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RESEARCH ARTICLE

Lewis Pair Polymerization of Alkyl Methacrylate by Amidinato Silicon Compounds and Tris(pentafluorophenyl)borane

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Abstract: 0.5 mol% of the amidinato disilyne $[LSi:]_2$ (**1**, L = PhC(N*t*Bu)$_2$) and 1 mol% of $B(C_6F_5)_3$ cooperatively polymerized methyl methacrylate (MMA) to form poly(MMA) with the H and $CH_2C(=CH_2)COMe$ end groups (**P1**, M_n = 3.1 ×10^3 $gmol^{-1}$; repeating unit, n = 31; polydispersity index, Đ: 1.55). The catalytic mechanism is proposed, where compound **1** could react with MMA and $B(C_6F_5)_3$ to form a zwitterionic active species $[LSi\{CH_2C(Me)=C(OMe)O\}B(C_6F_5)_3]_2$. The latter could activate MMA molecules affording poly(MMA) chains on the silicon centers. The methyl group of the last enolate of a poly(MMA) chain on a silicon center could then react with the Si-C bond of the adjacent poly(MMA) chain to form **P1**, as well as regenerate compound **1** and $B(C_6F_5)_3$. When compound **1** was replaced by the amidinato amidosilylene $[LSiN(SiMe_3)_2]$ (**2**), 1 mol% of compound **2** and 1 mol% of $B(C_6F_5)_3$ mediated living MMA polymerization in toluene to form the poly(MMA) **P2** (M_n = 1.04 ×10^4 $gmol^{-1}$; Đ: 1.97).

Introduction

Low-oxidation state silicon compounds with a formal oxidation state of +2, +1 and 0 are of particular interest due to possession of donor and acceptor valence orbitals with small energy gaps.[1] These electronic properties enable some of them showing transition metal like reactivity in small molecules activation,[2] in particular reversible oxidative addition and reductive elimination.[3] The activation of small molecules is also achievable when low-oxidation state silicon compounds formed a frustrated Lewis pair with Lewis acids.[4] However, the use of stable low-oxidation state silicon compounds for catalytic organic synthesis was seldom reported. It is possibly due to the activated small molecules hardly undergo further transformation to form new products, which can be subsequently eliminated from the silicon centers.[5] Only the cyclopentadienyl silyliumylidene cation $[Cp^*Si]^+$ (Cp^* = C_5Me_5) and NHC-silyliumylidene cation $[(I_{Me})_2SiH]^+$ (I_{Me} = $:C\{N(Me)C(Me)\}_2$) were shown to catalyze the controlled degradation of oligo(ethyleneglycol) diethers, hydrosilylation of olefins, Piers-Rubinsztajn reaction, hydroboration of carbon dioxide, carbonyl compounds and pyridine derivatives, as well as N-formylation of amines, respectively.[6] It is indispensable to discover more application of low-oxidation state silicon compounds in catalytic organic reactions, which would greatly advance sustainable catalysis due to the high abundance and relatively low toxicity of silicon.

Recently, Lewis bases such as N-heterocyclic carbenes, N-heterocyclic olefins, phosphines and phosphazenes were paired with Lewis acids such as $B(C_6F_5)_3$, $Al(C_6F_5)_3$, $MeAl(BHT)_2$ (BHT =

2,6-di-tert-butyl-4-methylphenoxide) and silylium ions to cooperatively polymerize a diversity of polar vinyl monomers such as methacrylates, polar divinyl monomers, acrylamides, dialkyl vinylphosphonate, vinyl pyridine and 2-isopropenyl-2-oxazoline.[7] By fine tuning Lewis acidity, Lewis basicity and steric effect, the Lewis pairs facilitate customization, controllability and selectivity of polymerization to afford ultra-high molecular weight and topology-controlled polymers and copolymers.[8]

It is anticipated that the Lewis ambiphilic character and peculiar structure of low-oxidation state silicon compounds could bring out new features in Lewis pair polymerization. In this paper, we report an amidinato silylene and disilyne (also known as bis(silylene)) pairing with $B(C_6F_5)_3$ to catalyze polymerization of methacrylate compounds (Figure 1).

