the copolymerization of MBL and MMBL produced a randomly sequenced copolymer with \(M_n = 28.3 \text{ kg mol}^{-1}\) and \(D = 1.03\) (run 1, Table 2, Figure S23). On the other hand, sequential block copolymerization by polymerizing MMBL first with \([\text{MMBL}]/[\text{^{1}BuSKA}] / [\text{B}(\text{C}_6\text{F}_5)_3] = 100:1:1\) without quenching, followed by addition of another 100 equiv. of MBL, successfully afforded linear diblock copolymer PMMBL-b-PMBL. As can be seen from Figure 9, the GPC traces for the PMMBL produced during the initial MMBL polymerization shifted to a higher molecular weight region with low MWD value of 1.07, while the \(M_n\) increase from 13.2 kg mol\(^{-1}\) (black trace) for the homopolymer PMMBL to 25.7 kg mol\(^{-1}\) (red trace) for the diblock copolymer PMMBL-b-PMBL (run 2, Table 2), which provided further evidence for the formation of well-defined block copolymer by \(^{1}\text{BuSKA}/[\text{B}(\text{C}_6\text{F}_5)_3]\) system. Through the same sequential monomer addition method, well-defined triblock copolymer PMMBL-b-PMBL-b-PMMBL was also successfully prepared with a \(M_n\) value of 37.1 kg/mol and a \(D\) value of 1.06 (Figure 9, blue trace, run 3, Table 2). We also characterized both block copolymers and random copolymers by \(^{13}\text{C}-\text{NMR}\) analysis (Figure S21). In contrast to diblock copolymer PMMBL-b-PMBL showing two signals corresponding to the PMBL and PMMBL, the yielded random copolymer PMMBL-r-PMBL only exhibited one broad peak.
in the carbonyl signals, which is ranging between the signals for homopolymers PMBL and PMMBL. The combination of such conclusive \(^{13}\)C NMR results and GPC analyses should provide sufficient evidence for the formation of random and block copolymer from statistical and sequential block polymerization, respectively.

![Figure 9](image)

**Figure 9.** GPC traces of homopolymer PMMBL (black), diblock copolymer PMMBL-b-PMBL (red), and triblock copolymer PMMBL-b-PMBL-b-PMBL (blue) produced by \(^{13}\)BuSKA/B(C\(_6\)F\(_5\))\(_3\) in CH\(_2\)Cl\(_2\) at RT.

3. Materials and Methods

3.1. Materials, Reagents and Methods

All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or an inert gas-filled glovebox. Toluene, benzene, THF and hexane were refluxed over sodium/potassium alloy distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. CH\(_2\)Cl\(_2\) was refluxed over CaH\(_2\) distilled under nitrogen atmosphere, then stored over molecular sieves 4 Å. Benzene-\(d_6\) was dried over molecular sieves 4 Å. NMR spectra were recorded using an Avance II 500 (500 MHz, \(^1\)H; 126 MHz, \(^13\)C; 471 MHz, \(^19\)F) instrument (Bruker, Karlsruhe, Baden-Württemberg, Germany) in appropriate deuterated solvents at room temperature. Chemical shifts for \(^1\)H and \(^13\)C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe\(_4\), whereas \(^19\)F-NMR spectra were referenced to external CFCl\(_3\). Air sensitive NMR samples were conducted in Teflon-valve sealed J. Young-type NMR tubes.

