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High-Speed Living Polymerization of Polar Vinyl Monomers by **Self-Healing Silvlium Catalysts**

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Abstract: This contribution describes the development and demonstration of the ambient-temperature, high-speed living polymerization of polar vinyl monomers (M) with a low silvlium catalyst loading (< 0.05 mol % relative to M). The catalyst is generated in situ by protonation of a trialkylsilyl ketene acetal (^RSKA) initiator (I) with a strong Brønsted acid. The living character of the polymerization system has been demonstrated by several key lines of evidence, including the observed linear growth of the chain length as a function of monomer conversion at a given [M]/[I] ratio, near-precise polymer number-average molecular weight $(M_n, \text{ controlled by the } [M]/[I] \text{ ratio})$ with narrow molecular weight distributions (MWD), absence of an induction period and chain-termination reactions (as revealed by kinetics), readily achievable chain extension, and the successful synthesis of well-defined block copolymers. Fundamental steps of activation, initiation, propagation, and catalyst "self-repair" involved in this living polymerization system have been elucidated, chiefly featuring a propagation "catalysis" cycle consisting of a rate-limiting C-C bond formation step and fast release of the silvlium catalyst to the incoming monomer. Effects of acid activator, catalyst and monomer structure, and reaction temperature on

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polymerization characteristics have also been examined. Among the three strong acids incorporating a weakly coordinating borate or a chiral disulfonimide anion, the oxonium acid [H- $(Et_2O)_2$]⁺[B(C₆F₅)₄]⁻ is the most effective activator, which spontaneously delivers the most active R₃Si⁺, reaching a high catalyst turn-over frequency (TOF) of $6.0 \times 10^3 \text{ h}^{-1}$ for methyl methacrylate polymerization by Me₃Si⁺ or an exceptionally high TOF of 2.4× $10^5 h^{-1}$ for *n*-butyl acrylate polymerization by iBu_3Si^+ , in addition to its high (>90%) to quantitative efficiencies and a high degree of control over $M_{\rm n}$ and MWD (1.07–1.12). An intriguing catalyst "self-repair" feature has also been demonstrated for the current living polymerization system.

lyst-based stereochemical and architectural control, leading to advanced or new classes of polymeric materials, often op-Discrete metal complexes incorporating specifically deerated at ambient or higher polymerization temperature signed organic ligands have been increasingly utilized as (T_p) . In contrast, classical anionic polymerization, which is a highly efficient and active catalysts or initiators for coordikey technique used to polymerize polar vinyl monomers to nation polymerization of polar vinyl monomers such as technologically important functionalized vinyl polymers,^[2] (meth)acrylates and (meth)acrylamides.^[1] Such coordination often requires low T_p or additional additives to render discrete, single-site anionic active species,^[3] for achieving a polymerization is recognized as advantageous over other polymerization methods, thanks to its precision in the catagood control over the polymerization characteristics, such as the resulting polymer number average molecular weight

 $(M_{\rm p})$ and molecular weight distribution (MWD). Many strategies have been developed to achieve various degrees of control in anionic polymerization of polar vinyl monomers at ambient temperature, and the majority of them targeted the production of poly(methyl methacrylate) (PMMA) with controlled structure.^[4]

Of these strategies, one particularly successful, commercialized living/controlled polymerization process employs a

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Introduction

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silyl ketene acetal (SKA) initiator and a catalyst at ambient or higher T_p . This polymerization was developed by scientists of DuPont and termed group-transfer polymerization (GTP), based on the initially postulated associative propagation mechanism in which the silyl group that is coordinated with a nucleophilic catalyst is intramolecularly transferred to the incoming monomer through hypervalent anionic silicon species (path a, Scheme 1).^[5] However, it has been sug-



Scheme 1. Proposed associative (a) and dissociative (b) pathways for methyl methylacrylate (MMA) polymerization by using SKA.^[5-7]

gested^[6] that several key lines of experimental evidence are more consistent with a dissociative mechanism,^[7] which involves ester enolate anions as the propagating species and a rapid, reversible complexation (termination) of small concentrations of enolate anions with SKA or its polymer homologue (path b, Scheme 1). The elementary C-C bond coupling

step in GTP is that of the Mukaiyama-Michael reaction,^[8] but activation of the inactive SKA is the critical first step in either the associative or dissociative pathway described above. Such activation can be viewed as reductive activation of SKA for both pathways in GTP, namely, conversion of the inactive, neutral Si center to the active, anionic Si center. Regardless of the dispute over the mechanism, polymerization of MMA through GTP by using a SKA and a nucleophilic catalyst, such as a bifluoride or oxyanion with a low catalyst loading (0.1–1.0 mol% relative to initiator),^[9] readily produces PMMA with $M_{\rm n} \leq 20\,000\,{\rm g\,mol^{-1}}$ in a controlled fashion at $T_{\rm p}$ \geq ambient temperatures. However, the synthesis of PMMA with $M_{\rm n} \ge 60\,000~{\rm g\,mol^{-1}}$ following this procedure is considered difficult.^[6] (Recently, N-heterocyclic carbenes were utilized as nucleophilic catalysts in GTP, which can produce polymers with higher MWs.^[10]) On the other hand, polymerization of acrylates by using GTP requires the use of Lewis acidic catalysts, such as zinc halides or alkylaluminum chlorides, and a much higher catalyst loading (typically 10 mol% based on monomer) to achieve a reasonable degree of polymerization control.^[11]

Departing from the conventional GTP methodology and utilizing SKA as both the initiator and the source of cata-

lyst, we recently developed a new polymerization system, which is catalyzed by silvlium ions (R₃Si⁺), for a highly active, efficient, and living/controlled (meth)acrylate polymerization at room temperature.^[12] The highly active, ambiphilic propagating species contains both the nucleophilic SKA moiety and the electrophilic silvlium ion sites (Scheme 2). This propagator is generated by a unique "monomer-less" initiation involving oxidative activation of trialkylsilyl SKA (^RSKA) by a catalytic amount of [Ph₃C]⁺ $[B(C_6F_5)_4]^-$, leading to the R₃Si⁺-activated MMA derived from vinylogous hydride abstraction of ^RSKA by Ph₃C⁺ (i.e., the monomer is generated from the initiator), followed by subsequent Michael addition of RSKA to the activated MMA (or silvlated MMA), as shown in Scheme 2. A propagation "catalysis" cycle consists of a fast step of recapturing the silvlium catalyst from the ester group of the growing polymer chain by the incoming MMA, followed by the ratedetermining step (r.d.s.) of the C-C bond coupling by intermolecular Michael addition of the polymeric SKA to the silylated MMA (see Scheme 2). This polymerization is propa-



