Silylium Dual Catalysis in Living Polymerization of Methacrylates via *In Situ* Hydrosilylation of Monomer

Tieqi Xu,[1] Eugene Y.-X. Chen[2]

[1]State Key Laboratory of Fine Chemicals, College of Chemistry, Dalian University of Technology, No. 2 Linggong Road, Dalian 116024, China
[2]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872
Correspondence to: T. Xu (E-mail: tqxu@dlut.edu.cn) or E. Y.-X. Chen (E-mail: eugene.chen@colostate.edu)

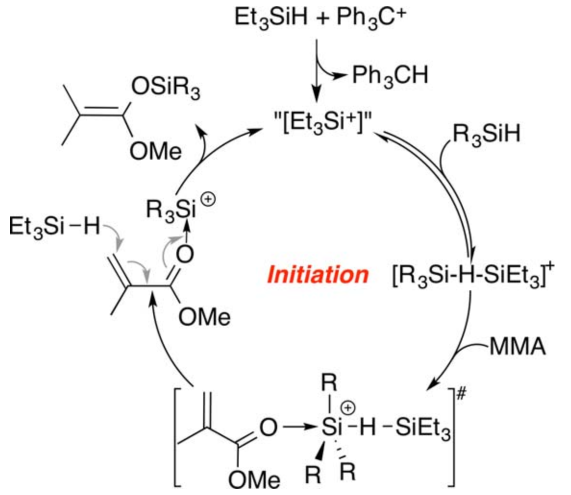
Received 10 February 2015; accepted 16 March 2015; published online 13 April 2015
DOI: 10.1002/pola.27641

ABSTRACT: Silylium ions (“R_3Si^+”) are found to catalyze both 1,4-hydrosilylation of methyl methacrylate (MMA) with R_3SiH to generate the silyl ketene acetal initiator *in situ* and subsequent living polymerization of MMA. The living characteristics of the MMA polymerization initiated by R_3SiH (Et_3SiH or Me_2PhSiH) and catalyzed by $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene), which have been revealed by four sets of experiments, enabled the synthesis of the polymers with well-controlled M_n values (identical or nearly identical to the calculated ones), narrow molecular weight distributions ($Đ = 1.05$–1.09), and well defined chain structures {H—$[MMA]_n$—H}. The polymerization is highly efficient too, with quantitative or near quantitative initiation efficiencies ($I^* = 96$–100%). Monitoring of the reaction of MMA + Me_2PhSiH + $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (0.5 mol%) by ^1H NMR provided clear evidence for *in situ* generation of the corresponding SKA, $Me_2C{=}C(OMe)OSiMe_2Ph$, via the proposed “Et_3Si^+”-catalyzed 1,4-hydrosilylation of monomer through “frustrated Lewis pair” type activation of the hydrosilane in the form of the isolable silylium-silane complex, $[Et_3Si{—}H{—}SiR_3]^+[B(C_6F_5)_4]^-$. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 1895–1903

KEYWORDS: living polymerization; methacrylate; hydrosilylation; group-transfer polymerization; silylium catalysts; methyl methacrylate

INTRODUCTION Silylium ions,[1] denoted as “R_3Si^+” herein, are highly reactive species and coordinated/stabilized in the condensed phase by even very weak bases or donors such as weakly coordinating anions, solvent molecules, monomers/substrates, or moieties in the ligand R itself. Such reactive species have been shown attractive utilities in organic synthesis[2] and catalysis.[3] Silylium ions have also been utilized to catalyze polymerization reactions for polymer synthesis. In this context, Olah et al.[4] and others[5,6] have realized the cationic ring-opening polymerization (ROP) of cyclosiloxanes mediated predominantly by trisilyloxonium ions generated by reacting R_3SiH with $[Ph_3C][B(C_6F_5)_4]$ in the presence of siloxanes. Olah et al.[7] have also achieved the ROP of 4-, 6-, and 7-membered lactones using silylium-generating reagents. Manners, Reed and coworkers[8] have reported the ROP of cyclic chlorophosphazene trimer $[N_3P_3Cl_6]$ catalyzed by silylium ions paired with weakly coordinating halogenated carborane anions.

To realize unique utilities of “R_3Si^+” in catalyzing polymerization reactions *other than* a ROP process, we[9] have demonstrated that “R_3Si^+,” generated either externally by $\{R_3SiH + [Ph_3C][B(C_6F_5)_4]\}$, or more intriguingly, by *in situ* reaction of a silyl ketene acetal [^{R}SKA, $Me_2C{=}C(OMe)OSiR_3$] with a catalytic amount of $[Ph_3C][B(C_6F_5)_4]$, catalyzes living anionic-addition polymerization of acrylic monomers such as methyl methacrylate (MMA) at room temperature (RT), producing poly(methyl methacrylate) (PMMA) with medium to high molecular weights ($M_n > 10^5$ g/mol) and narrow molecular weight distributions (MWD’s, defined by $Đ = M_w/M_n = 1.04$–1.12).[9] Subsequent structure–reactivity relationship studies have revealed a remarkable selectivity of ^{R}SKA for monomer structure.[10] Specifically, the small “Me_3Si^+” (0.05 mol %) is highly active and efficient for MMA polymerization, but it shows poor activity and efficiency for the polymerization of sterically less demanding, active α-proton-containing acrylates such as *n*-butyl acrylate (^{n}BA). In contrast, the larger “$^iBu_3Si^+$” catalyst exhibits low activity for the polymerization of MMA, but exceptional activity, efficiency, and control for the polymerization of ^{n}BA, achieving quantitative ^{n}BA conversion in 1 min at 25 °C and giving a very high catalyst turn-over frequency (TOF) of 1.2×10^5 h^{-1}.[10] Although this silylium-catalyzed addition polymerization uses ^{R}SKA, which are commonly employed as initiators in the group-transfer polymerization (GTP),[11] both chain initiation and propagation involved in the silylium-catalyzed



SCHEME 1 Proposed catalytic cycle for *in situ* generation of the ^{R}SKA initiator through the "Et_3Si^{+}"-catalyzed 1,4-hydrosilylation of MMA with hydrosilane R_3SiH. The anion $[B(C_6F_5)_4]^-$ was omitted for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerization, as outlined in Scheme 1, are different than those fundamental steps of the conventional GTP. Furthermore, the silylium-catalyzed polymerization offers advantages over the conventional GTP in terms of its ability to readily produce high MW poly(methacrylate)s and also effects living polymerization of acrylates under ambient temperature and low catalyst loading conditions.[9,10] The silylium-catalyzed GTP method has also enabled high-speed, living polymerization of renewable α-methylene-γ-butyrolactones, producing homo and random or block copolymers with controlled low to high MW (M_n up to 5.43×10^5 kg/mol) and narrow MWD's ($Đ = 1.01$–1.06).[12] Covalently linked dinuclear, bifunctional silylium-SKA active species have also been developed to circumvent the limitation of the bimolecular, activated monomer propagation mechanism imposed on polymerizations under highly dilute initiator or catalyst conditions and on the stereochemical control of polymerization.[13]