Methyl methacrylate (MMA) was purchased from J&K (Beijing, China), while \(\alpha\)-methylene-\(\gamma\)-butyrolactone (MBL) and \(\gamma\)-methyl-\(\alpha\)-methylene-\(\gamma\)-butyrolactone (MMBL) were purchased from TCI (Tokyo, Japan). These monomers were first degassed by three freeze-pump-thaw cycles and dried over CaH\(_2\) for 12 h, followed by vacuum distillation. Further purification of MMA involved titration with tri(\(n\)-octyl)aluminum (Strem Chemicals, Newburyport, MA, USA) to a yellow end point [56], followed by distillation under reduced pressure. All purified monomers were stored in brown bottles inside a glovebox freezer at \(-30^\circ\)C. Dimethylphenylsilane (Me\(_2\)PhSiH), and triphenylsilane (Ph\(_3\)SiH) were purchased from TCI. Triisobutylsilane (iBu\(_3\)SiH), dimethylethylsilane (Me\(_2\)EtSiH), dimethylketene methyl trimethylsilyl acetal (\(^{13}\)BuSKA) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Butylated hydroxytoluene (BHT-H, 2,6-di-tert-butyl-4-methylphenol), triethylsilane (Et\(_3\)SiH), chlorodimethyl-silane (Me\(_2\)ClSiH), bromopentafluorobenzene were purchased from J&K. Boron trichloride (1.0 M solution in hexanes) and \(n\)-BuLi (2.5 M solution in hexanes)
were purchased from Energy Chemical (Shanghai, China). Tris(pentafluorophenyl)borane, B(C₆F₅)₃, was prepared according to literature procedures.[57,58] Literature procedures were also employed for the preparation of the following compounds: dimethylketene methyl triethyloxysilic acid (Me₂SKA) [49], dimethylketene methyl triphenylsilyl acetal Me₂C=C(OH)OSiPh₃ (PhSKA) [50], dimethylketene methyl trisobutylsilyl acetal Me₂C=C(OH)OSi(iBu)₃ (iBuSKA) [50], dimethylketene methyl dimethyl-phenylsilyl acetal Me₂C=C(OH)OSiMe₂ (Mes₂SKA) [54].

3.2. Synthesis of Dimethylketene Methyl Chlorodimethylsilane Acetal Me₂C=C(OH)OSiMe₂Cl (Me₂ClSKA)

In an inert gas-filled glovebox, solution containing B(C₆F₅)₃ (128 mg, 0.250 mmol) and MMA (2.65 mL, 25.0 mmol) in dry CH₂Cl₂ (50 mL) was charged in a 100 mL Schlenk flask equipped with a stir bar. This flask was sealed with a rubber septum, removed from the glovebox, interfaced to a Schlenk line, and brought to −78 °C for at least 15 min. Chlorodimethylsilane (2.78 mL, 25.0 mmol) was added dropwise to the above flask under nitrogen atmosphere. The resulting mixture was allowed to warm up to room temperature slowly and then subjected to vacuum. The residue was purified by vacuum distillation to afford the final product as colorless oil. Yield: 3.84 g (79%).

1H-NMR (500 MHz, benzene-d₆) δ 3.35 (s, 3H, OCH₃), 1.64 (s, 3H, =CMe), 1.61 (s, 3H, =CMe), 0.36 (s, 6H, SiMe₂Cl).

13C-NMR (126 MHz, benzene-d₆) δ 149.2, 92.8, 57.2, 17.1, 16.4, 2.3.

3.3. Synthesis of Chloro(ethoxy)dimethylsilane Me₂(EtO)SiCl

Literature procedures [59] were modified for the preparation of Me₂(EtO)SiCl. In an inert gas-filled glovebox, solution of B(C₆F₅)₃ (461 mg, 0.90 mmol) and EtOH (5.08 mL, 90.0 mmol) in dry CH₂Cl₂ (100 mL) was charged in a 200 mL Schlenk flask equipped with a stir bar. This flask was sealed with a rubber septum, removed from the glovebox, interfaced to a Schlenk line, and brought to −78 °C for at least 20 min. Chlorodimethylsilane (1.00 mL, 90.0 mmol) was added dropwise to the flask under nitrogen atmosphere. The resulting mixture was allowed to warm up to room temperature slowly and then subjected to vacuum. The residue was purified by distillation to afford the product as colorless oil. Yield: 12.48 g (91%).

1H-NMR (500 MHz, benzene-d₆) δ 3.61 (q, J = 7.0 Hz, 2H, OCMe), 1.72 (s, 3H, =CMe), 1.68 (s, 3H, =CMe), 1.13 (t, J = 7.0 Hz, 3H, OCH₂CH₃), 0.26 (s, 6H, SiMe₂).

13C-NMR (126 MHz, benzene-d₆) δ 149.8, 90.7, 58.6, 56.6, 18.5, 17.1, 16.5, −2.5.