Scheme 2. Living/controlled (meth)acrylate polymerization catalyzed by R₃Si⁺.^[12,14]

gated in the same fashion as by using MeSKA and the exteradded silylium catalyst, [Et₃Si(toluene)]⁺[Bnallv $(C_6F_5)_4]^{-,[13]}$ generated from the in situ reaction of Et₃SiH and $[Ph_3C]^+[B(C_6F_5)_4]^-$ in toluene.^[12] Our subsequent structure-reactivity relationship studies have revealed a remarkable selectivity of ^RSKAs (R = Me, Et, *i*Bu, Ph, trimethylsilyl (TMS)) on the monomer structures for the polymerization of (meth)acrylates by ^RSKA/[Ph₃C]⁺[B(C₆F₅)₄]⁻.^[14] Specifically, the Me₃Si⁺ catalyst, derived from ^{Me}SKA that bears a small silvl group, is highly active and efficient for the polymerization of MMA but inefficient for the polymerization of the sterically less demanding n-butyl acrylate (nBA). In contrast, the iBu₃Si⁺ catalyst, derived from ^{iBu}SKA that bears a bulky silyl group, exhibits low activity in the polymerization of MMA but exceptional activity, efficiency, and control for the polymerization of nBA.^[14] Overall, this novel polymerization system can readily produce controlled lowto-high molecular weights $(M_n > 10^5 \,\mathrm{g \, mol^{-1}})$ and well-defined $(M_w/M_n = 1.04 - 1.12)$ homo and copolymers of (meth)acrylates; thereby achieving a high silvlium catalyst turn-over frequency (TOF) up to $1.5 \times 10^3 \text{ h}^{-1}$ for methacrylates and an exceptionally high TOF up to $1.2 \times 10^5 \text{ h}^{-1}$ for acrylates, with the reaction completed within 1 min, at 25 °C with a

low catalyst loading (typically 0.05 mol% based on monomer).

In organic catalysis, Yamamoto and coworkers^[15] have extensively utilized strong Brønsted acids^[16] such as trifluoromethanesulfonimide (HNTf₂) for the catalytic Mukaiyama aldol and Michael reactions involving nucleophiles, such as enol silyl ethers or SKAs, and acceptors, such as aldehydes, ketones, or their α , β -unsaturated derivatives. Since our cur-



rent work, which is focused on the development of an alternative method for delivering the R₃Si⁺ catalyst by using strong Brønsted acids, including the oxonium acid [H(Et₂O)₂]⁺[B- $(C_6F_5)_4]^-$ (1),^[17] [HN(Me₂)Ph]⁺ (2),^[18] and the $[B(C_6F_5)_4]^$ chiral acid 3 that has the chiral disulfonimide counteranion (which recently achieved the asymmetric Mukaiyama aldol reaction),^[19] was in progress, Kakuchi et al.^[20] reported the

use of HNTf₂ to activate SKA (thus, generating Me₃SiNTf₂ in situ, which is a superior carbonyl activator to Me₃SiOTf^[21]) for living polymerization of MMA through the same silvlium-catalyzed propagation process described above (see Scheme 2). However, the polymerization by the SKA/HNTf₂ system typically employed a reaction time of 24 h and led to PMMA with low $M_{\rm n}$ of $\leq 17000 \,{\rm g mol^{-1}}$ (but with excellent control, having $M_w/M_n = 1.03-1.08$), thus, giving a low catalyst TOF of typically only $\approx 80 \text{ h}^{-1}$. Intriguingly, the previously reported, highly effective, acid-catalyzed "GTP" systems by using SKA as initiator and additionally employing different combinations of a Lewis acid and a Me₃Si-containing reagent, such as Me₃SiOTf/B- $(C_6F_5)_3$,^[22] Me₃SiI/HgI₂,^[23] or Me₃SiI/RAl(OAr)₂,^[24] may also involve the silvlium-catalyzed process as demonstrated in the SKA/ $[Ph_3C]^+[B(C_6F_5)_4]^-$ system,^[12,14] thereby pointing to potentially broad implications of such a silylium-catalyzed process in polymerization.

The central objective of our current study was to investigate the characteristics of polymerizations of polar vinyl monomers catalyzed by silvlium ions that are derived from the reaction of SKA with the strong Brønsted acids 1, 2, and 3. Our choice of these three acids in this study, in which we were seeking more active and controlled silylium catalyst systems for polymerization of polar vinyl monomers, was motivated by the following four established facts: 1) acids 1 and 2 have been widely used as potent activators in metalcatalyzed polymerization of olefins^[25] and polar vinyl monomers;^[26] 2) the counteranion $[B(C_6F_5)_4]^-$ in acids 1 and 2 is among the least coordinating anions;^[25,27] 3) the silvlium cation chemistry is largely dictated by the coordinating nature of the counteranion;^[28] and 4) specifically designed chiral counteranions, such as that in 3 or its variants, can powerfully mediate asymmetric catalysis^[29] by silvlium cations^[19] or transition-metal cations.^[30]

Results and Discussion

Generation of silylium catalysts: Protonation of ^{Me}SKA by acid **1** in CD_2Cl_2 at ambient temperature is instantaneous and produces cleanly the base-separated silylium ion pair $[Me_3Si\cdots L]^+[B(C_6F_5)_4]^-$ (**4**), where L is the coproduct $Me_2CHC(OMe)=O$ or Et_2O (Scheme 3). The base-stabilized



Scheme 3. Generation of the silylium catalyst Me_3Si^+ by protonation of ^{Me}SKA with strong Brønsted acids.

Me₃Si⁺ cation exhibits a characteristic ¹H NMR signal at $\delta = 0.68$ ppm (s, 9H; Si*Me*₃) and a ²⁹Si NMR (HSQCAD) signal at $\delta = 68.5$ ppm, whereas the noncoordinated borate anion is readily characterized by its ¹⁹F NMR spectrum [$\delta = -131.4$ (brs, 8F; *o*-F), -161.9 (t, J = 20.3 Hz, 4F; *p*-F), -165.8 ppm (t, J = 18.0 Hz, 8F; *m*-F)].^[12] Interestingly, the isolated, dried product showed a 3:1 mixture of **4a** (L= Me₂CHC(OMe)=O) and **4b** (L=Et₂O), whereas the crystals grown slowly over a period of one week were those of pure **4b** (see the Experimental Section). Also noteworthy here is that protonation of ^{Me}SKA with the chiral acid **3** forms cleanly the silylated disulfonimide, Me₃Si-[**3**-H], and the ester coproduct is uncoordinated to the silylium ion, indicative for the coordinating nature of the chiral disulfonimide anion in acid **3**.

As efforts to solve the molecular structure of the (twin) crystals of 4b by X-ray diffraction analysis were unsuccessful, we examined the same reaction by using acid 2, which produces Me₂NPh as the coproduct, a stronger base than the ester or ether from the reaction with acid 1. Indeed, the resulting silvlium cation in 5 coordinates only to N,N-dimethyl aniline and, gratifyingly, colorless single crystals of 5 were found suitable for X-ray diffraction analysis, yielding a well-solved structure (Figure 1; goodness-of-fit on $F^2 = 1.022$ and final $R_1 = 0.0381$). The base-stabilized Si center adopts a distorted tetrahedral geometry with the sum of the C-Si-C angles being 337.59°. The average C-Si-C angle of $\approx 113^{\circ}$ in 5 compares to 113° in $[Me_3Si(py)]^+I^-$ (py=pyridine),^[31] 114° in $[Me_3Si(thf)]^+[B(C_6F_5)_4]^{-[12]}$ and in $[Et_3Si(toluene)]^+[B (C_6F_5)_4$ ⁻,^[13] 115° in [*i*Pr₃Si(MeCN)]⁺[Br₅CB₀H₅]⁻,^[32] 117° in $i Pr_3 Si(Br_6 CB_{11}H_6)$,^[33] and 118° in $[Me_3 Si]^+ [C_2 H_5 CB_{11}F_{11}]^-$;^[34] the last structure of this series has an angle close to 120° for a nearly trigonal-planar trimethyl silyl cation. The three Si-