Besides $[Ph_3C][B(C_6F_5)_4]$, several additional types of activators have also been used to deliver the silylium catalyst *in situ* while activating ^{R}SKA. Kakuchi and coworkers[14] utilized a strong BrØnsted acid, trifluoromethanesulfonimide ($HNTf_2$),[15] to activate ^{R}SKA for *in situ* generation of Me_3SiNTf_2,[16] leading to the silylium-catalyzed living polymerization of MMA, and to activate dialkylaminosilyl enol ether for the living polymerization of *N,N*-dimethylacrylamide.[17] Kakuchi et al.[18] also reported Me_3SiNTf_2-catalyzed living GTP of ^{n}BA with functional initiators and/or terminators to produce well-defined end-functionalized polymers. We[19] employed strong BrØnsted acids paired with weakly coordinating perfluorophenylborate anions,[20] $[H(Et_2O)_2][B(C_6F_5)_4]$,[21] $[HN(Me_2)Ph][B(C_6F_5)_4]$,[22] and a strong BrØnsted acid bearing a chiral disulfonimide counteranion,[2d] to deliver the R_3Si^+ catalyst that effects high-speed living polymerization with a unique "self-repair" features in the presence of water.[19] Also worth noting here are the observations that the more advanced GTP systems using the ^{R}SKA initiator and additionally employing different combinations of a Lewis acid and a Me_3Si-containing reagent, such as $[Me_3SiOTf + B(C_6F_5)_3]$,[23] $[Me_3SiI + HgI_2]$,[24] or $[Me_3SiI + RAl(OAr)_2]$,[25] are considerably more active than the typical GTP system using no such combinations, which may indicate their possible involvement of the silylium-catalyzed process similar to what has been demonstrated for the ^{R}SKA + $[Ph_3C][B(C_6F_5)_4]$[9,10] and ^{R}SKA + $[H(Et_2O)_2][B(C_6F_5)_4]$ systems.[19]

The above overviewed "R_3Si^{+}"-catalyzed, GTP-type polymerization systems have one thing in common: they all utilize the preformed SKA as initiator. As the SKA initiator is sensitive to moisture and protic impurities, it would be desirable to develop an advanced GTP process without directly employing SKA. In this context, *in situ* generation of the SKA initiator via 1,4-hydrosilylation of α,β-unsaturated esters (acrylic monomers) using a hydrosilane (R_3SiH)[26] offers an attractive approach. Piers et al. reported the first $B(C_6F_5)_3$-catalyzed hydrosilylation of aromatic aldehydes, ketones, and esters,[27] as well as 1,4-hydrosilylation of α,β-unsaturated ketones.[28] Mechanistic studies revealed that this hydrosilylation proceeds through the so-called frustrated Lewis pair (FLP)[29] activation of the hydrosilane in the form of an unstable intermediate $[R_3Si\text{–}H \rightarrow B(C_6F_5)_3]$, rather than activation of the more basic carbonyl function in the form of the more stable classical Lewis adduct $[>C{=}O \rightarrow B(C_6F_5)_3]$.[30] Accordingly, we hypothesized that this facile $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl substrates could provide a new, convenient GTP process for polymerization of acrylic monomers directly using R_3SiH, instead of the sensitive SKA. In fact, while our work on this front was still in progress, Kakuchi and coworkers reported the living/controlled GTP of acrylate ^{n}BA by the *in situ* generated SKA initiator through $B(C_6F_5)_3$-catalyzed hydrosilylation of ^{n}BA with R_3SiH.[31] However, in our hands this $R_3SiH/B(C_6F_5)_3$ system exhibited no activity for polymerization of less reactive, sterically bulkier methacrylate monomers such as MMA.[32] Subsequently, we found that the system consisting of the stronger silylium Lewis acid, $R_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene or Et_3SiH), enables the first successful example of the silylium-catalyzed living methacrylate polymerization by the *in situ* generated SKA initiator through the "R_3Si^{+}"-catalyzed 1,4-hydrosilylation of MMA with R_3SiH. This contribution presents a full account of this study.

EXPERIMENTAL

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, on a high-vacuum line, or in an inert gas (Ar or N_2)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. HPLC-grade organic solvents were first sparged extensively with nitrogen during filling solvent reservoirs and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-d_6 and toluene-d_8 were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas $CDCl_3$ was dried over activated Davison 4 Å molecular sieves. HPLC-grade fluorobenzene and 1,2-difluorobenzene were degassed and dried over CaH_2 overnight, followed by vacuum distillation (CaH_2 was removed before distillation). NMR spectra were recorded on a Varian Inova 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 282 MHz, ^{19}F) or a Varian 400 MHz spectrometer. 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 $CFCl_3$.

MMA was purchased from Sigma-Aldrich Co.; it was first degassed and dried over CaH_2 overnight, followed by vacuum distillation. Further purification of MMA involved titration with neat tri(*n*-octyl) aluminum to a yellow end point, followed by distillation under reduced pressure. The purified monomer was stored in a brown bottle and stored inside a glovebox freezer at −30 °C. Triethylsilane (Et_3SiH) and dimethylphenylsilane (Me_2PhSiH) were purchased from TCI. These silanes were first degassed and dried over CaH_2 overnight, followed by vacuum distillation. Butylated hydroxytoluene (BHT-H) was purchased from Sigma-Aldrich and recrystallized from hexanes prior to use. Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ and trityl tetrakis(pentaflurophenyl)-borate $[Ph_3C][B(C_6F_5)_4]$ were purchased from Beijing Innochem Co.; the borane was further purified by recrystallization from hexanes at −30 °C. Literature procedures were employed or modified for the preparation of the following silylium complexes: $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$ [1r] and $[Et_3Si–H–SiEt_3]^+[B(C_6F_5)_4]^-$[1c].

In Situ Generation of $Me_2C{=}C(OMe)OSiMe_2Ph$ (^{Me2Ph}SKA) by Silylium-Catalyzed 1,4-Hydrosilylation of MMA

In an argon-filled glovebox, an NMR tube was charged with 10 mg (0.1 mmol) of MMA, 13.6 mg (0.1mmol) Me_2PhSiH, and 0.5 mL of C_7D_8. A 0.5 mL fluorobenzene solution of $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) (0.50 μ mol) was slowly added to this NMR tube via a syringe at RT, and the resulting reaction mixture was analyzed immediately by NMR. In the ^{1}H NMR spectrum of the mixture, the signals at δ 5.49 and 6.09 ppm characteristic of the $=CH_2$ protons for MMA completely disappeared and those signals at δ 4.58 and 0.41 ppm characteristic of H and Me protons for Me_2PhSiH diminished greatly (but not completely disappeared, vide infra), whereas the signals at δ 3.31 and 0.46 ppm characteristic of the OMe and $SiMe_2$ protons for ^{Me2Ph}SKA[26b] appeared. It is noted here that Me_2PhSiH was not completely consumed because this silylium-catalyzed hydrosilylation is accompanied by the competing reaction of the relatively fast silylium-catalyzed oligomerization/polymerization that takes place as soon as ^{Me2Ph}SKA is generated. This competition resulted in imbalanced consumption between MMA and Me_2PhSiH; thus, this reaction afforded predominantly the desired Me_2PhSKA, along with a small amount of the unconsumed Me_2PhSiH and oligomeric SKAs (Fig. 4).