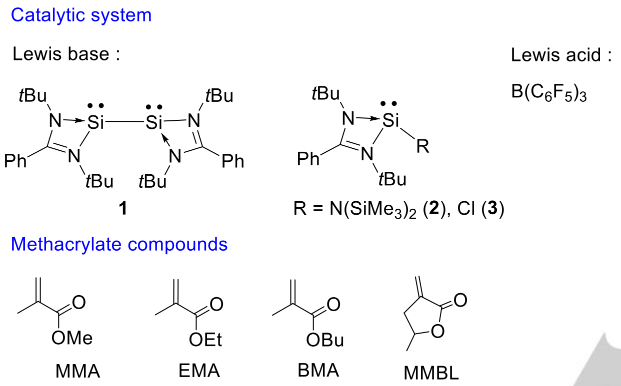


Figure 1. Catalytic systems and methacrylate compounds.

Results and Discussion

Considering that the amidinato disilyne $[LSi:]_2$ (**1**, L = PhC(N*t*Bu)$_2$) was capable of cooperating with Lewis acid namely $FeBr_2{\cdot}thf_2$ to catalyze the hydroboration of carbonyl compounds,[9] compound **1** was selected to be a Lewis base component in Lewis pair polymerization.

0.5 mol% of **1** was reacted with methyl methacrylate (MMA) in toluene (6 mL) for 1 day yielded the poly(MMA) with low molecular weight ($M_n = 1.1 \times 10^3$ gmol^{-1}; repeating unit, n = 11; polydispersity index, Đ: 1.11; Table 1). However, only 3% conversion of MMA was achieved. The results suggest that compound **1** marginally activated MMA to afford the polymer with low yield. The reactivity of **1** was compared with that of NHCs and phosphines in MMA polymerization. In case of NHCs, 1,3,4-triphenyl-4,5-dihydro-1H-1,2,4-triazol-5-ylidene (TPT) was capable of catalyzing dimerization of MMA instead of polymerization.[10] Another NHC, namely 1,3-di-tert-butylimidazolin-2-ylidene (I*t*Bu, $\{HCN(tBu)\}_2C$:) non-catalytically mediated MMA polymerization in DMF to form poly(MMA) with medium-high-molecular weight ($M_n = 33.2 \times 10^3$ gmol^{-1}), but no polymerization was observed when the solvent was changed to toluene and THF.[10] In case of phosphines, they were not feasible to promote MMA polymerization.[11]

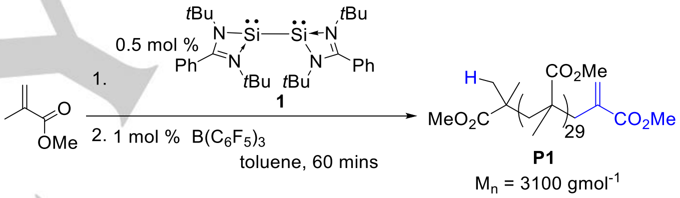
In addition, 1 mol% of $B(C_6F_5)_3$ was treated with MMA in C_6D_6 or toluene for 1 day, but no reaction was observed. This suggests that the Lewis acid $B(C_6F_5)_3$ alone cannot polymerize MMA.

$B(C_6F_5)_3$ (0.1 mol%) and **1** (0.5 mol%) were used (Run 3, Table 1) to mediate MMA polymerization, resulting in the formation of poly(MMA) with medium-high molecular weight ($M_n = 28.3 \times 10^3$ gmol^{-1}, n = 283, Đ: 2.11). Although the conversion of MMA was 20% only, the result illustrates that $B(C_6F_5)_3$ cooperates with compound **1** to polymerize MMA.

Table 1. MMA polymerization mediated by the Lewis pair of **1** and $B(C_6F_5)_3$.[a]

Run	[MMA]:[**1**]:[$B(C_6F_5)_3$]	Reaction Time (hr)	Conv. (%)	M_n ($\times 10^3$ gmol^{-1})	Đ (M_w/M_n)
1	200:1:0	24	3	1.1	1.11
2	200:0:2	24	0	-	-
3	200:1:0.2	24	20	28.3	2.11
4	200:1:2	1	100	3.1	1.55
5[b]	200:1:2	1	100	3.2	1.55
	50:1:2	1.5	100	0.85	1.21

[a] All polymerizations were performed at room temperature in toluene (6 mL). MMA conversion (%) is measured by ^{1}H NMR spectroscopy. M_n and Đ were determined by gel permeation chromatography (GPC) relative to poly(MMA) standards. [b] The reaction was conducted in a [MMA]:[**1**]:[$B(C_6F_5)_3$] ratio of 200:1:2 first. After consuming all MMA, second portion of 50 equivalents of MMA was added to the reaction mixture.