Figure 1. X-ray crystal structure of $[Me_3Si \cdots N(Me_2)Ph]^+[B(C_6F_5)_4]^-$ (5). Selected bond lengths [Å] and angels [°]: Si(1)–N(1) 1.9211(11), Si(1)–C(1) 1.8386(16), Si(1)–C(2) 1.8335(16), Si(1)–C(3) 1.8402(15), B(1)–C(11) 1.6572(19), B(1)–C(21) 1.6553(19), B(1)–C(31) 1.6524(19), B(1)–C(41) 1.6513(19); C(1)-Si(1)-C(2) 113.03(10), C(1)-Si(1)-C(3) 112.58(8), C(2)-Si(1)-C(3) 111.93(8), N(1)-Si(1)-C(1) 106.73(7), N(1)-Si(1)-C(2) 105.39(6), N(1)-Si(1)-C(3) 106.54(6). Hydrogen atoms are omitted for clarity.

C bonds in the cation of **5** have an essentially identical bond length (1.837 Å average), as do the four B–C bonds (1.655 Å average) in the unassociated borate anion that has essentially identical metric parameters to the same anion found in [Me₃Si(thf)]⁺[B(C₆F₅)₄]⁻.^[12] The Si–N bond length of 1.921(1) Å in **5** is ≈ 0.06 Å longer than that found in [Me₃Si(py)]⁺I^{-[31]} (1.858(9) Å), and significantly longer than a typical covalent Si–N bond (≈ 1.75 Å) in a tetracoordinated silicon center, indicative of a dative Si–N bonding in **5**. Overall, the structural analysis of **5** confirms the proposed protonation reaction of SKA with the acid, which generates the silylium catalyst from the initiator SKA; hence, the SKA in this polymerization system serves as both the initiator and the catalyst source.

Characteristics of homopolymerizations: In the current polymerization system, the added acid activator converts an equimolar amount of the initiator SKA to the silylium catalyst (Scheme 3). Hence, for a polymerization with an $x[M]_0/$



Figure 2. Comparisons of the MMA polymerization by method A (\blacktriangle ; slope = -0.0217, R^2 =0.996) and method B (\triangle ; slope = -0.0311, R^2 = 0.996) in zero-order plots of [M]/[M]₀ versus time. Conditions: solvent = CH₂Cl₂, T_p =25 °C, [MMA]₀=0.935 M, [^{Me}SKA]₀=5.14 mM, [**1**]₀= 0.467 mM, [MMA]₀/[^{Me}SKA]₀/[**1**]₀=400/2.2/0.2, [M]/[I]=200.

activation). Two observations are worth noting: first, both procedures give the polymerization kinetics of a clearly zero-order dependence on [M], as shown in Figure 2; second, under otherwise identical conditions as listed in the caption of Figure 2, the polymerization by method B (i.e., when the silvlium catalyst is generated in the presence of the monomer) is ≈ 1.4 times faster than that by method A (where the silvlium catalyst is preformed followed by addition of the monomer). However, it should be pointed out that both methods achieved a quantitative monomer conversion and produced PMMA with targeted MW ($M_n = 2.26 \times$ 10^4 gmol⁻¹ as determined by the [M]/[I] ratio of 200) and a narrow MWD ($M_w/M_n = 1.08$), achieving a high initiator efficiency (I^*) of ≈ 90 %. Considering a similarly high degree of control and efficiency of the polymerization by both methods but faster reaction and more convenient procedures possessed by method B, we accordingly adopted this method for the rest of the current studies.

Table 1 summarizes the selected results of the MMA polymerization by ^{Me}SKA and acid **1** at ambient temperature. As can be seen from Table 1, the polymerization at all investigated [M]/[I] ratios (100–800, runs 1–5) consumed all monomer while using a low catalyst loading of 0.05 mol%

 $y[SKA]_0/z[acid]_0$ ratio, the real equivalency of the initiating SKA is y-z, thus, giving an actual [monomer (M)]/[initiator (I)] ratio of x/(y-z). Keeping this in mind, we initially compared the activity and efficiency of the MMA polymerization by MeSKA and acid 1 by using two different polymerization procedures detailed in the Experimental Section: method A (preactivation) versus method B (in-reactor

Table 1. Selected results of MMA polymerization by ^{Me}SKA and acid 1 (0.05 mol % based on MMA).^[a]

Run	[M]/[I]	t [min]	Conv. ^[b] [%]	$M_{\rm w}/M_{\rm n}^{\rm [c]}$	$M_n^{[c]}$ [kgmol ⁻¹]	$M_{n(calcd)}$ [kg mol ⁻¹]	I* ^[d] [%]	[<i>rr</i>] ^[b] [%]	[<i>mr</i>] ^[b] [%]	[<i>mm</i>] ^[b] [%]
1	100	20	100	1.07	11.3	10.1	90	71.7	26.6	1.7
2	133	35	100	1.07	14.4	13.4	93	72.2	26.0	1.8
3	200	40	100	1.08	22.1	20.1	91	72.2	25.9	1.9
4	400	75	100	1.07	42.0	40.2	96	71.5	26.5	2.0
5	800	180	100	1.12	74.7	80.2	107	72.4	25.6	2.0

[a] Conditions: solvent = CH₂Cl₂, T_p =25°C, [MMA]₀=0.935 M, [1]₀=0.467 mM, varied [^{Me}SKA]₀ to adjust the [M]/[I] ratio to 100, 133, 200, 400, and 800. [b] Monomer conversions and PMMA methyl triad distributions measured by ¹H NMR spectroscopy. [rr]=syndiotactic racemo triad, [mr]=heterotactic triad, and [mm]=isotactic meso triad. [c] M_n and MWD determined by GPC relative to PMMA standards. [d] Initiator efficiency (I^*)= M_n (calcd)/ M_n (expti), where M_n (calcd)=MW(MMA)×[MMA]_0/[I]_0×conversion %+MW of chain-end groups.

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based on monomer, in relative short time periods, thus, giving rise to a high silvlium catalyst TOF of $\approx 6000 \text{ h}^{-1}$. This TOF value represents an approximately 4-fold rate enhancement over the $^{Me}SKA/[Ph_3C]^+[B(C_6F_5)_4]^-$ system and 80-fold over the ^{Me}SKA/HNTf₂ system (see above), highlighting the importance of the chosen method for delivering the silylium catalyst, when comparing the protonation of SKA by the acid to the vinylogous hydride abstraction of SKA by the trityl salt; and the coordinating nature of the counteranion, when comparing the weakly coordinating [B- $(C_6F_5)_4$ ⁻ anion to the coordinating [NTf₂]⁻ anion. This polymerization also exhibits a high degree of control over the resulting polymer MW with the [M]/[I] ratio, as shown by a linear relationship between the polymer M_n and the [M]/[I] ratio (Figure 3), thus, achieving nearly targeted M_n 's and narrow MWD's of 1.07-1.12 (Figure 4). Also noteworthy is the high efficiency of this catalyst system, affording high



Figure 3. Plot of M_n of PMMA versus the $[M]_0/[I]_0$ ratios. The M_n and PDI (M_w/M_n) values for each $[M]_0/[I]_0$ ratio are included in parentheses (M_n, PDI) .