Conversely, the borane-catalyzed 1,4-hydrosilylation of MMA in a 1:1:0.1 ratio of MMA/Me_2PhSiH/$B(C_6F_5)_3$ at 20 °C in $CDCl_3$, following the above procedure, afforded cleanly the corresponding ^{Me2Ph}SKA without contamination with the unconsumed silane and/or the oligomeric species (Fig. 5), because there are no competing oligomerization/polymerization reactions for the $R_3SiH/B(C_6F_5)_3$ system under the current conditions.[32]

General Polymerization Procedures

Polymerizations were performed in 20 mL oven-dried glass reactors inside the glovebox under ambient conditions (*ca.* 20 °C). Two different polymerization procedures were employed. In the first procedure, which was adopted by the majority of this study, initiator Et_3SiH or Me_2PhSiH and monomer MMA (0.20 g) were premixed in a predetermined ratio in 1.0 mL C_6H_5F for 5 min, followed by rapid addition of the catalyst solution of $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) in 1.0 mL C_6H_5F to start the polymerization. In the second procedure, which was used for some comparative or control runs, a predetermined amount of MMA (0.20 g) was first dissolved in 1.0 mL of solvent inside a glovebox, and the polymerization was started by rapid addition of a measured amount of the corresponding mixture of catalyst and initiator in 1.0 mL of C_6H_5F via a gastight syringe to the MMA solution under vigorous stirring. In both procedures, after the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 2-mL vial containing 0.6 mL of “wet” $CDCl_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ^{1}H NMR to obtain the percent monomer conversion data. The polymerization was immediately quenched, after the removal of the aliquot, by addition of 5 mL 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Monomer conversions $\{1–[M]_t/[M]_0\}$ were obtained from ^{1}H NMR analysis of aliquots. The ratio of $[MMA]_0$ to $[MMA]_t$ at a given time t, $[M]_0/[M]_t$, was determined by integration of the peaks for MMA (5.2 and 6.1 ppm for the vinyl signals; 3.4 ppm for the OMe signal in $CDCl_3$) and PMMA (centered at 3.4 ppm for the OMe signals in $CDCl_3$) according to $[M]_0/[M]_t = 2A_{3.4}/3A_{5.2+6.1}$, where $A_{3.4}$ is the total integrals for the peaks centered at 3.4 ppm (typically in the region 3.2−3.6 ppm) and $A_{5.2+6.1}$ is the total integrals for both peaks at 5.2 and 6.1 ppm.

Polymer Characterizations

Polymer number-average molecular weights (M_n) and MWDs ($Đ = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at 35 °C and a flow rate of 1.0 mL/min with DMF as the eluent, on a Agilent 1260 GPC instrument coupled with a Waters RI detector and equipped with two PL gel 5 μm mixed-C columns (Polymer Laboratories; linear range of molecular weight = 200–2,000,000). The instrument was calibrated with 10 PMMA standards, and

TABLE 1 Selected Results of MMA Polymerization by $Et_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene)[a]

Run no.	Time (min)	conv. [b] (%)	M_n [c] (kg/mol)	$Đ$ [c] (M_w/M_n)	$M_{n\ (calcd)}$ [d] (kg/mol)	I^* [e] (%)
1	4	9	3.50	1.05	3.52	101
2	5	10	4.10	1.05	4.05	99
3	10	18	7.20	1.05	7.25	101
4	15	25	10.1	1.08	10.1	100
5	20	34	13.4	1.06	13.6	101
6	25	39	15.7	1.06	15.7	100
7	30	50	20.0	1.05	20.1	101
8	50	76	30.5	1.07	30.5	100
9	70	100	42.0	1.09	40.1	96

[a] Conditions: solvent = C_6H_5F (2.0 mL), T_p = RT (~20 °C), $[MMA]_0 = 1.0$ M (0.2 mmol), $[MMA]_0/[Et_3SiH]_0/[Et_3Si(L)]^+[B(C_6F_5)_4]^- = 400:1:1$.

[b] Monomer conversions measured by ^1H NMR.

[c] M_n and $Đ$ determined by gel-permeation chromatography (GPC) relative to PMMA standards in DMF.

[d] $M_n(\text{calcd}) = \text{MW(MMA)} \times [MMA]_0/[I]_0 \times \text{conversion\%} + \text{MW of chain-end groups}$, where $[I]_0 = [Et_3SiH]_0$ and chain ends = 2 H.

[e] Initiation efficiency (I^*) = $M_n(\text{calcd})/M_n(\text{exptl})$.

chromatograms were processed with Agilent Empower software (version 2002).

Low molecular-weight MMA oligomers produced by the catalyst system $Et_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) in fluorobenzene at RT were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS). The experiment was performed on a Micro MX MALDI-TOF mass spectrometer (Waters) operated in a positive ion and reflector mode using a 1.2 kV accelerating voltage. The sample (1 μL in THF) was mixed with 1 μL of α-cyano-4-hydroxycinnamic acid (CHCA, 10 mg/ml in THF). The mixture was spotted on the MALDI target and allowed to air dry. External calibration was done using a peptide calibration mixture (4 to 6 peptides) on a spot adjacent to the sample.

RESULTS AND DISCUSSION

Characteristics of MMA Polymerization by $R_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$

At the outset, we carried out necessary control MMA polymerization runs using all the reagents involved in the present system (i.e., silane, activator, silylium complex), either an individual reagent alone or when combined together in different ratios. Although other solvents may also be appropriate for this polymerization system involving the highly reactive and sensitive silylium ions, we settled to fluorobenzene (C_6H_5F) as the solvent due to the suitable solubility and stability of “R_3Si^+” in this solvent. Thus, control MMA polymerization runs at RT using hydrosilane (Et_3SiH or Me_2PhSiH) or the activator $[Ph_3C][B(C_6F_5)_4]$ alone yielded no polymer formation up to 24 h. The 1:1 mixture of $Et_3SiH + [Ph_3C][B(C_6F_5)_4]$ in toluene after being stirred for 10 min, followed by addition of MMA, also exhibited no polymerization activity, but the 2:1 mixture brought about rapid polymerization. Next, the polymerization using the isolated silylium complex, $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$, yielded two contrasting results, depending on how the complex was prepared; when it was prepared from the 1:1 reaction of $Et_3SiH + [Ph_3C][B(C_6F_5)_4]$ in toluene, followed by extensive washing with toluene and hexanes (to remove any possible excess Et_3SiH and/or $[Ph_3C][B(C_6F_5)_4]$), the isolated pure complex, $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$,[1r] exhibited no polymerization activity. In contrast, when the silylium complex was actually impure (i.e., containing a small amount of Et_3SiH) or prepared from the reaction using excess Et_3SiH,[1r,u] it polymerized MMA rapidly. Finally, the isolated pure silylium-silane complex, $[Et_3Si–H–SiEt_3]^+[B(C_6F_5)_4]^-$,[1c,f] rapidly polymerized MMA. Overall, the above control experiments clearly showed that the active polymerization system was brought about by the combination of Et_3SiH and $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$, or in the form of a single component silylium-silane complex, $[Et_3Si–H–SiEt_3]^+[B(C_6F_5)_4]^-$. From a practical point of view, the polymerization by $R_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) is more convenient and controlled, which was the protocol adopted for this study.