3.4. Synthesis of Dimethylketene Methyl Ethoxymethylsilyl Acetal Me₂C=C(-OMe)OSiMe₂(EtO) (Me₂EtO)SKA

Literature procedures for the general synthesis of ketene trialkysilyl acetals [60,61] were modified for the preparation of Me₂(EtO)SKA. In an inert gas-filled glovebox, a solution of diisopropylamine (7.05 mL, 5.06 g, 50.0 mmol) in dry THF (100 mL) was charged in a 200 mL Schlenk flask equipped with a stir bar. This flask was sealed with a rubber septum, removed from the glovebox, interfaced to a Schlenk line, and placed in a 0 °C ice-water bath for at least 15 min. n-Butyllithium (32.0 mL, 1.6 M in hexane, 51.2 mmol) was added dropwise to the above flask under nitrogen atmosphere. After stirring at 0 °C for 30 min, methyl isobutyrate (5.74 mL, 5.11 g, 50.0 mmol) was added slowly. The reaction mixture was stirred at this temperature for 30 min, after which Chloro(ethoxy)dimethylsilane (7.61 g, 50.0 mmol) was added. The mixture was allowed to warm slowly to room temperature and stirred overnight, after which all volatiles were removed in vacuum and hexanes (50 mL) was added. The resulting precipitates were filtered off under nitrogen atmosphere, the solvent of the filtrate was removed under reduced pressure. The residue was purified by distillation under vacuum to afford the product as colorless oil. Yield: 8.79 g (86%).

1H-NMR (500 MHz, benzene-d₆) δ 3.72 (q, J = 7.0 Hz, 2H, OCH₂CH₃), 3.39 (s, 3H, OMe), 1.72 (s, 3H, =CMe), 1.68 (s, 3H, =CMe), 1.13 (t, J = 7.0 Hz, 3H, OCH₂CH₃), 0.21 (s, 6H, SiMe₂).

13C-NMR (126 MHz, benzene-d₆) δ 149.8, 90.7, 58.6, 56.6, 18.5, 17.1, 16.5, −2.5.
3.5. Isolation of Adduct B(C₆F₅)₃·MMA

To a solution of B(C₆F₅)₃ (512 mg, 1.0 mmol) in hexane (15 mL) was added MMA (110 mg, 1.1 mmol) at room temperature with reacting for 30 min. The solution was brought to −30 °C in glovebox freezer for 1 h. After filtration and removal of organic solvents in vacuo, the B(C₆F₅)₃·MMA was obtained as a white powder (546 mg, 89%). ¹H-NMR (benzene-d₆) δ 5.91 (s, 1H, =CH), 5.05–5.03 (3H, =CH), 5.39 (s, 3H, OMe), 1.63 (s, 3H, Me). ¹⁹F-NMR (benzene-d₆) δ −130.18 (d, J = 20.2 Hz, 6F, o-F), −144.90 (t, J = 20.8 Hz, 3F, p-F), −160.70 (m, 6F, m-F).

3.6. Isolation of Adduct B(C₆F₅)₃·MMBL

The B(C₆F₅)₃·MMBL adduct was isolated as a white powder in 91% yield using the same procedure as described for the isolate of the adduct B(C₆F₅)₃·MMA. ¹H-NMR (500 MHz, benzene-d₆) δ 6.06 (t, J = 3.0 Hz, 1H, =CH), 4.86 (t, J = 2.7 Hz, 1H, =CH), 3.67 (ddq, J = 8.0, 6.3, 5.7 Hz, 1H, OCH), 1.56 (ddt, J = 17.3, 8.0, 2.7 Hz, 1H, CH₂), 1.10 (ddt, J = 17.3, 5.7, 2.9 Hz, 1H, CH₂), 0.26 (d, J = 6.3 Hz, 3H, Me). ¹⁹F-NMR (471 MHz, benzene-d₆) δ −134.81 (dd, J = 23.2, 7.3 Hz, 6F, o-F), −156.72 (t, J = 20.7 Hz, 3F, p-F), −163.93 (m, 6F, m-F).