Figure 4. Overlay of GPC traces of the PMMAs reported in Table 1. M_n [kgmol⁻¹] and PDI for the traces from right (low MW) to left (high MW) are: 11.3, 1.07; 14.3, 1.07; 22.1, 1.08; 42.0, 1.07; and 74.7, 1.12.

 $(\geq 90\%)$ to near quantitative *I**. All PMMAs produced by this catalyst system at ambient temperature are syndio-rich, having a syndiotacticity of $\approx 72\%$ *rr*.

Selected plots (Figures 5 and 6) of the kinetic profile of the MMA polymerization by ^{Me}SKA and acid **1** clearly show a strictly linear increase of M_n with an increase in MMA



Figure 5. Plots of M_n (\triangle) and PDI (\blacktriangle) versus MMA conversion. Conditions: [M]/[I]=100, CH₂Cl₂, 25 °C (R^2 =0.998).



Figure 6. Plots of M_n (\triangle) and PDI (\blacktriangle) versus MMA conversion. Conditions: [M]/[I]=200, CH₂Cl₂, 25 °C (R^2 =0.999).

conversion, whereas the MWD remains narrow and nearly constant for all conversions. Overall, all results (those discussed above and further results on kinetics, chain extension, and well-defined block copolymer formation to be discussed below) demonstrate the living characters of this polymerization catalyzed by the silylium catalyst.

Polymerization kinetics and mechanism: Table 2 compiles some selected kinetic results of the MMA polymerization by ^{Me}SKA and acid **1** (0.05 mol% relative to monomer) in

Table	2. Sel	ected kinetic	data	for MMA pol	lyme	rization by	^{Me} SKA	and 1	l
(0.05 1	nol %	based on MM	(A)	in CH ₂ Cl ₂ at 2	5°C.	[a]			
Run	[1]	[M]/[I].	t	Conv	М	М	WD	<i>I</i> *	

Run	[I]	$[M]/[I]_0$	t	Conv.	$M_{ m n}$	MWD	I^*
	[тм]		[min]	[%]	$[kg mol^{-1}]$	$(M_{\rm w}/M_{\rm n})$	[%]
1	9.35	100	1	17.1	1.74	1.04	104
2			3	28.0	2.63	1.09	110
3			5	39.4	3.89	1.08	104
4			7	49.6	5.31	1.12	96
5			10	71.8	7.72	1.10	95
6			13	86.9	9.17	1.08	96
7			16	97.8	10.3	1.07	96
8	7.01	133	1	10.2	1.69	1.03	86
9			3	19.3	2.44	1.07	109
10			5	25.8	3.63	1.11	- 98
11			7	34.5	4.76	1.11	99
12			10	51.0	6.87	1.07	100
13			15	67.6	9.70	1.08	94
14			20	87.0	12.2	1.08	96
15			30	98.7	14.3	1.07	92
16	4.67	200	5	21.6	4.30	1.08	103
17			10	35.8	7.96	1.06	92
18			20	66.9	15.0	1.09	90
19			30	95.2	20.9	1.08	92
20			40	100	22.1	1.08	91
21	2.34	400	5	14.5	4.60	1.09	128
22			10	19.2	8.24	1.06	94
23			20	34.9	14.9	1.07	95
24			30	51.7	22.9	1.09	91
25			45	74.7	32.5	1.08	93
26			60	93.9	38.2	1.08	99
27			75	100	4.20	1.07	96
28	1.17	800	5	5.6	4.12	1.09	110
29			10	8.8	7.64	1.12	93
30			20	15.8	13.2	1.08	97
31			30	23.3	20.2	1.09	93
32			45	36.9	32.1	1.08	92
33			60	48.1	41.5	1.07	93
34			90	72.3	60.8	1.08	95
35			120	91.4	72.6	1.10	101
26							

[[]a] See footnotes of Table 1 for explanations of abbreviations and methods.

 CH_2Cl_2 at 25 °C with five different [M]/[I] ratios ranging from 100 to 800. Overall, these more detailed studies further confirm the living character of the polymerization manifested in Table 1 and reveal that all polymerizations, from low to high monomer conversions and in all [M]/[I] ratios investigated, are well controlled, thereby producing PMMA with targeted M_n 's and narrow MWD's (1.04–1.12) and achieving high to near quantitative initiator efficiencies.

In one set of kinetic experiments, we employed a constant $[M]_0/[I]_0$ ratio of 200 by adjusting relative amounts of $[^{Me}SKA]_0$ and $[1]_0$ (thus, the Me₃Si⁺ catalyst concentration). Kinetic plots of these polymerizations clearly showed no induction period and a strict zero-order dependence on [M] for all the polymerizations investigated herein (Figure 7). However, the polymerization is first order with respect to the catalyst concentration [Me₃Si⁺], given by the slope of 1.13 from the double logarithm plot (Figure 8) of k_{app} as a function of $[1]_0$ (i.e., $[Me_3Si^+]$), thereby establishing an activated monomer polymerization (i.e., silylium catalysis). As expected, the catalyst concentration does not affect the re-



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Figure 7. Zero-order plots of $[M]_{t}/[M]_{0}$ versus time for the MMA polymerization by ^{Me}SKA and **1** in CH₂Cl₂ at 25 °C and varied concentrations of acid **1** (thus, the Me₃Si⁺ catalyst): $[MMA]_{0}=0.935 \text{ M}$, $[^{Me}SKA]_{0}=6.08 \text{ mM} (\blacktriangle)$, 5.61 mM ($\bigtriangleup)$, 5.14 mM (\blacksquare), 4.91 mM (\square), 4.79 mM (\blacklozenge); $[\mathbf{1}]_{0}=1.402 \text{ mM} (\bigstar)$, 0.935 mM (\bigtriangleup), 0.467 mM (\blacksquare), 0.234 mM (\square), 0.117 mM (\blacklozenge).



Figure 8. Plot of $\ln(k_{app})$ versus $\ln([\mathbf{1}]_0)$ (slope = 1.13, $R^2 = 0.972$).

sulting PMMA's syndiotacticity, with a constant syndiotacticity of 72 % rr upon variations of [Me₃Si⁺] from 0.0125 to 0.15 mol % relative to monomer.

In another set of kinetic experiments, we kept $[M]_0$ and $[1]_0$ constant but varied $[^{Me}SKA]_0$ (thus, the initiator concentration) as $[I] = [^{Me}SKA]_0 - [1]_0$. These kinetic experiments with $[M]_0/[I]_0$ ratio = 100, 133, 200, 400, and 800, again revealed that the polymerization follows the strict zero-order kinetics with respect to [M] (Figure 9) and also the first-order dependence on [I], given by the slope of 0.95 from a plot of $\ln(k_{app})$ versus $\ln[I]$ (Figure 10). These results indi-



Figure 9. Zero-order plot of $[M]/[M]_0$ versus time for the MMA polymerization by ^{Me}SKA and 1 in CH₂Cl₂ at 25 °C and varied SKA concentrations: $[MMA]_0 = 0.935 \text{ M}$, $[\mathbf{1}]_0 = 0.467 \text{ mM}$, $[^{Me}SKA]_0 = 9.82 \text{ mM}$ (\blacktriangle , $R^2 = 0.993$), 7.48 mM (\bigtriangleup , $R^2 = 0.995$), 5.14 mM (\blacksquare , $R^2 = 0.999$), 2.80 mM (\square , $R^2 = 0.998$), 1.64 mM (\blacklozenge , $R^2 = 0.999$).