Table 1 summarizes the results of the MMA polymerization by $Et_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) in a 400/1/1 ratio (i.e., with a silylium catalyst loading of 0.25 mol % relative to monomer). It can be seen from the table, the polymerization went smoothly to completion in less than 70 min in a living/controlled manner. The monomer conversion increased gradually with time and the M_n of the polymer increased linearly with monomer conversion (Fig. 1), while the MWD remained narrow throughout the entire course of the polymerization ($Đ = 1.05–1.09$). The measured M_n values were identical or nearly identical to those calculated ones based on the monomer-to-initiator ratio ($[MMA]_0/[Et_3SiH]_0$) and conversion data, thereby affording essentially quantitative initiation efficiencies ($I^* \geq 96\%$) for all conversion points analyzed in this study (see Table 1). These results highlighted the high degree of control and efficiency possessed by this silylium-catalyzed polymerization system.

The living characteristics of the silylium-catalyzed polymerization were further revealed by the results obtained from investigating effects of the monomer-to-initiator ratio on the

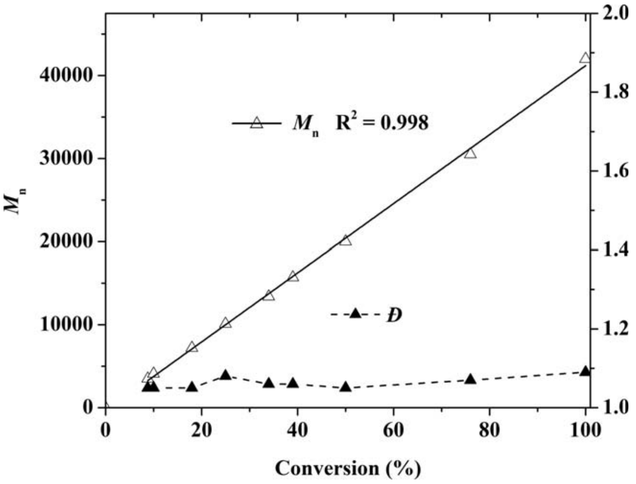


FIGURE 1 Plots of PMMA M_n and Đ values versus monomer conversion. Data taken from Table 1.

resulting polymer M_n values and from the chain-extension experiments. Thus, when the $[MMA]_0/[Et_3SiH]_0$ ratio was varied from 100:1, 200:1, 300:1, to 400:1, the M_n value of the resulting PMMA increased linearly from $M_n = 1.04 \times 10^4$ g/mol ($Đ = 1.10$, $I^* = 96\%$), 2.04×10^4 g/mol ($Đ = 1.06$, $I^* = 98\%$), 3.05×10^4 g/mol ($Đ = 1.07$, $I^* = 98\%$), to 4.20×10^4 g/mol ($Đ = 1.09$, $I^* = 96\%$), respectively, (Fig. 2). Worth noting also are the nearly quantitative initiation efficiencies and narrow MWD's achieved for all the ratio runs (*vide supra*) by this polymerization method. Furthermore, a sequential chain-extension experiment was performed by addition of another 200 equiv of MMA to the end of the polymerization that started with a $[MMA]_0/[Et_3SiH]_0$ ratio of 200:1, which produced PMMA with $M_n = 4.32 \times 10^4$ g/mol and $Đ = 1.07$ (Fig. 3); this M_n was approximately double of the MW of the PMMA produced by the first sequence ($M_n = 2.13 \times 10^4$ g/mol, $Đ = 1.09$) and agreed well with the M_n of the PMMA produced by the polymerization directly using a $[MMA]_0/[Et_3SiH]_0$ ratio of 400:1.

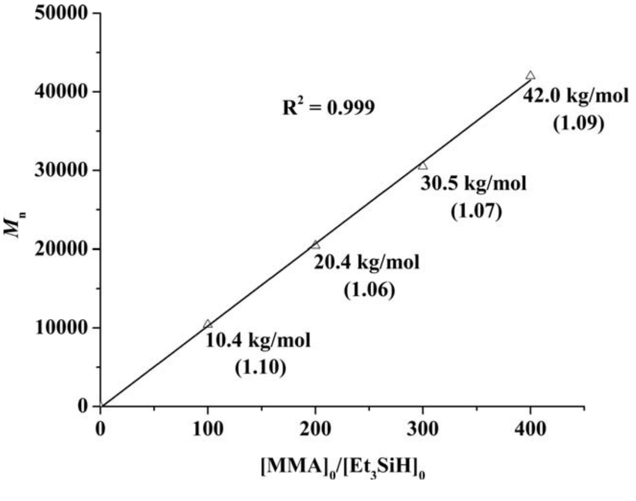


FIGURE 2 Plot of PMMA M_n versus $[MMA]_0/[Et_3SiH]_0$ ratio.

Interestingly, under the same conditions (RT, C_6H_5F, 0.25 mol% loading of $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$), the MMA polymerization with Me_2PhSiH was noticeably faster than that using Et_3SiH but the degree of polymerization control is more or less the same. Thus, the monomer conversion after 50 min was 76.2% with Et_3SiH (run 8, Table 1), whereas the conversion was 100% with Me_2PhSiH, at which time the PMMA produced had $M_n = 4.23 \times 10^4$ g/mol and $Đ = 1.08$, which were nearly identical to those values of the PMMA produced by Et_3SiH at quantitative monomer conversion (run 9, Table 1).

"Et_3Si^+"-Catalyzed Hydrosilylation of MMA for In Situ Generation of ^{R}SKA

The SKA initiator $Me_2C{=}C(OMe)OSiMe_2Ph$ (^{Me2Ph}SKA) can be prepared by the Rh-catalyzed 1,4-hydrosilylation of MMA with Me_2PhSiH.[26b] To demonstrate *in situ* generation of the initiator ^{Me2Ph}SKA in the current polymerization system starting with $Me_2PhSiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene), we carried out the model reaction of MMA + Me_2PhSiH + $[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ in a 1:1:0.005 ratio at 20 °C in fluorobenzene + toluene-d_8. The ^{1}H NMR spectrum obtained immediately after mixing of these reagents clearly showed the formation of ^{Me2Ph}SKA [δ 7.64 (m, 2H, Ph), 7.39 (m, 3H, Ph), 3.42 (s, 3H, OMe), 1.57 (s, 3H, $=CMe_2$), 1.51 (s, 3H, $=CMe_2$), 0.48 (s, 6H, $SiMe_2$)], along with a small amount of the unconsumed Me_2PhSiH and oligomeric SKAs (Fig. 4). The inevitable presence of the latter two types of species from this reaction is due to the relatively fast silylium-catalyzed oligomerization/polymerization that takes place as soon as ^{Me2Ph}SKA is generated, which competes with the hydrosilylation reaction; hence, such competing reaction products were unavoidable regardless of the reaction conditions (from RT to −80 °C in toluene-d_8 or fluorobenzene + toluene-d_8), the catalyst loading (from 0.1 to 10 mol %), and the nature of hydrosilanes (Et_3SiH or

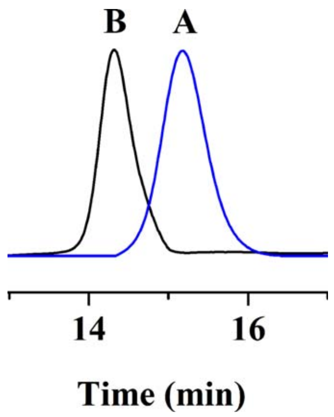


FIGURE 3 Overlay of GPC traces of the PMMA samples produced by the sequential addition of MMA. **A**: PMMA obtained after consuming the first 200 equiv of MMA ($M_n = 2.13 \times 10^4$ g/mol, $Đ = 1.09$); **B**: PMMA obtained after consuming the second 200 equiv of MMA ($M_n = 4.32 \times 10^4$ g/mol, $Đ = 1.07$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