Scheme 1. Synthesis of **P1** (Run 4, Table 1). End groups of **P1** are highlighted in blue color.

The catalytic amounts of **1** and $B(C_6F_5)_3$ were increased to a ratio of 1:2 (Run 4), where 0.5 mol% of **1** and 1 mol% of $B(C_6F_5)_3$ were reacted with MMA in toluene (6 mL) at room temperature for 1h to afford poly(MMA) with low molecular weight (**P1**, $M_n = 3.1 \times 10^3$ gmol^{-1}; repeating unit, n = 31; polydispersity index, Đ: 1.55; Scheme 1, Table 1). The conversion of this reaction is 100%. The MALDI-TOF mass spectrum of **P1** showed a set of fragments at an interval of *m*/*z* 100, which corresponds to a MMA unit (Figure 2). This illustrates that **P1** does not comprise **1** and $B(C_6F_5)_3$ in the skeleton. Moreover, its ^{1}H NMR spectrum showed signals at δ 6.15, 5.23 and 3.41 ppm in an integral ratio of 1:1:104 attributable to the alkenyl protons $C{=}C(H_a)(H_b)$ and methoxide protons O*Me*, respectively. The integral ratio indicates that there are 35 OMe groups in **P1**, which is in good agreement with the repeating units analyzed by gel permeation chromatography (GPC, Table 1). The presence of alkenyl protons suggests that the end groups of **P1** are H and $CH_2C(=CH_2)CO_2Me$ (Scheme 1). Same end-groups were observed, when **P1** was isolated before and after quenching the reaction mixture. Comparing the structure of **P1** with other poly(MMA)s, the initiator AIBN and catalytic chain transfer agent $[(iPr)(H_2O)Co(dmgBF_2)_2]$ ($dmgBF_2$ = difluoroboryldimethylglyoxime) can produce poly(MMA) with the same end groups of H and $CH_2C(=CH_2)CO_2Me$.[12] On the basis of the molecular structure of **P1**, the Lewis pair of **1** and $B(C_6F_5)_3$ catalyzed the MMA polymerization. The conclusion is further supported by the initiator efficiency (I*) of 332% ($I^* = M_n(\text{calcd})/M_n(\text{exptl})$, where $M_n(\text{calcd}) = \text{MW(M)} \times [\text{M}]/[\text{I}] \times \text{conversion (\%)} + \text{MW(chain-end groups)}$),[10] which shows a catalytic polymerization system through chain transfer to monomer in the absence of any chain transfer agents.

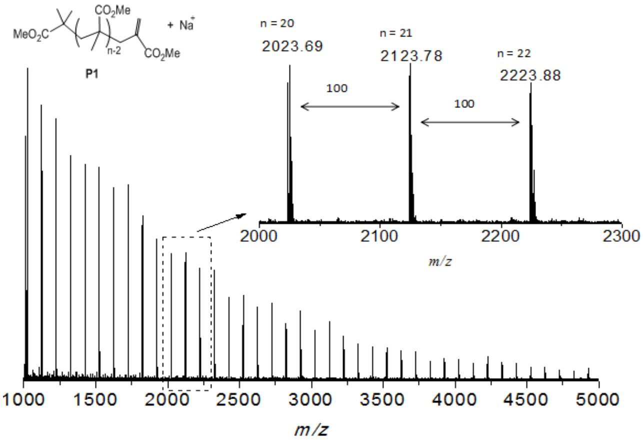


Figure 2. MALDI-TOF spectrum of **P1** from m/z 1000 - 5000.

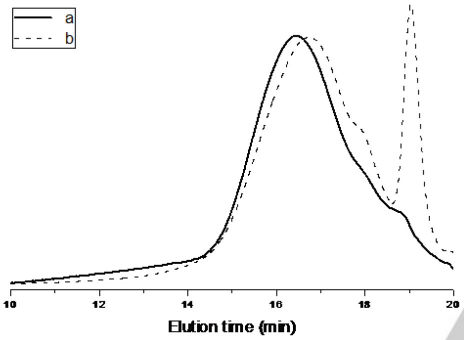


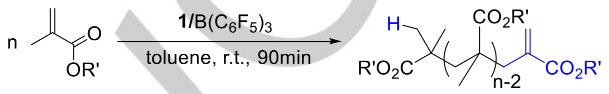
Figure 3. GPC profiles of (a) **P1** from Run 4, Table 1, (b) poly(MMA)s from Run 5, Table 1.