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Figure 10. Plot of $\ln(k_{app})$ versus $\ln([I])$, where $[I] = [M^{e}SKA]_{0} - [1]_{0}$ (slope = 0.95, $R^{2} = 0.998$).

cate that the propagation mechanism ("catalysis" cycle) is



Scheme 4. Fundamental steps of activation, initiation, propagation, and catalyst "self-repair" involved in the living polymerization catalyzed by R_3Si^+ -An⁻ (An = B(C_6F_5)_4).

firmed by the following chain-extension and copolymeriza-

tion experiments. In the chain-extension experiment, the

first 200 equiv of MMA were polymerized by ^{Me}SKA and acid 1 in CH₂Cl₂ at 25 °C to give the precisely controlled

PMMA with $M_n = 19.9 \text{ kg mol}^{-1}$, MWD = 1.08, $I^* = 101 \%$,

and $T_g = 128$ °C (run 1, Table 3). Subsequently, the second

200 equiv of the MMA feed was added, and the polymeri-

zation resumed to give the precisely chain-extended PMMA

the same as that proposed for the polymerization by SKA/ $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Scheme 2), in which the C–C bond formation step through intermolecular Michael addition of the polymeric SKA to the silylium-activated (or silylated) MMA is the rate-determining step, and the release of the silylium catalyst from the ester group of the growing polymer chain to the incoming MMA is relatively fast, thereby highlighting the high efficiency of the silylium catalysis in this polymerization.

Being highly reactive and moisture-sensitive species, silylium catalysts, R₃Si⁺, can be consumed by even an extremely low level of protic impurities.

Significantly, our catalyst "selfrepair" study (see the Experimental Section) clearly demonstrated the self-healing ability of the silylium catalyst. Specifically, the reaction of H_2O (as a protic impurity) with equimolar amounts of catalyst **4**, derived from protonation of ^{Me}SKA by acid **1**, showed the clean regeneration of acid **1** and formation of Me₃SiOH. Upon addition of another equivalent of ^{Me}SKA, catalyst **4** was regenerated,

Table 3. Selected copolymerization results by ^RSKA and acid 1 at 25 °C.^[a]

Run	^R SKA (R)	Solvent	M_1	M ₂	<i>t</i> ₁ , <i>t</i> ₂ [min]	Conv. [%]	$M_{n(\text{total})}$ [kg mol ⁻¹]	$\frac{\text{MWD}}{(M_{\rm w}/M_{\rm n})}$	I* [%]	Т _g [°С]
1	Me	CH_2Cl_2	MMA	none	35	100	19.9	1.08	101	128
2	Me	CH_2Cl_2	MMA	MMA	35, 115	100	41.1	1.09	99	n.d. ^[b]
3	Me	CH_2Cl_2	none	BMA	140	100	44.3	1.07	64	n.d.
4	Me	CH_2Cl_2	MMA	BMA	270	100	69.0	1.07	70	70
5	<i>i</i> Bu	toluene	MMA	none	210	100	20.0	1.08	100	n.d.
6	<i>i</i> Bu	toluene	none	nBA	1	100	23.2	1.08	110	n.d.
7	<i>i</i> Bu	toluene	MMA	nBA	210, 1	100	42.5	1.08	108	122, -46

[a] Conditions: $[M_1]/[M_2]/[I] = 200:200:1$; [1] = 0.05 mol % based on the first monomer feed, or 0.025 mol % based on the total monomer feed. [b] n.d. = not determined.

which exhibited a similar polymerization activity to the originally generated catalyst before the "self-repair" process. Overall, a combination of the detailed kinetic results with the activation and catalyst "self-repair" studies led to the proposed mechanism for the MMA polymerization by ^RSKA and acid **1**, outlined in Scheme 4. Although the propagation proceeds in the same fashion as that proposed for the polymerization by ^RSKA/[Ph₃C]⁺[B(C₆F₅)₄]⁻, the current ^RSKA/acid **1** system, which is faster and more effective, proceeds through a different activation (catalyst generation) pathway, and exhibits a unique catalyst self-healing feature, thereby offering more attractive polymerization catalysis features.

Chain extension and copolymerization: The living character of the current polymerization system has been further conwith M_n =41.4 kg mol⁻¹, MWD=1.09, and I^* =99% (run 2, Table 3). The doubled MW after the chain extension is shown in the overlaid GPC traces of the PMMA before and after the chain extension depicted in Figure 11. The polymerization of the bulkier *n*-butyl methacrylate (BMA) is slower but, nonetheless, proceeds to completion in 140 min (run 3, Table 3), and the resulting poly(*n*-butyl methyl acrylate) (PBMA) has a higher syndiotacticity (78% *rr*) than the PMMA (72% *rr*) produced by this catalyst system. We also showed that statistical copolymerization of the well-defined, random copolymer with a narrow MWD of 1.07 and a T_g of 70°C, which is approximately the midpoint of the T_g 's for PMMA and PBMA.

Guided by our previous structure-reactivity relationship studies on the $^{R}SKA/[Ph_{3}C]^{+}[B(C_{6}F_{5})_{4}]^{-}$ system, $^{[14]}$ we

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Figure 11. Overlay of GPC traces of the PMMA before and after the chain-extension experiment reported in Table 3 (right: run 1, left: run 2).



Figure 12. Overlay of GPC traces of P(nBA) (right: run 6, Table 3) and PMMA-*b*-P(*n*BA) (left: run 7, Table 3).

turned to the iBu_3Si^+ catalyst derived from ${}^{iBu}SKA$ for the polymerization of *n*BA. Indeed, this catalyst exhibits a lower activity for MMA polymerization than Me_3Si^+, whereas it maintains the excellent control and quantitative efficiency (run 5, Table 3), but an exceptional activity and control for polymerization of *n*BA (run 6, Table 3). Built upon the living character Table 4. Selected polymerization results by MeSKA and different acids.^[a]

		1	2		2								
Run	Acid	$T_{\rm p}$	М	[M]/[I]	t	Conv.	TOF	M _n	$M_{\rm w}/M_{\rm n}$	I^*	[<i>rr</i>]	[mr]	[mm]
		[°C]			[min]	[%]	$[h^{-1}]$	[×10 ³]		[%]	[%]	[%]	[%]
1	1	25	MMA	200	40	100	6000	22.1	1.08	91	72.2	25.9	1.9
2	1	0	MMA	200	180	91.4	1 2 2 0	20.0	1.09	92	75.3	22.9	1.8
3	1	-40	MMA	200	1980	8.9	10	3.41	1.13	55	86.9	11.0	2.1
4	2	25	MMA	200	900	97.6	260	18.5	1.07	106	70.4	27.4	2.2
5	3	25	MMA	200	1440	0	0						
6	1	25	DMAA	800	15	100	64000	102	1.09	78			
7	3	25	DMAA	200	20	100	12000	30.2	1.13	66	61	1.5	38.5

[a] Conditions: [acid] = 0.05 mol % based on monomer, solvent = CH_2Cl_2 .

exhibited by the iBu_3Si^+ catalyst for both MMA and nBA homopolymerizations, the block copolymerization by this catalyst led to the well-defined block copolymer, PMMA-*b*-P(*n*BA), with a targeted M_n and a narrow MWD of 1.08 (run 7, Table 3), as found in the GPC traces shown in Figure 12. The copolymerization is also highly efficient with a near quantitative efficiency and, as expected, the block copolymer exhibits two T_g 's of 122 °C and -46 °C, corresponding to the hard PMMA and soft P(*n*BA) blocks, respectively.