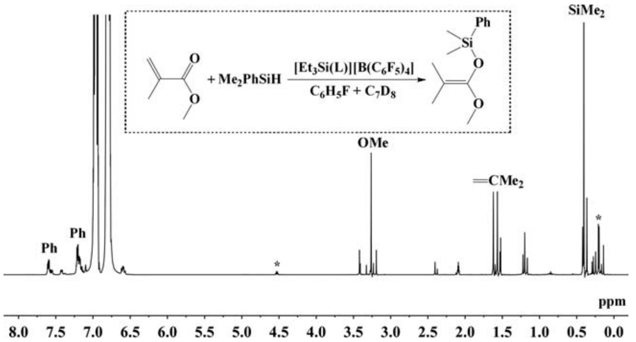


FIGURE 4 ^{1}H NMR spectrum for *in situ* generation of ^{Me2Ph}SKA from the 1:1:0.005 ratio reaction of MMA/Me_2PhSiH/$[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) at 20 °C in fluorobenzene + toluene-d_8. Unlabeled peaks were attributed to a small amount of the unconsumed Me_2PhSiH (marked with an *), oligomers, and NMR solvents.

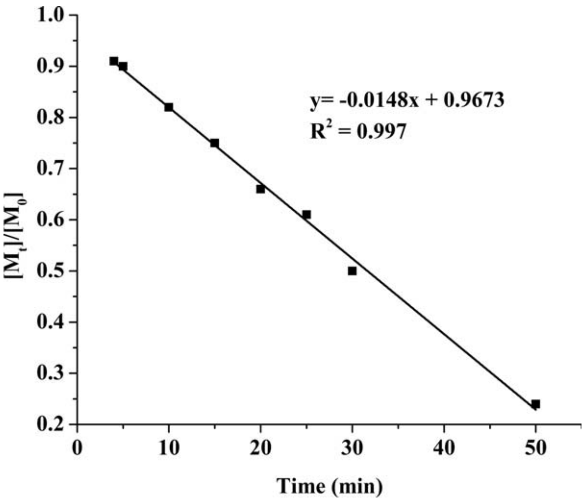


FIGURE 6 Zero-order plot of $[M]_t/[M]_0$ versus time for polymerization of MMA ($[MMA]_0 = 0.909$ M in C_6H_5F) by Et_3SiH/$[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ (L = toluene) at 20 °C in a MMA/Et_3SiH/$[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ ratio of 400:1:1.

Me_2PhSiH). Nonetheless, in all cases the *in situ* generation of ^{R}SKA was clearly confirmed.

In contrast, 1,4-hydrosilylation of MMA catalyzed by $B(C_6F_5)_3$ generates cleanly the corresponding ^{R}SKA without contamination with the unconsumed silane and/or the oligomeric species. For example, the 1:1:0.1 ratio reaction of $Me_2PhSiH + MMA + B(C_6F_5)_3$ at 20 °C in $CDCl_3$ afforded cleanly ^{Me2Ph}SKA (Fig. 5), thanks to the fact that the R_3SiH/$B(C_6F_5)_3$ system exhibited no activity for polymerization of MMA under the current conditions;[32] therefore, there was no imbalanced consumption between MMA and R_3SiH and no oligomer formation either. This result also provided insight into why the $R_3SiH/B(C_6F_5)_3$ system exhibited no activity in MMA polymerization, which is due to the inability of this borane Lewis acid to promote subsequent repetitive iterations of Mukaiyama-Michael addition of the SKA to monomer in the chain propagation cycle.

Overall, the above study supported the hypothesis that the silylium-catalyzed 1,4-hydrosilylation of MMA with R_3SiH generates *in situ* the ^{R}SKA initiator. This hydrosilylation catalyzed by the strongly Lewis acidic silylium ion "Et_3Si^+" resembles that catalyzed by the strong Lewis acid $B(C_6F_5)_3$,[27–30] and the similar mechanism invoking the FLP activation of the hydrosilane by the Lewis acid,[30] now in the form of the isolable silylium-silane complex, $[Et_3Si–H–SiR_3]^+[B(C_6F_5)_4]^-$,[1c,f] is outlined in Scheme 1.

Kinetics and Mechanism of Polymerization by R_3SiH/$[Et_3Si(L)]^+[B(C_6F_5)_4]^-$

Our previous detailed kinetic studies on the acrylic polymerization catalyzed by silylium ions "R_3Si^+," generated by *in situ* oxidative activation of ^{R}SKA with a catalytic amount of $[Ph_3C][B(C_6F_5)_4]$, showed that such silylium-catalyzed living anionic-addition polymerization of acrylics followed first-order kinetics with respect to the catalyst $[R_3Si^+]$ and initiator [^{R}SKA] concentrations, but zero-order kinetics with respect to monomer [M] concentration.[9,10,12] Noteworthy is that such polymerization kinetics (i.e., zero-order dependence on [M] and first- order dependence on initiator and Lewis acid catalyst concentrations) were also observed in the GTP-type polymerization catalyzed by zirconocenium cations.[33] Such kinetics are consistent with the propagation mechanism in that the C—C bond forming step via intermolecular Mukaiyama-Michael addition of the propagating species to the Lewis acid-activated monomer is the rate-

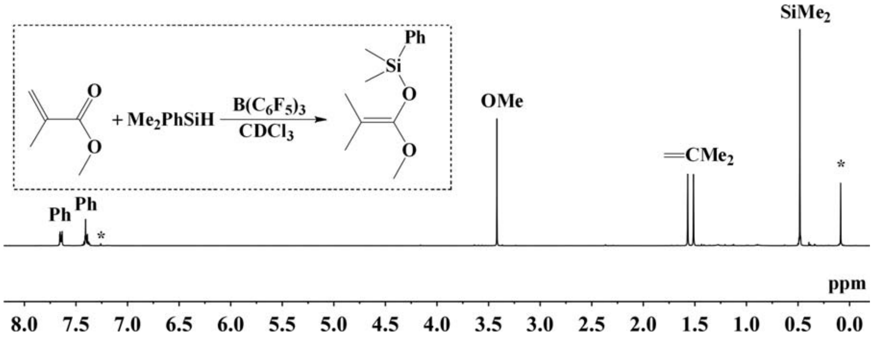
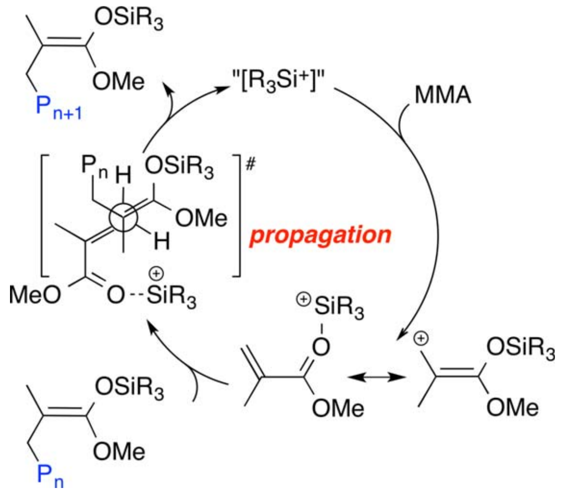


FIGURE 5 ^{1}H NMR spectrum for *in situ* generation of ^{Me2Ph}SKA from the 1:1:0.1 ratio reaction of $Me_2PhSiH + MMA + B(C_6F_5)_3$ at 20 °C in $CDCl_3$. Peaks marked with an * were due to the NMR solvent and silicon grease.