3.7. NMR Reaction of Me₂C=CM(O)MeSiMe₂ (MeSKA) with B(C₆F₅)₃

In an inert gas-filled glovebox, solution of MeSKA (1.74 mg, 0.01 mmol) in 0.3 mL of C₆D₆ was charged in a Teflon-valve-sealed J. Young-type NMR tube. A 0.3 mL C₆D₆ solution of B(C₆F₅)₃ (5.12 mg, 0.01 mmol) was added to this tube via pipet at room temperature and allowed to react for ~15 min before the NMR spectra were recorded, which showed there were no reaction between MeSKA and B(C₆F₅)₃. ¹H-NMR (500 MHz, benzene-d₆) δ 3.33 (s, 3H, OMe), 1.73 (s, 3H, =CM), 0.65 (s, 3H, =CM), 0.18 (s, 9H, SiMe₃). ¹⁹F-NMR (471 MHz, benzene-d₆) δ −128.82 (d, J = 21.7 Hz, 6F, o-F), −141.81 (t, J = 21.3 Hz, 3F, p-F), −160.06 (m, 6F, m-F).

3.8. NMR Reaction of MeSKA with B(C₆F₅)₃·MMA

In an inert gas-filled glovebox, solution of MeSKA (1.74 mg, 0.01 mmol) in 0.3 mL of C₆D₆ was charged in a Teflon-valve-sealed J. Young-type NMR tube. A 0.3 mL C₆D₆ solution of B(C₆F₅)₃·MMA (6.12 mg, 0.01 mmol) was slowly added to this tube via pipet at room temperature and allowed to react for ~15 min before the NMR spectra were recorded. The resulting mixture showed the clean formation of the species Me₃SiO(O)Me=C(Me)CH₂Me₂C(Me)=O·…B(C₆F₅)₃ (I) as two isomers (Z/E) in 3:2 ratio: major isomer 1A and minor isomer 1B, plus a small amount of unreacted starting materials. 1A: ¹H-NMR (500 MHz, benzene-d₆) δ 3.395 (s, 3H, OMe), 3.25 (s, 3H, COOMe), 2.53 (s, 2H, CH₂), 1.65 (s, 3H, Me), 1.31 (s, 6H, Me₂), 0.18 (s, 9H, SiMe₃); 1B: δ 3.392 (s, 3H, OMe), 3.30 (s, 3H, COOMe), 2.46 (s, 2H, CH₂), 1.72 (s, 3H, Me), 1.32 (s, 6H, Me₂), 0.16 (s, 9H, SiMe₃); ¹⁹F-NMR (471 MHz, benzene-d₆) δ −129.03 (br, 6F, o-F), −142.24 (br, 3F, p-F), −160.09 (s, 6F, m-F). ¹³C-NMR (126 MHz, benzene-d₆) δ 178.30, 178.2, 153.3, 152.2, 149.4, 147.4, 138.7, 136.7, 92.1, 91.6, 57.2, 55.6, 51.4, 51.3, 43.14, 43.05, 42.5, 42.4, 25.8, 16.5, 15.4, 0.3, 0.1.

3.9. NMR Reaction of Me₂C=CM(O)MeSi('Bu)₃ (iBuSKA) with B(C₆F₅)₃

This reaction was carried out in the same manner as the reaction of MeSKA with B(C₆F₅)₃, which showed there were no reaction between iBuSKA and B(C₆F₅)₃. ¹H-NMR (500 MHz, benzene-d₆) δ 3.38 (s, 3H, OMe), 1.98 (sept, J = 6.6 Hz, 3H, CHMe₂), 1.70 (s, 3H, =CM), 1.69 (s, 3H, =CM), 1.05 (d, J = 6.6 Hz, 18H, CHMe₂), 0.84 (d, J = 6.8 Hz, 6H, SiCH₂). ¹⁹F-NMR (471 MHz, benzene-d₆) δ −128.82 (d, J = 21.7, 6F, o-F), −141.83 (t, J = 20.9 Hz, 3F, p-F), −160.07 (m, 6F, m-F).