Effects of reaction temperature and catalyst structure: Owing to the chain-end-controlled nature of this polymerization (i.e., 4 $[mm][rr]/[mr]^2 \approx 1$), the T_p should have a great influence on the resulting polymer tacticity. Accordingly, decreasing T_p from 25 °C (72.2 % rr, run 1, Table 4) to 0 °C (75.3 % rr, run 2, Table 4) resulted in an increase in syndiotacticity of 3 %, but at the expense of an approximately 5fold activity reduction. A further drop in T_p to -40 °C gave a syndiotactic PMMA with 87 % rr (run 3, Table 4), but the polymerization activity was drastically diminished by more than two orders of magnitude.

The structure of the silylium catalyst in the current polymerization system is determined by both the SKA and the

acid structures (see Scheme 3). On one hand, the initiating ^RSKA delivers the cation of the catalyst, R₃Si⁺. On the other hand, the activator acid delivers the anion of the catalyst. Hence, we examined the effects of both cation and anion on the polymerization characteristics. Consistent with what we have previously observed for the SKA/[Ph₃C]⁺[B- $(C_6F_5)_4$ ⁻ system,^[14] there is a remarkable selectivity of ^RSKA on monomer structure. Thus, the small Me₃Si⁺ catalyst derived from ^{Me}SKA and acid 1 is highly active (TOF= 6000 h^{-1}), efficient ($I^* > 90\%$), and living for the polymerization of MMA (run 1, Table 4), but ill-controlled for the polymerization of the sterically less demanding nBA (e.g., at 45% conversion, the polymer produced gave a relatively broad MWD of 1.53). In sharp contrast, the bulkier iBu₃Si⁺ catalyst derived from 'BuSKA and acid 1 exhibits lower activity in the polymerization of MMA (TOF= $2000 h^{-1}$, run 5, Table 3), but exceptional activity (TOF= $2.4 \times 10^5 \text{ h}^{-1}$), efficiency, and control for the polymerization of nBA (run 6, Table 3).

Staying with the initiator ^{Me}SKA but switching the activating acid from **1** to **2** resulted in a 23-fold reduction in activity (run 4 vs. run 1, Table 4). As both acids are paired with the same anion $[B(C_6F_5)_4]^-$ and both react with ^{Me}SKA to instantaneously deliver the cation Me₃Si⁺, the observed con-

trast in activity must be attributed to the strong coordinating N,N-dimethyl aniline, the coproduct from acid 2 (see above), that significantly hampers the catalyst reactivity. When the anion employed becomes too coordinating, as in the case of the chiral disulfonimide anion in acid 3 (see above), the MMA polymerization shuts down completely (run 5, Table 4). To overcome this problem, we reasoned that utilizing a monomer that is basic enough to outcompete the anion for coordination to the silylium catalyst could lead to an active polymerization system by using 3. Indeed, the polymerization of N,N-dimethyl acrylamide (DMAA, a stronger base than MMA) by MeSKA and acid 3 in CH₂Cl₂ is highly active, reaching a high TOF of 12000 h⁻¹ and producing poly(N,N-dimethyl acrylamide) (PDMAA) with a narrow MWD of 1.13 (run 7, Table 4). However, the resulting polymer is essentially atactic, with a triad distribution of 38.5% mm and 61.5% rr/mr as determined by ¹³C NMR spectroscopy, and the polymerization is still about 6 times slower than the same polymerization in the presence of acid **1** paired with the weakly coordinating anion $[B(C_6F_5)_4]^-$ (run 7 vs. run 6, Table 4). The same polymerization by ^{Me}SKA and acid 3, but carried out in toluene, is much slower, requiring 22 h to reach completion, but the resulting PDMAA has a similar tacticity of 37.2 % mm and 62.8 % rr/ mr.

Conclusion

In summary, this contribution presents a full account of our investigation into the ambient-temperature, high-speed living polymerization of polar vinyl monomers (e.g., methacrylates, acrylates, and acrylamides), catalyzed by silvlium ions derived from the spontaneous protonation of the SKA initiator with the strong Brønsted acids 1, 2, and 3-which incorporate the noncoordinating $[B(C_6F_5)_4]^-$ anion or the chiral disulfonimide anion. The living character of the current polymerization system has been demonstrated by several key lines of evidence, including the observed linear growth of the chain length as a function of monomer conversion at a given [M]/[I] ratio, near-precise polymer M_n (controlled by the [M]/[I] ratio) with narrow MWD, absence of an induction period and chain-termination reactions (as revealed by polymerization kinetics), readily achievable chain extension, and the successful synthesis of the well-defined block copolymers. We have also elucidated the fundamental steps of activation, initiation, propagation, and catalyst "self-repair" involved in this living polymerization system. Key findings of this study are summarized as follows: Among the three strong Brønsted acids investigated in this study, the oxonium acid 1 is the most effective activator, in that it delivers the most active silylium catalyst, R₃Si⁺, thanks to 1) its least coordinating counteranion $[B(C_6F_5)_4]^$ and 2) the weak basic coproduct (ether and ester) relative to monomer. Hence, the MMA polymerization by MeSKA and 1 at ambient temperature with a low catalyst loading of 0.05 mol% (based on monomer) exhibits a high activity

(catalyst TOF=6000 h⁻¹), a high efficiency (>90% to quantitative I^* values), and a high degree of control (near-precise M_n as determined by the [M]/[I] ratio and narrow MWD's of 1.07–1.12). Acid **2** is much less effective, due to its strong coordinating coproduct *N*,*N*-dimethyl aniline formed upon protonation of SKA, whereas acid **3** is ineffective for MMA polymerization, due to its coordinating disulfonimide anion. However, a high activity of the ^{Mc}SKA/**3** system has been achieved in the polymerization of DMAA (TOF= 12000 h⁻¹), attributed to the ability of this monomer to outcompete the anion for coordination to the silylium ion.

The structure of the silylium ions also exerts a strong effect on polymerization activity and control, as revealed by a remarkable selectivity of ^RSKA on monomer structure. Thus, the small Me₃Si⁺ catalyst derived from ^{Me}SKA and acid **1** is highly active, efficient, and living for the polymerization of MMA, but it is ill-controlled for the polymerization of *n*BA. On the other hand, the larger *i*Bu₃Si⁺ catalyst derived from ^{*i*Bu}SKA and acid **1** exhibits lower activity in the polymerization of MMA, but exceptional activity (TOF= 2.4×10^5 h⁻¹), efficiency, and control for the polymerization of *n*BA. This system also enabled the synthesis of well-defined methacrylate-*b*-acrylate (MMA-*b*-*n*BA) block copolymers.