SCHEME 2 Proposed "R_3Si^{+}"-catalyzed chain propagation cycle via repetitive iterations of Mukaiyama-Michael addition of the growing SKA chain to the activated monomer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

limiting step and the release of the Lewis acid catalyst from its coordinated last inserted monomer unit in the growing polymer chain to the incoming monomer is relatively fast.[34]

A survey of kinetics of the current "R_3Si^{+}"-catalyzed living polymerization system with the *in situ* generated ^{R}SKA initiator through the "R_3Si^{+}"-catalyzed hydrosilylation of MMA with R_3SiH also showed clearly the zero-order dependence on monomer concentration (Fig. 6). Hence, the chain propagation mechanism proposed for this polymerization system, as outlined in Scheme 2, follows that already established for other silylium-catalyzed polymerization processes.[9,10,12] Consistent with this mechanistic picture, the PMMA produced by the current catalyst/initiator system is a syndiotactic-biased material (71% *rr*).

Lastly, if the current "Et_3Si^{+}"-catalyzed living methacrylate polymerization follows the initiation and propagation mechanisms proposed in Schemes 1 and 2, respectively, the resulting PMMA should have a linear chain structure of H—[MMA]$_n$—H, where the initiation end (H) is derived from the hydrosilylation of MMA by R_3Si—H and the termination end (H) is derived from hydrolysis of the SKA chain end [–$CH_2C(Me){=}C(OMe)OSiEt_3$] through quenching and/or matrix preparation procedures (see Experimental). To confirm this hypothesis, we used matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) to analyze the chain-end groups of a low-MW oligomer sample with $M_n = 2.80$ kg/mol and $Đ = 1.08$ (measured by GPC), which was prepared by $Et_3SiH/[Et_3Si(L)]^{+}[B(C_6F_5)_4]^{-}$ (L = toluene) at 20 °C in C_6H_5F with $MMA/Et_3SiH/[Et_3Si(L)]^{+}[B(C_6F_5)_4]^{-} = 25/1/0.1$ and quenched with wet hexanes. As can be seen from Figure 7, the MALDI-TOF MS spectrum of the sample consisted of two series of molecular ion peaks, with the spacing between the two neighboring molecular ion peaks within each series being that of the exact molar mass of the oligomer repeat unit, MMA (*m/z* = 100.03). Further analysis of the *m/z* values of the same molecular ion series clearly indicated that series (a) corresponds to the structure of $[H{-}[MMA]_n{-}H + Li]^{+}$, whereas series (b) corresponds to the structure of $[H{-}[MMA]_n{-}H + Na]^{+}$ (Fig. 7); for example, the observed and the calculated (in parenthesis) *m/z* values of 1509.77 (1509.82) and 1525.68 (1525.79) agreed well with each other for the 15-mer structures of $[H{-}[MMA]_{15}{-}H + Li]^{+}$ and $[H{-}[MMA]_{15}{-}H + Na]^{+}$, respectively, (ions from the MALDI matrix). Overall, this result provides an additional piece of critical evidence to support not only the above proposed initiation and propagation mechanisms, but also the living characteristics of this silylium-catalyzed methacrylate polymerization that produces the well-defined and controlled PMMA.

CONCLUSIONS

To the best of our knowledge, this work represents the first successful silylium-catalyzed living polymerization of

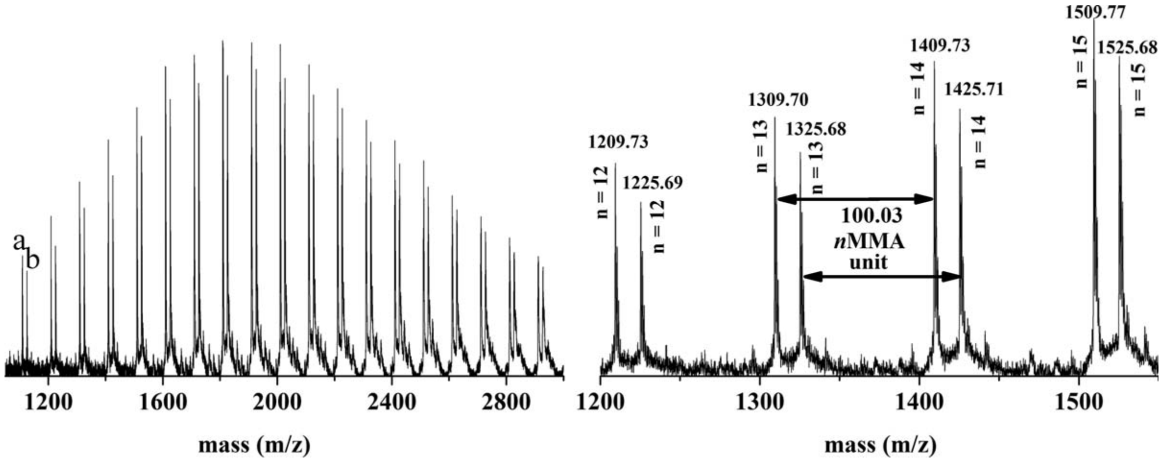


FIGURE 7 MALDI-TOF Mass Spectrum of a low-MW oligomer sample prepared by $Et_3SiH/[Et_3Si(L)]^{+}[B(C_6F_5)_4]^{-}$ (L = toluene) at 20 °C in C_6H_5F with $MMA/Et_3SiH/[Et_3Si(L)]^{+}[B(C_6F_5)_4]^{-} = 25/1/0.1$ and quenched with wet hexanes: H–(MMA)$_n$–H + Li^{+} (**a**) and H–(MMA)$_n$–H + Na^{+} (**b**).

methacrylates (represented by MMA in this study) by the *in situ* generated SKA initiator through the “Et_3Si^+”-catalyzed 1,4-hydrosilylation of monomer with R_3SiH. Although the living/controlled GTP of *acrylates* (represented by ^{n}BA) by the *in situ* generated SKA through $B(C_6F_5)_3$-catalyzed hydrosilylation of monomer with R_3SiH became known while this study was still progress,[31] in our hands the $R_3SiH/B(C_6F_5)_3$ system exhibited no activity for polymerization of less reactive, sterically bulkier methacrylate monomers such as MMA. In contrast, the present system consisting of the stronger silylium Lewis acid, $R_3SiH/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$, catalyzes high-speed and living methacrylate polymerization. The living characteristics of the MMA polymerization by $[Et_3SiH]/[Et_3Si(L)]^+[B(C_6F_5)_4]^-$ were revealed by four sets of experiments. First, the monomer conversion increased gradually with time and the M_n of the polymer increased linearly with monomer conversion, while the MWD remained narrow throughout the polymerization ($Đ = 1.05–1.09$). Second, the measured M_n values were identical or nearly identical to those calculated ones, which yielded essentially quantitative initiation efficiencies for all the conversion points and varied monomer-to-initiator ratio runs, thereby further highlighting the high degree of control and essentially no chain termination or transfer events in this silylium-catalyzed polymerization system. Third, the M_n of the polymer was found to increase linearly with increasing the monomer-to-initiator ratio without broadening the polymer MWD, and sequential additions of monomer feeds successfully extended the polymer chain. Fourth, the well-defined chain structure of $H—[MMA]_n—H$ was confirmed by MALDI-TOF MS analysis of the MMA oligomers.