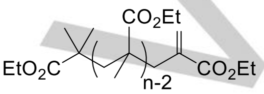
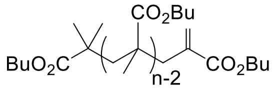
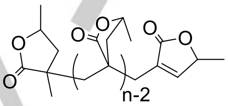
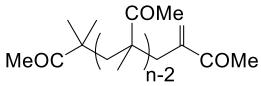
The Lewis pair of compound **1** and $B(C_6F_5)_3$ is one of metal-free systems that polymerizes MMA. Other metal-free Lewis pairs I*t*Bu/$B(C_6F_5)_3$, $PPh_3/B(C_6F_5)_3$ and $Et_3N/B(C_6F_5)_3$ are capable of polymerizing MMA and γMMBL.[13]

To evidence the chain transfer mechanism in the polymerization, 0.5 mol% of **1** and 1 mol% of $B(C_6F_5)_3$ were reacted with MMA in toluene (i.e. [MMA]:[**1**]:[$B(C_6F_5)_3$]: 200:1:2; Run 5, Table 1). After 90 mins, another 50 equivalents of MMA were further added in the reaction mixture and the resulting mixture was stirred for another 90 mins (Run 5, Table 1). GPC analysis showed two poly (MMA)s of $M_n = 3.2 \times 10^3$ gmol^{-1}, n = 32 and $M_n = 0.85 \times 10^3$ gmol^{-1}, n = 9 (Figure 3b). The former polymer was formed by the [MMA]:[**1**] ratio of 200:1, being consistent with **P1** (Run 4, Table 1, $M_n = 3.1 \times 10^3$ gmol^{-1}, Figure 3a), while the latter polymer was formed by the [MMA]:[**1**] ratio of 50:1. This study shows that compound **1** and $B(C_6F_5)_3$ were regenerated after the first MMA polymerization and subsequently polymerized the 50 equivalents of MMA. In addition, the first poly(MMA) ($M_n = 3.2 \times 10^3$ gmol^{-1}), which was formed by the 200 equivalents of MMA, did not further undergo propagation in the reaction mixture after the second addition of 50 equivalents of MMA.

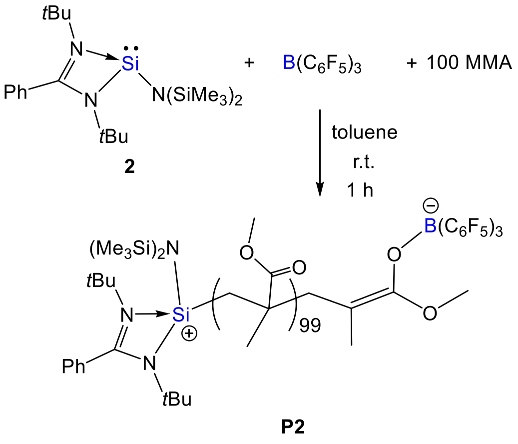
Other methacrylates, namely ethyl methacrylate (EMA), butyl methacrylate (BMA) and α-methylene-γ-valerolactone (MMBL) were also polymerized by the Lewis pair of **1** and $B(C_6F_5)_3$ in toluene for 90 mins to form the corresponding polymers with end groups of H and $CH_2C(=CH_2)CO_2R$. Moving on to isopropenyl methyl ketone (MIK), it was polymerized by the Lewis pair of **1** and $B(C_6F_5)_3$ to form the poly(MIK) with the end groups of H and $CH_2C(=CH_2)COMe$.