Results of kinetic studies showed that the polymerization by ^{Me}SKA and acid **1** is zero order in monomer concentration and first order in the concentrations of initiator [SKA] and catalyst [Me₃Si⁺]. These results are consistent with the propagation mechanism ("catalysis" cycle) as depicted in Scheme 4, in which the C–C bond formation step through Michael addition of the polymeric SKA to the silylium-activated MMA is the rate-determining step and the release of the silylium catalyst from the ester group of the growing polymer chain to the incoming MMA is relatively fast, thereby highlighting the high efficiency of the silylium catalysis in this polymerization. Another interesting feature of this polymerization is its unique catalyst "self-repair" feature, as outlined in the catalyst healing cycle of Scheme 4.

All PMMAs produced by this catalyst system at ambient temperature are syndio-rich polymers with a syndiotacticity of \approx 72% *rr*, although the syndiotacticity of PBMA is higher (78% *rr*). The syndiotacticity of PMMA can be enhanced to 75% *rr* and 87% *rr*, at the expense of substantially reduced activity, by lowering T_p to 0°C and -40°C, respectively. Utilization of the chiral disulfonimide anion, in attempts to regulate the MMA polymerization stereochemistry, was hampered by its inactivity. Efforts to achieve a stereoselective polymerization catalyzed by chiral silylium catalysts are currently underway.

Experimental Section

Materials, reagents, and methods: All syntheses and manipulations of airand moisture-sensitive materials were carried out in flamed-dried Schlenk-type glassware on a dual-manifold Schlenk line, on a highvacuum line (from 10^{-5} – 10^{-7} Torr), or in an argon-filled glove box (typi-

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cally < 1.0 ppm oxygen and moisture). NMR-scale reactions (typically in a 0.02 mmol scale) were conducted in Teflon-valve-sealed J. Young-type NMR tubes. High performance liquid chromatography (HPLC) grade organic solvents were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina (for diethyl ether (Et₂O), tetrahydrofuran (THF), and CH₂Cl₂) followed by passage through Q-5-supported copper catalyst (for toluene and hexane) stainless steel columns. [D₆]Benzene and [D₈]toluene were dried over sodium/potassium alloy and distilled in vacuum or filtered, whereas C₆D₅Br, CD₂Cl₂, and CDCl₃ were dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F) or a Varian Inova 400 spectrometer. Chemical shifts for $^1\mathrm{H}$ and $^{13}\mathrm{C}\,\mathrm{NMR}$ spectra were referenced to internal solvent resonances and are reported as parts per million (ppm) relative to SiMe₄, whereas ¹⁹F NMR spectra were referenced to external CFCl₃. Si NMR chemical shifts were obtained from ¹H/²⁹Si HSQC or HSQCAD experiments on a MR400-VNMRs400 (400 MHz, ¹H; 79.4 MHz, ²⁹Si) spectrometer.

Methyl methacrylate (MMA, 99%) and *n*-butyl methacrylate (BMA, 99%) were purchased from Aldrich Chemical, *N*,*N*-dimethyl acrylamide (DMAA, 98%) from TCI America, and *n*-butyl acrylate (*n*BA) from Acros. These monomers were first degassed and dried over CaH₂ overnight, followed by vacuum distillation. Final purification of MMA involved titration with neat tri(*n*-octyl)aluminum (Strem Chemicals) to a yellow end point,^[35] followed by vacuum distillation. The purified monomers (checked by NMR spectroscopy) were stored in brown bottles inside a glove box freezer at -30 °C.

Butylated hydroxytoluene (BHT-H, 2,6-di-tert-butyl-4-methylphenol, 99%) was purchased from Aldrich Chemical and recrystallized from hexane prior to use. Tris(pentafluorophenyl)borane, B(C₆F₅)₃, trityl tetrakis(pentafluorophenyl)borate, $[Ph_3C]^+[B(C_6F_5)_4]^-$, and dimethylanilinium tetrakis(pentafluorophenyl)borate, $[HN(Me_2)Ph]^+[B(C_6F_5)_4]^-$ (2), were obtained as a research gift from Boulder Scientific. B(C₆F₅)₃ was further purified by recrystallization from hexane at -30 °C, whereas [Ph₃C]+[B- $(C_6F_5)_4]^-$ and **2** were used as received. Trimethylsilyl dimethylketene methyl acetal (^{Me}SKA, 98%), diisopropylamine (\geq 99%), methyl isobutyrate (99%), chlorotriisobutylsilane (99%), and bromopentafluorobenzene (99%) were purchased from Aldrich Chemical and dried over CaH₂, followed by vacuum distillation. Boron trichloride (1.0 m in hexane) and HCl (2.0 M in diethyl ether) were purchased from Aldrich Chemical and used as received. Literature procedures were employed for the preparation of triisobutylsilyl dimethylketene methyl acetal Me₂C=C- $(OMe)OSi(iBu)_3$ (^{iBu}SKA),^[14] [Li(Et₂O)]⁺[B(C₆F₅)₄]⁻,^[36] and (R)-3,3'-bis-[3,5-bis(trifluoromethyl)phenyl]-1,1'-binaphthly-2,2'-disulfonimide (3).^[19]

Preparation of $[H(Et_2O)_2]^+[B(C_6F_5)_4]^-$ (1): Oxonium acid 1 was prepared by modification of the literature procedure that employs HClg.^[17] A solution of $[Li(Et_2O)]^+[B(C_6F_5)_4]^-$ (3.00 g, 3.95 mmol) in diethyl ether (10 mL) was added to a reactor that contains a solution of HCl in diethyl ether (1.0 M, 20 mL, 20 mmol) at -30 °C. The mixture was stirred at this temperature for 4 H; after which it was filtered and the filtrate was concentrated to ≈ 10 mL, which were then added to another solution of HCl in diethyl ether (1.0 m, 20 mL, 20 mmol) at -30 °C. This procedure was repeated three times. The solvent of the filtrate was removed in vacuo, and the solid residue was dissolved in CH_2Cl_2 (10 mL). The filtrate was layered with hexane (20 mL) and diethyl ether (5 mL) and stored in a freezer inside the glove box at -30°C overnight. Filtration and drying under vacuum of the resulting colorless crystalline solid yielded 1.30 g (39.8%) of the pure title compound. ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): $\delta = 16.5$ (s, 1H; H), 4.08 (q, J = 7.2 Hz, 8H; OCH₂CH₃), 1.43 ppm (t, J =7.2 Hz, 12 H; OCH₂CH₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): $\delta = -131.9$ (brs, 8F; o-F), -162.4 (t, J=20.4 Hz, 4F; p-F), -166.4 ppm (t, J=17.8 Hz, 8F; m-F).