The real initiator of the polymerization system, ^{R}SKA, is generated *in situ* through the “Et_3Si^+”-catalyzed 1,4-hydrosilylation of monomer with R_3SiH, as evidenced by monitoring the reaction with ^{1}H NMR. This silylium-catalyzed hydrosilylation was proposed to proceed via FLP-type activation of the hydrosilane in the form of the isolable silylium-silane complex, $[Et_3Si—H—SiR_3]^+[B(C_6F_5)_4]^-$, a mechanism similar to the well-established hydrosilylation of carbonyl compounds catalyzed by the strong Lewis acid $B(C_6F_5)_3$.[30] However, there is a key difference between these two Lewis acid-catalyzed 1,4-hydrosilylation systems: while 1,4-hydrosilylation of MMA catalyzed by $B(C_6F_5)_3$ generates cleanly the corresponding ^{R}SKA, the hydrosilylation catalyzed by “R_3Si^+” produces ^{R}SKA predominantly, together with a small amount of the unconsumed silane and/or the oligomeric species, due to the ability of “R_3Si^+” to catalyze the subsequent, relatively fast oligomerization/polymerization of MMA once the real polymerization initiator ^{R}SKA is generated.

Polymerization kinetics of the present system are consistent with the previously established “R_3Si^+”-catalyzed propagation mechanism in that the C—C bond forming step via intermolecular Mukaiyama-Michael addition of the propagating species to the R_3Si^+-activated monomer is the rate-limiting step and the release of the “R_3Si^+” catalyst to the incoming monomer is relatively fast. The polymer end groups, determined by analysis of oligomeric MMA samples with MALDI-TOF MS, are also consistent with the above proposed chain initiation and propagation mechanisms.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (NSFC- No. 21274015) and the Fundamental Research Funds for the Central Universities (No. DUT14LK28) for the study carried out at DLUT, as well as by the US National Science Foundation (NSF-1150792) for the study carried out at CSU.

REFERENCES AND NOTES

1 Selected recent examples and reviews: (a) R. J. Wehmschulte, K. K. Laali, G. L. Borosky, D. R. Powell, *Organometallics* **2014**, *33*, 2146−2149; (b) K. Müther, P. Hrobarik, V. Hrobarikova, M. Kaupp, M. Oestreich, *Chem. Eur. J.* **2013**, *19*, 16579–16594; (c) S. J. Connelly, W. Kaminsky, D. M. Heinekey, *Organometallics* **2013**, *32*, 7478−7481; (d) A. Schäfer, M. Reißmann, S. Jung, A. Schäfer, W. Saak, E. Brendler, T. Müller, *Organometallics* **2013**, *32*, 4713–4722; (e) A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase, T. Müller, *Angew. Chem. Int. Ed.* **2011**, *50*, 12636–12638; (f) M. Nava, C. A. Reed, *Organometallics* **2011**, *30*, 4798−4800; (g) K. Müther, R. Fröhlich, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2011**, *133*, 12442−12444; (h) C. A. Reed, *Acc. Chem. Res.* **2010**, *43*, 121−128; (i) H. F. T. Klare, K. Bergander, M. Oestreich, *Angew. Chem. Int. Ed.* **2009**, *48*, 9077–9079; (j) S. Duttwyler, Q.-Q. Do, A. Linden, K. K. Baldridge, J. S. Siegel, *Angew. Chem. Int. Ed.* **2008**, *47*, 1719–1722; (k) T. Küppers, E. Bernhardt, R. Eujen, H. Willner, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2007**, *46*, 6346−6349; (l) T. A. Kochina, D. V. Vrazhnov, E. N. Sinotova, M. G. Voronkov, *Russ. Chem. Rev.* **2006**, *75*, 95−110; (m) T. Müller, *Adv. Organomet. Chem.* **2005**, *53*, 155−215; (n) K.-C. Kim, C. A. Reed, D. W. Elliott, L. J. Mueller, F. Tham, L. Lin, J. B. Lambert, *Science* **2002**, *297*, 825−827; (o) J. B. Lambert, Y. Zhao, S. M. Zhang, *J. Phys. Org. Chem.* **2001**, *14*, 370−379; (p) C. A. Reed, *Acc. Chem. Res.* **1998**, *31*, 325−332; (q) Z. Xie, A. Benesi, C. A. Reed, *Organometallics* **1995**, *14*, 3933−3941; (r) J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994**, *13*, 2430−2443; (s) Z. Xie, D. J. Liston, T. Jelínek, V. Mitro, R. Bau, C. A. Reed, *J. Chem. Soc., Chem. Commun.* **1993**, 384−386; (t) J. B. Lambert, S. Zhang, *J. Chem. Soc., Chem. Commun.* **1993**, 383−384; (u) J. B. Lambert, S. Zhang, C. L. Stern, J. C. Huffman, *Science* **1993**, *260*, 1917−1918.

2 Selected recent examples: (a) L. Ratjen, M. van Gemmeren, F. Pesciaioli, B. List, *Angew. Chem. Int. Ed.* **2014**, *53*, 8765−8769; (b) M. Mahlau, P. García-García, B. List, *Chem. Eur. J.* **2012**, *18*, 16283−16287; (c) O. Allemann, S. Duttwyler, P. Romanto, K. K. Baldridge, J. S. Siegel, *Science* **2011**, *332*, 574−577; (d) P. García-García, F. Lay, P. García-García, C. Rabalakos, B. List, *Angew. Chem. Int. Ed.* **2009**, *48*, 4363−4366; (e) C. H. Cheon, H. Yamamoto, *J. Am. Chem. Soc.* **2008**, *130*, 9246−9247; (f) K. Hara, R. Akiyama, M. Sawamura, *Org. Lett.* **2005**, *7*, 5621−5623.

3 Selected recent examples: (a) K. Müther, J. Mohr, M. Oestreich, *Organometallics* **2013**, *32*, 6643−6646; (b) A. Schulz, A. Villinger, *Angew. Chem. Int. Ed.* **2012**, *51*, 4526–4528; (c) R. K. Schmidt, K. Müther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* **2012**, *134*, 4421−4428; (d) K. Leszczynska, A. Mix, R. J. F. Berger, B. Rummel, B. Neumann, H.-G. Stammler, P. Jutzi, *Angew. Chem. Int. Ed.* **2011**, *50*, 6843–

6846; (e) K. Müther, M. Oestreich, *Chem. Commun.* **2011**, *47*, 334−336; (f) F. M. Ibad, P. Langer, A. Schulz, A. Villinger, *J. Am. Chem. Soc.* **2011**, *133*, 21016−21027; (g) H. F. T. Klare, M. Oestreich, *Dalton Trans.* **2010**, *39*, 9176−9184; (h) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* **2010**, *132*, 4946−4953; (i) S. Duttwyler, C. Douvris, N. L. P. Fackler, F. S. Tham, C. A. Reed, K. K. Baldridge, J. S. Siegel, *Angew. Chem. Int. Ed.* **2010**, *49*, 7519–7522; (j) C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188−1190; (k) R. Panisch, M. Boldte, T. Müller, *J. Am. Chem. Soc.* **2006**, *128*, 9676–9682.