3.10. NMR Reaction of iBuSKA with B(C₆F₅)₃·MMA

This reaction was carried out in the same manner as the reaction of MeSKA with B(C₆F₅)₃·MMA, forming cleanly iBu₃SiO(O)Me=C(Me)CH₂Me₂C(OMe)=O·…B(C₆F₅)₃ (3) as two isomers (Z/E) in
4:3 ratio: major isomer 2A and minor isomer 2B. 2A: 1H-NMR (500 MHz, benzene-d$_6$) δ 3.401 (s, 3H, OMe), 3.30 (s, 3H, COOMe), 2.52 (s, 2H, CH$_2$), 1.98 (m, 3H, CHMe$_2$), 1.71 (s, 3H, Me$_2$), 1.32 (s, 6H, CMe$_2$), 1.05 (d, $J = 6.5$ Hz, 18H, CHMe$_2$), 0.85 (d, $J = 6.9$ Hz, 6H, SiCH$_2$)$_3$; 2B: δ 3.397 (s, 3H, OMe), 3.37 (s, 3H, COOMe), 2.56 (s, 2H, CH$_2$), 1.98 (m, 3H, CHMe$_2$), 1.68 (s, 3H, Me$_2$), 1.36 (s, 6H, CMe$_2$), 1.04 (d, $J = 6.8$ Hz, 18H, CHMe$_2$), 0.82 (d, $J = 6.9$ Hz, 6H, SiCH$_2$)$_3$; 19F-NMR (471 MHz, benzene-d$_6$) δ –128.84 (br, 6F, o-F), –141.82 (br, 3F, p-F), –159.99 (m, 6F, m-F). 13C-NMR (126 MHz, benzene-d$_6$) δ 149.4, 147.4, 138.7, 136.7, 92.5, 58.6, 56.9, 51.3, 51.3, 43.0, 42.4, 42.3, 26.8, 26.7, 26.5, 26.4, 25.9, 25.7, 24.5, 16.6, 15.1.

3.11. General Polymerization Procedures

Polymerizations were performed in 20 mL glass reactors inside the inert gas-filled glovebox for ambient temperature (ca. 25 °C) runs. In a typical procedure, a predetermined amount of B(C$_6$F$_5$)$_3$ and monomer (1 mL for MMA, 250 μL for MMBL or 205 μL for MBL, 200 equiv. relative to the SKA) were dissolved in dry CH$_2$Cl$_2$. A solution of a SKA (1 equiv. of a LA) in 1.0 mL of solvent were added rapidly via a gastight syringe to the solution of B(C$_6$F$_5$)$_3$-monomer. The amount of the monomer was fixed for all polymerizations. After stirring for the measured time, a 0.1 mL aliquot was withdrawn from the reaction mixture and quickly quenched into 0.6 mL of undried “wet” CDCl$_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by 1H-NMR to obtain the monomer conversion. After the polymerization was stirred for the stated reaction time then the reactor was taken our of the glovebox, and quenched by addition of 10 mL of 5% HCl-acidified methanol. The quenched mixture was isolated by filtration and dried in vacuo overnight at room temperature to a constant weight.

3.12. Polymerization Kinetics

Kinetic experiments were carried out in a stirred glass reactor at ambient temperature (ca. 25 °C) inside an inert gas-filled glovebox using the polymerization procedure already described above, with the [B(C$_6$F$_5$)$_3$]/[iBuSKA] ratio was 0.5/1, 1/1, 2/1, 4/1, [MMBL]$_0$ was fixed at 0.936 M and [iBuSKA]$_0$ was fixed at 2.34 mM, where [B(C$_6$F$_5$)$_3$] = 1.17, 2.34, 4.68, 9.36 mM in 2.5 mL mixture solutions. At appropriate time intervals, 0.1 mL aliquots were taken from the reaction mixture and quickly quenched into 0.6 mL of undried “wet” CDCl$_3$ mixed with 250 ppm BHT-H. The quenched aliquots were analyzed by 1H-NMR for determining the [MMBL]$_t$ at a given time $t$ and Ln([MMBL]$_t$/[MMBL]$_0$). Apparent rate constants ($k_{app}$) were extracted from the slopes of the best fit lines to the plots of Ln([MMBL]$_t$/[MMBL]$_0$) vs. time. Another set of kinetic experiments were carried out to determine the kinetic order with respect to [iBuSKA]. In these experiments, with the [B(C$_6$F$_5$)$_3$]/[iBuSKA] ratio was 1/0.5, 1/1, 1/2, 1/4, [MMBL]$_0$ was fixed at 0.936 M and [B(C$_6$F$_5$)$_3$]$_0$ was fixed at 2.34 mM, where [iBuSKA] = 1.17, 2.34, 4.68, 9.36 mM in 2.5 mL mixture solutions. The rest of the procedure was same as the described above.