Table 2. Catalytic polymerization mediated by the Lewis pair of **1** and $B(C_6F_5)_3$



 **Poly(EMA)**	 **Poly(BMA)**
M_n[a]=5.8; n=58; yield=100%; Đ=2.34	M_n=5.6; n=56; yield=100%; Đ=2.15
 **Poly(MMBL)**	 **Poly(MIK)**
M_n=1.3; n=15; yield=100%; Đ = 1.05	M_n=9.8; n=87; yield=100%; Đ=1.21

[a] unit of M_n: $\times 10^3$ gmol^{-1}, [b] poly(EMA) and poly(BMA), Lewis pair loading: 0.5 mol% of **1** and 1 mol% of $B(C_6F_5)_3$, [c] poly(MMBL) and poly(MIK), Lewis pair loading: 2.5 mol% of **1** and 35 mol% of $B(C_6F_5)_3$



Scheme 2. MMA polymerization mediated by the Lewis pair of **2** and $B(C_6F_5)_3$.

To understand the effect of mono- and dinuclear low oxidation state silicon compounds, the amidinato amidosilylene [LSiN(SiMe$_3$)$_2$][14] (**2**) replaced compound **1** in the Lewis pair. 1 mol% of compound **2** and 1 mol% of $B(C_6F_5)_3$ (i.e. [MMA]:[**2**]:[$B(C_6F_5)_3$]: 100:1:1) were used to mediate MMA polymerization in toluene at room temperature for 1h, whereby medium molecular weight poly(MMA) **P2** [Figure 4a, M_n = 1.04

$\times10^4$ $gmol^{-1}$; Đ: 1.97] was afforded. The nearly quantitative initiator efficiency of I* = 96% illustrates that no chain transfer occurred. In other words, the end groups of **P2** are compound **2** and $B(C_6F_5)_3$. Moreover, the ^1H NMR spectrum of **P2** does not have any signals for H and $CH_2C(=CH_2)CO_2Me$ of **P1**. To further support our conclusion, 1 mol% of compound **2** and 1 mol% of $B(C_6F_5)_3$ were reacted with MMA in toluene (i.e. [MMA]:[**2**]:[$B(C_6F_5)_3$]: 100:1:1). After 60 mins, another 25 equivalents of MMA were further added to the reaction mixture and the resulting mixture was stirred for another 1.5 hr. GPC analysis showed that only one poly(MMA) was afforded [Figure 4b, M_n = 1.29 $\times10^4$ $gmol^{-1}$; Đ: 2.02]. No chain transfer was occurred. In addition, the increment of M_n is in accordance with the amount of MMA added, that is, 100 equivalents of MMA led to M_n = 1.04 $\times10^4$ $gmol^{-1}$, while 100+25 equivalents resulted in M_n = 1.29 $\times10^4$ $gmol^{-1}$. The results show that the Lewis pair of compound **2** and $B(C_6F_5)_3$ mediated living MMA polymerization.

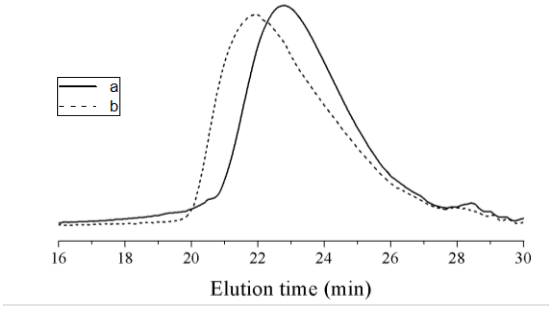
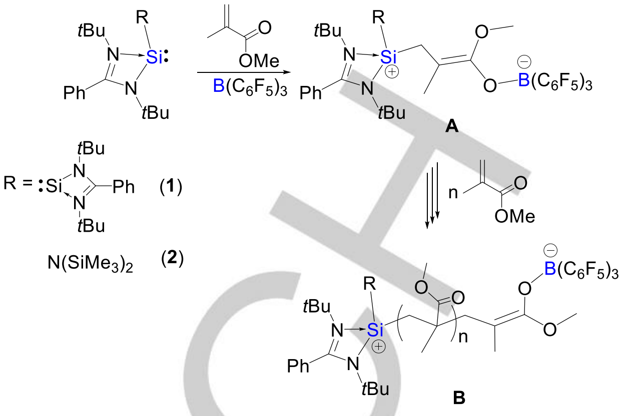


Figure 4. GPC profiles of (a) **P2**, (b) **P2**+25 equivalents of MMA

Compound **2** and $B(C_6F_5)_3$ is one of the Lewis pair systems that enable living polymerization. Other examples are the Lewis pair of N-heterocyclic olefin (NHO) and $MeAl(BHT)_2$ in methacrylates polymerization,[15] NHO/silyl ketene acetal and $Al(C_6F_5)_3$ in lactones polymerization,[16] NHO and $AlPh_3$ in acrylamides polymerization.[17]