4 (a) Q. Wang, H. Zhang, G. K. S. Prakash, T. E. Hogen-Esch, G. A. Olah, *Macromolecules* **1996**, *29*, 6691−6694; (b) G. A. Olah, X.-Y. Li, Q. Wang, G. Rasul, G. K. S. Prakash, *J. Am. Chem. Soc.* **1995**, *117*, 8962−8966.

5 G. Toskas, M. Moreau, M. Masure, P. Sigwalt, *Macromolecules* **2001**, *34*, 4730−4736.

6 M. Cypryk, J. Chojnowski, J. Kurjata, *ACS Symp. Ser.* **2007**, *964*, 10−26.

7 G. A. Olah, Q. Wang, X.-Y. Li, G. Rasul, G. K. S. Prakash, *Macromolecules* **1996**, *29*, 1857−1861.

8 Y. Zhang, K. Huynh, I. Manners, C. A. Reed, *Chem. Commun.* **2008**, 494−496.

9 Y. Zhang, E. Y.-X. Chen, *Macromolecules* **2008**, *41*, 36−42.

10 Y. Zhang, E. Y.-X. Chen, *Macromolecules* **2008**, *41*, 6353−6360.

11 (a) K. Fuchise, Y. Chen, T. Satoh, T. Kakuchi, Polym. Chem. **2013**, *4*, 4278−4291; (b) M. Rikkou-Kalourkoti, O. W. Webster, C. S. Patrikios, *Encyclopedia of Polymer Science and Technology*; Wiley: New York, **2013**; Vol. *99*, pp 1−77; (c) O. W. Webster, *Adv. Polym. Sci.* **2004**, *167*, 1–34; (d) D. Y. Sogah, W. R. Hertler, O. W. Webster, G. M. Cohen, *Macromolecules* **1987**, *20*, 1473–1488; (e) O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, T. V. RajanBabu, *J. Am. Chem. Soc.* **1983**, *105*, 5706–5708.

12 G. M. Miyake, Y. Zhang, E. Y.-X. Chen, *Macromolecules* **2010**, *43*, 4902–4908.

13 Y. Zhang, L. O. Gustafson, E. Y.-X. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 13674–13684.

14 R. Kakuchi, K. Chiba, K. Fuchise, R. Sakai, T. Satoh, T. Kakuchi, *Macromolecules* **2009**, *42*, 8747−8750.

15 (a) H. Yamamoto, *Tetrahedron* **2007**, *63*, 8377–8412; (b) M. B. Boxer, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 48–49; (c) K. Ishihara, Y. Hiraiwa, H. Yamamoto, *Syn Lett.* **2001**, 1851–1854.

16 B. Mathieu, L. Ghosez, *Tetrahedron Lett.* **1997**, *38*, 5497−5500.

17 K. Fuchise, R. Sakai, T. Satoh, S.-I. Sato, A. Narumi, S. Kawaguchi, T. Kakuchi, *Macromolecules* **2010**, *43*, 5589−5594.

18 K. Takada, K. Fuchise, T. Kubota, T. Ito, Y. Chen, T. Satoh, T. Kakuchi, *Macromolecules* **2014**, *47*, 5514−5525.

19 Y. Zhang, F. Lay, P. García-García, B. List, E. Y.-X. Chen, *Chem. Eur. J.* **2010**, *16*, 10462–10473.

20 E. Y.-X. Chen, T. J. Marks, *Chem. Rev.* **2000**, *100*, 1391–1434.

21 P. Jutzi, C. Müller, A. Stammler, H. Stammler, *Organometallics* **2000**, *19*, 1442–1444.

22 (a) E. B. Tjaden, D. C. Swenson, R. F. Jordan, *Organometallics* **1995**, *14*, 371–386; (b) H. W. Turner, G. G. Hlatky, R. R. Eckman, U.S. Patent 5,198,401, **1993**.

23 K. Ute, H. Ohnuma, T. Kitayama, *Polym. J.* **2000**, *32*, 1060–1062.

24 R. Zhuang, A. H. E. Müller, *Macromolecules* **1995**, *28*, 8035–8042; 8043–8050.

25 K. Ute, H. Ohnuma, I. Shimizu, T. Kitayama, *Polym. J.* **2006**, *38*, 999–1003.

26 For examples of SKA synthesis by metal-catalyzed hydrosilylation of α,β-unsaturated esters, see: (a) Hydrosilylation, A Comprehensive Review on Recent Advances, B. Marciniec,; Springer, **2009**; Chapter *9*, pp 289–339; (b) G. Z. Zheng, T. H. Chan, *Organometallics* **1995**, *14*, 70–79; (c) A. Revis, T. K. Hilty, *J. Org. Chem.* **1990**, *55*, 2972–2973; (d) I. Ojima, M. Kumagai, *J. Orgmet. Chem.* **1976**, *111*, 43–60.

27 D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441.

28 J. M. Blackwell, D. J. Morrison, W. E. Piers, *Tetrahedron* **2002**, *58*, 8247–8254.

29 Selected reviews: (a) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316; (b) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625−2641; (c) *Frustrated Lewis Pairs I & II*; D. W. Stephan, G. Erker, Eds.; Topics in Current Chemistry; Springer: New York, **2013**; Vols. *332* & *334*; (d) G. Erker, *Pure Appl. Chem.* **2012**, *84*, 2203−2217; (e) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740−5746; (f) G. Erker, *Dalton Trans.* **2011**, *40*, 7475−7483; (g) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46−76; (h) D. W. Stephan, *Dalton Trans.* **2009**, 3129−3136; (i) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535−1539.

30 (a) A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers, H. M. Tuononen, *Nat. Chem.* **2014**, *6*, 983–988; (b) S. Rendler, M. Oestreich, *Angew. Chem. Int. Ed.* **2008**, *47*, 5997−6000; (c) D. J. Parks, J. M. Blackwell, W. E. Piers, *J. Org. Chem.* **2000**, *65*, 3090–3098.

31 K. Fuchise, S. Tsuchida, K. Takada, Y. Chen, T. Satoh, T. Kakuchi, *ACS Macro Lett.* **2014**, *3*, 1015–1019.

32 MMA polymerizations by $Et_3SiH/B(C_6F_5)_3$ in a MMA/$Et_3SiH/B(C_6F_5)_3$ ratio of 400/1/1 in C_6H_5F (i.e., the standard monomer-to-initiator-to-catalyst ratio and conditions employed in this work) or 30/1/0.01 in CH_2Cl_2 (i.e., the standard conditions employed in ref. 31), yielded no polymer formation at RT for up to 24 h.

33 (a) G. Stojcevic, H. Kim, N. J. Taylor, T. B. Marder, S. Collins, *Angew. Chem. Int. Ed.* **2004**, *43*, 5523−5526; (b) Y. Li, D. G. Ward, S. S. Reddy, S. Collins, *Macromolecules* **1997**, *30*, 1875−1883.

34 E. Y.-X. Chen, *Chem. Rev.* **2009**, *109*, 5157–5214.