3.13. Polymer Characterizations

Number-average molecular weight ($M_n$) and molecular weight distributions ($D = M_w/M_n$) of polymers were measured by gel permeation chromatography (GPC) at 35 °C and a flow rate of 1 mL/min, with DMF (HPLC grade, containing 50 mmol/L LiBr) as an eluent on a Waters 1515 instrument (Milford, MA, USA) equipped with a Waters 4.6 × 30 mm guard column and three Waters WAT054466, WAT044226, WAT044223 columns (Polymer Laboratories, Milford, MA, USA; linear range of molecular weight = 500 to 4 × 10$^6$). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Breeze 2 software (version: 6.01.2154.026; Milford, MA, USA). Tacticities of PMMA was measured by 1H-NMR in CDCl$_3$, while 13C-NMR of P(M)MBL (co)polymers were recorded in DMSO-d$_6$.

The isolated low-MW polymer samples were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS); the experiment was performed on a Bruker Autoflex speed TOF/TOF mass spectrometer (Karlsruhe, Baden-Württemberg, Germany) in linear, positive ion, reflector mode using a 25 KV accelerating voltage. A thin layer of
1% CF$_3$COONa solution was first deposited on the target plate, followed by 0.6 µL of both sample and matrix (trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB), 20 mg/mL in THF). The spectra of the sample was externally calibrated using a peptide calibration mixture (4–6 peptides). The raw data were processed in the Bruker Daltonics FlexAnalysis 3.3.80.0 software (Karlsruhe, Baden-Württemberg, Germany).

4. Conclusions

In summary, FLPs based on bulky organo-LA, B(C$_6$F$_5$)$_3$, and SKAs either preformed or in-situ generated from the hydrosilylation with R$_3$SiH, were employed for GTP of polar vinyl monomers, including linear MMA as well as the cyclic renewable monomers MMBL and MBL. Although the polymerizations of MMA by both R$_3$SiH/B(C$_6$F$_5$)$_3$ and SKA/B(C$_6$F$_5$)$_3$ systems are sluggish, SKA/B(C$_6$F$_5$)$_3$ system promotes the living/controlled GTP of MMBL and MBL, achieving polymers with predicted $M_n$ values and narrow $D$ values.

The formation of FLP was confirmed by in situ NMR reactions of SKA with B(C$_6$F$_5$)$_3$. Detailed investigations into the characterization of key reaction intermediates, polymerization kinetics and polymer structures have led to a GTP polymerization mechanism, in which the reaction was initiated with the intermolecular Michael addition of the SKA enolate group to vinyl group of B(C$_6$F$_5$)$_3$-activated monomer, while the silyl group is transferred to the carbonyl group of the monomer to generate the SKA analogues and release B(C$_6$F$_5$)$_3$ which reenters the next catalytic cycle for the activation of incoming monomer. The living features of such iBuSKA/B(C$_6$F$_5$)$_3$FLP system enabled us to successfully synthesize well-defined diblock, triblock copolymer PMMBL-b-PMBL and PMMBL-b-PMBL-b-PMMBL with predicted $M_n$ by using such iBuSKA/B(C$_6$F$_5$)$_3$ FLP system.

Supplementary Materials: Supplementary materials are available online.

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Author Contributions: Lu Hu carried out the synthesis of all silyl ketene acetals (SKAs), and SKA/B(C$_6$F$_5$)$_3$ Lewis Pair-catalyzed (co)polymerization of all monomers, investigation of polymerization kinetics, characterization through in situ NMR reaction and MALDI-TOF MS analyses and draft the manuscript. Wuchao Zhao measured both the number average molecular weight ($M_n$) and molecular weight distributions ($D = M_w/M_n$) of yielded polymers by GPC. Jianghua He analyzed and summarized all data. Yuetao Zhang supervised the whole research work, and finalized the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: Samples of the compounds are available from the authors.