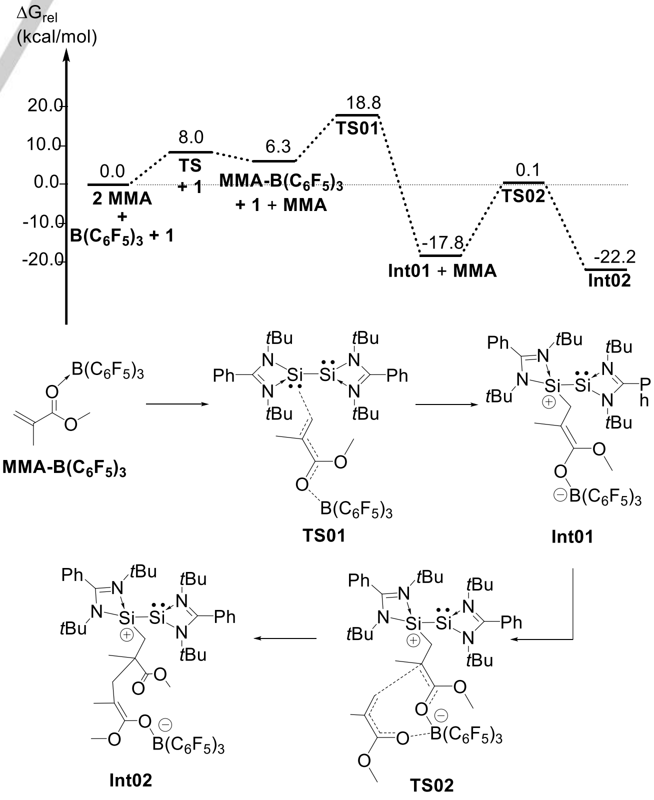
When the $N(SiMe_3)_2$ substituent in compound **2** was replaced by chloride substituent, the Lewis pair of the amidinato chlorosilylene [LSiCl][18] (**3**) and $B(C_6F_5)_3$ cannot polymerize MMA. The results show that the distinctive steric and electronic property of compounds **1** – **3** affect their capability in MMA polymerization.[19]

On the basis of **P2**, the mechanism for MMA polymerization should be similar to other Lewis pair-mediated methacrylates polymerization,[7] where the low oxidation state silicon center(s) in compound **1** or **2** reacted with MMA and $B(C_6F_5)_3$ to form a zwitterionic active species $[LSi\{CH_2C(Me)=C(OMe)O\}B(C_6F_5)_3]_2$ or $L\{(Me_3Si)_2N\}Si\{CH_2C(Me)=C(OMe)O\}B(C_6F_5)_3$ (**A**, Scheme 4), respectively. It then activated MMA molecules, leading to chain propagation.

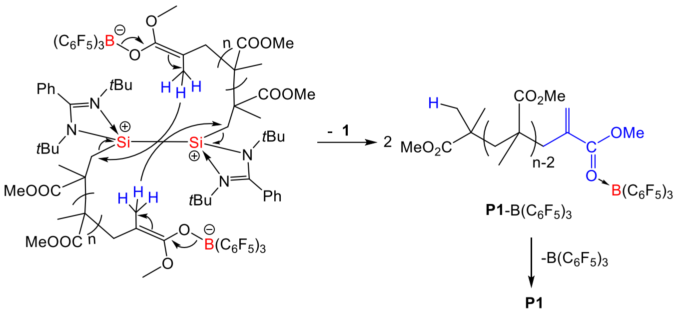


Scheme 4. Chain-propagation mechanism

The proposed chain propagation was verified by DFT calculations (M06-2X/def2-SVP, Scheme 5). In the simplified model, a Si^I center in compound **1** is reacted with two MMA molecules and a $B(C_6F_5)_3$ molecule in order to understand how a polymer chain grows between the silicon and boron center. Firstly, MMA reacts with a $B(C_6F_5)_3$ molecule to form a Lewis acid-base adduct, which is endergonic (ΔG = 6.3 kcal/mol). The Si^I center in compound **1** then attacks the C=C double bond of the adduct to form a zwitterionic intermediate **Int01** ($\Delta G_{1\rightarrow Int01}$= -17.8 kcal/mol) via a kinetic barrier of 12.5 kcal/mol. **Int01** subsequently undergoes nucleophilic attack with another MMA molecule, which proceeds via **TS02** (free energy of activation: 17.7 kcal/mol), to produce zwitterionic **Int02** ($\Delta G_{Int01\rightarrow\ Int02}$= -22.2 kcal/mol). The overall exergonic gain in energy (ΔG = 22.2 kcal/mol) suggests that the MMA chain propagation via the active zwitterionic species **A** is feasible.



Scheme 5. DFT calculations of MMA chain propagation (M06-2X/def2-SVP).



Scheme 6. Proposed mechanism for the termination step.

The poly(MMA) chain on the Si center in compounds **1** and **2** underwent different termination steps. In case of the Lewis pair of compound **1** and $B(C_6F_5)_3$, the end groups of **P1** are H and $CH_2C(=CH_2)CO_2Me$, suggesting that the gauche bent geometry of the Si-Si skeleton could induce the methyl group of the last enolate of a poly(MMA) chain reacting with the Si-C bond of the adjacent poly(MMA) chain to form **P1,** as well as regenerate compound **1** and $B(C_6F_5)_3$ (Scheme 6). In case of the Lewis pair of compound **2** and $B(C_6F_5)_3$, the polymer is living, indicating that the last enolate unit cannot attack the Si-C bond of the same poly(MMA) chain.

Conclusion

The Lewis pair of the amidinato disilyne **1** and $B(C_6F_5)_3$ mediated methyl methacrylate (MMA) polymerization to form the poly(MMA) **P1** with the H and $CH_2C(=CH_2)CO_2Me$ end groups. In the proposed polymerization mechanism, compound **1** could react with MMA and $B(C_6F_5)_3$ to form a zwitterionic active species $[LSi\{CH_2C(Me)=C(OMe)O\}B(C_6F_5)_3]_2$, which could activate MMA molecules affording poly(MMA) chains on the silicon centers. The methyl group of the last enolate of a poly(MMA) chain on a silicon center could then react with the Si-C bond of the adjacent poly(MMA) chain to form **P1** ($M_n = 3.1 \times 10^3$ $gmol^{-1}$; repeating unit, n = 31; polydispersity index, Đ: 1.55), as well as regenerate compound **1** and $B(C_6F_5)_3$. On the other hand, the Lewis pair of the amidinato amidosilylene **2** and $B(C_6F_5)_3$ mediated living MMA polymerization in toluene to form the poly(MMA) **P2** ($M_n = 1.04 \times 10^4$ $gmol^{-1}$; Đ: 1.97).

Experimental Section

All manipulations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Toluene was dried over and distilled over Na/K alloy prior to use. $B(C_6F_5)_3$, methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), α-methylene-γ-valerolactone (MMBL) and isopropenyl methyl ketone (MIK) were purchased from TCI. MMA, EMA, BMA, MMBL and MIK were dried with CaH_2 before use. $[LSi:]_2$ (**1**)[9] (L = PhC(N*t*Bu)$_2$) and $[LSiN(SiMe_3)_2]$ (**2**)[14] were prepared according to the literature procedures. C_6D_6 was dried and distilled over K metal prior to use. The NMR spectra were recorded on a JEOL ECA 400 spectrometer and Bruker 400 spectrometer.

Synthesis of P1: Compound **1** (0.0026 g, 0.005 mmol) was added to toluene (6 mL) and MMA (0.10 g, 1.0 mmol) mixture in a 10 mL dried vial. Then, $B(C_6F_5)_3$ (0.0051 g, 0.010 mmol) was rapidly added under stirring. Subsequent procedures follow method A or B: *Method A*: The reaction mixture was stirred for 60 mins and dried under vacuum to obtain **P1** as white solid. Isolated yield: 0.095 g, 95 %. *Method B*: The reaction was stirred for 60 mins. **P1(quenched)** was precipitated by adding the reaction solution into 40 mL of 5% HCl-acidified *n*-hexane. **P1(quenched)** was filtered. It was then washed with hexane, and dried under vacuum. Yield: 0.091 g (91 %).^{1}H NMR (395.9 MHz, 25 °C, C_6D_6, ppm): δ 6.15 (m, =CH_2 of the $CH_2C(=CH_2)CO_2Me$ end-group), 5.23 (m, =CH_2 of the $CH_2C(=CH_2)CO_2Me$ end-group), 3.41-3.33 (m, O*Me*), 2.21-2.00 (br m, CH_2), 1.17-1.01 (m, *Me*). GPC, M_n ($gmol^{-1}$): 3100; Đ: 1.55.

To prove the chain transfer mechanism, the above procedure was repeated. After that MMA (0.025 g, 0.25 mmol) was added in the reaction mixture and the resulting mixture was stirred for another 90 mins until all MMA was converted. The reaction solution was dried under vacuum to afford the poly(MMA) as white solid. GPC showed two groups of poly(MMA): M_n ($gmol^{-1}$): 3200/850; Đ: 1.55/1.21.

Synthesis of P2: Compound **2** (0.0042 g, 0.01 mmol) was added to 6 mL of toluene and MMA (0.10 g, 1.0 mmol) mixture in a 10 mL dried vial. Then, $B(C_6F_5)_3$ (0.0051 g, 0.010 mmol) was rapidly added under stirring. The reaction mixture was stirred for 60 mins to afford the poly(MMA) **P2**. ^{1}H NMR (395.9 MHz, 25 °C, C_6D_6, ppm): δ 3.71 (s, OMe), 1.96 (br m, CH_2), 1.34-1.09 (m, Me). GPC: $M_n = 1.04 \times 10^4$ $gmol^{-1}$; Đ = 1.55.

To prove that **P2** is a living polymer, the above procedure was repeated. After that, MMA (0.025 g, 0.25 mmol) was added in the reaction mixture, which was then stirred for another 90 mins. GPC: $M_n = 1.29 \times 10^4$ $gmol^{-1}$; Đ: 2.02.

Experimental procedures for the polymerization in Table 1 and 2 are provided in the supporting Information.

Gel Permeation Chromatography. Molecular weights (M_n) and polydispersity (M_w/M_n, PDI) were determined by gel permeation chromatography (GPC) with THF as the eluent (1.0 mL min^{-1}) at 30 ºC (both the columns and detector), and equipped with a Waters 717 plus auto sampler, a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Shodex K-805, K-804, and K-802.5 columns in series. For polymer samples that can dissolve in N,N-dimethylformamide (DMF): Molecular weights (M_n) and polydispersity (M_w/M_n, PDI) were determined by gel permeation chromatography (GPC) with DMF as the eluent (1.0 mL min^{-1}) at 30 ºC (both the columns and detector) by PL-GPC 50 integrated system (Agilent Technologies). We used tandem three columns in the GPC to make the data more solid and trustworthy. Three column set up resulted in a sample requiring more time to flow through, which afford a wide/board curve even the sample with a relatively low polydispersity. The column system was calibrated with standard poly(methyl methacrylate)s (PMMAs). The M_n of PMMA standards used to calibrate samples with M_n in the range of 645-51800 g/mol.

MALDI-TOF-Mass Spectrometry. The matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were recorded on a JMS-S3000 SpiralTOF (JEOL Ltd., Japan) at an accelerating potential of 20 kV in the positive spiral mode. We prepared the polymer solution (polymer: 10 mg/mL in THF), matrix solution (DCTB: 10 mg/mL in THF), and cationization agent solution (NaTFA: 10 g/L in THF). The MALDI-TOF-MS samples were prepared by the dried droplet method. Polymer sample, matrix, and cationization agent solution (all in THF) were mixed together in a ratio of 1/5/1 (v/v/v) for polymer/DCTB/NaTFA. Then, 5 µL of the mixed solution was deposited on the target plate and dried in the air at room temperature.

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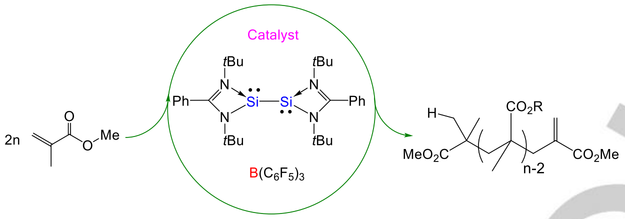

A Lewis pair of the amidinato disilyne and $B(C_6F_5)_3$ polymerized methyl methacrylate to form the polymer comprising H and $CH_2C(=CH_2)CO_2Me$ end groups.