Reaction of ^{Me}SKA with acid 1: In an argon-filled glove box, a Teflonvalve-sealed J. Young-type NMR tube was charged with ^{Me}SKA (3.5 mg, 0.02 mmol) and CD₂Cl₂ (0.3 mL). A solution of **1** (16.6 mg, 0.02 mmol) in CD₂Cl₂ (0.3 mL) was added to this tube by a pipette at ambient temperature. The mixture was allowed to react for \approx 15 min before NMR spectra were recorded, which showed the clean formation of base-separated ion

pair $[Me_3Si\cdots L]^+[B(C_6F_5)_4]^-$ (4, $L=Me_2CHC(OMe)=O$ or Et_2O). ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): $\delta = 3.86$ (s, 3H; OMe), 3.79 (q, J =7.2 Hz, 8H; OCH₂CH₃), 2.67 (sept, J = 7.2 Hz, 1H; CHMe₂), 1.29 (t, J =7.2 Hz, 12H; OCH₂CH₃), 1.22 (d, J=7.2 Hz, 6H; CHMe₂), 0.68 ppm (s, 9H; SiMe₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): $\delta = -131.4$ (brs, 8F; o-F), -161.9 (t, *J*=20.3 Hz, 4F; *p*-F), -165.8 ppm (t, *J*=18.0 Hz, 8F; *m*-F). Subsequently, the reaction mixture was dried under vacuum to remove all volatiles. The white, solid residue was washed with hexane and then dissolved in CD₂Cl₂ after being dried in vacuo for 2 h. The NMR spectra showed that neither the ester nor the ether was completely removed and that the product was a mixture of $[Me_3Si\cdots L]^+[B(C_6F_5)_4]^-$ in a 3:1 ratio of 4a (L=Me₂CHC(OMe)=O)/4b (L=Et₂O). 4a: ¹H NMR (CD₂Cl₂, 400 MHz, 23 °C): δ = 4.33 (s, 3H; OMe), 2.95 (brs, 1H; CHMe₂), 1.40 (d, J = 7.2 Hz, 6H; CHMe₂), 0.67 ppm (s, 9H; SiMe₃); 4b: ¹H NMR (CD₂Cl₂, 400 MHz, 23 °C): $\delta = 4.54$ (q, J = 7.2 Hz, 4H; OCH₂CH₃), 1.57 (t, J =7.2 Hz, 6H; OCH₂CH₃), 0.67 ppm (s, 9H; SiMe₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): $\delta = -131.4$ (brs, 8F; o-F), -162.0 (t, J = 20.3 Hz, 4F; p-F), -165.9 ppm (t, J=18.3 Hz, 8F; m-F).

It is interesting to note that the colorless crystals, obtained from layering a solution of 1 equiv of ^{Me}SKA in hexane onto a solution of 1 in CH₂Cl₂ at -30 °C inside a freezer in the glove box over a one week, were those of pure **4b**, as shown by NMR spectroscopy. ²⁹Si NMR (CD₂Cl₂, 79.4 MHz, HSQCAD): δ =68.48 ppm (SiMe₃). Unfortunately, X-ray diffraction analysis of these single crystals did not yield a satisfactory structure due to twining.

Reaction of ^{Me}SKA with acid 2: This reaction was carried out in the same manner as the reaction of ^{Me}SKA with 1, forming cleanly [Me₃Si···N-(Me₂)Ph]⁺[B(C₆F₅)₄]⁻ (5) and Me₂CHC(OMe)=O. ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): δ = 7.59 (brs, 3H; Ph), 7.37–7.35 (m, 2H; Ph), 3.70 (s, 3H; OMe), 3.33 (brs, 6H; NMe₂), 2.60 (sept, *J* = 7.2 Hz, 1H; CHMe₂), 1.16 (d, *J* = 7.2 Hz, 6H; CHMe₂), 0.52 ppm (s, 9H; SiMe₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): δ = -131.5 (brs, 8F; *o*-F), -161.9 (t, *J* = 20.4 Hz, 4F; *p*-F), -165.8 ppm (t, *J* = 18.2 Hz, 8F; *m*-F).

The colorless single crystals of **5** were obtained from layering solution of 1 equiv of ^{Me}SKA in hexane onto a solution of **2** in CH₂Cl₂ inside a freezer in the glove box at -30 °C over one week. The ¹H NMR spectrum of the isolated crystals was the same as that of **5** generated in situ from the NMR-scale reaction (minus those peaks due to the ester, which was removed). ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): δ =7.63–7.61 (m, 3H; Ph), 7.36–7.34 (m, 2H; Ph), 3.33 (s, 6H; NMe₂), 0.52 ppm (s, 9H; SiMe₃); ¹³C NMR (CD₂Cl₂, 75 MHz, 23 °C): δ =131.2, 130.8, 120.9 (Ph), 48.17 (NMe₂), -2.47 ppm (SiMe₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): δ = -131.8 (brs, 8F; *o*-F), -161.9 (t, *J*=20.6 Hz, 4F; *p*-F), -165.9 ppm (t, *J*=18.0 Hz, 8F; *m*-F); ²⁹Si NMR (CD₂Cl₂, 79.4 MHz, HSQCAD): δ = 55.65 ppm (SiMe₃). The molecular structure of **5** was characterized by single-crystal X-ray diffraction analysis.

Reaction of ^{Me}SKA with acid 3: This reaction was carried out in the same manner as the reaction of ^{Me}SKA with **1**, forming Me₃Si-[**3**-H] and the free (uncoordinated) Me₂CHC(OMe)=O. ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): δ =8.10–8.05 (m, 4H), 8.00–7.95 (m, 6H), 7.80–7.71 (m, 2H), 7.53–7.44 (m, 2H), 7.29–7.16 (m, 2H), 3.63 (s, 3H; OMe), 2.53 (sept, *J*= 6.9 Hz, 1H; CHMe₂), 1.13 (d, *J*=6.9 Hz, 6H; CHMe₂), 0.19, -0.20 ppm (s, 9H; SiMe₃); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): δ =-62.85, -62.91 ppm (CF₃); ²⁹Si NMR (CD₂Cl₂, HSQC): δ =39.86, 24.51 ppm (SiMe₃).

Study of catalyst "self-repair": This study was carried out in three stages. First, to a solution of catalyst 4 (0.017 mol) in CD₂Cl₂ (0.5 mL) an equimolar amount of was added equimolar at ambient temperature. The mixture was allowed to react for \approx 15 min before NMR spectra were recorded, which showed the clean formation of Me₃SiOH, regeneration of acid 1, and Me₂CHC(OMe)=O. ¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): δ =14.8 (s, 1H; H), 3.97 (q, *J*=6.9 Hz, 8H; OCH₂CH₃), 3.70 (s, 3H; OMe), 2.58 (sept, *J*=6.9 Hz, 1H; CHMe₂), 1.38 (t, *J*=6.9 Hz, 12H; OCH₂CH₃), 1.16 (d, *J*=6.9 Hz, 6H; CHMe₂), 0.42 (s, 1H; SiOH), 0.07 ppm (brs, Me₃SiO); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): δ =-131.4 (brs, 8F; *o*-F), -162.0 (t, *J*=20.3 Hz, 4F; *p*-F), -165.9 ppm (brs, 8F; *m*-F). Second, another equivalent of ^{Me}SKA (0.017 mmol) was added to this reaction mixture. The resulting NMR spectra clearly showed the regeneration of catalyst **4**.

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¹H NMR (CD₂Cl₂, 300 MHz, 23 °C): δ =3.78 (s, 6 H; OMe), 3.69 (q, *J*= 6.9 Hz, 8H; OCH₂CH₃), 2.62 (sept, *J*=6.9 Hz, 2H; CHMe₂), 1.25 (t, *J*= 6.9 Hz, 12 H; OCH₂CH₃), 1.19 (d, *J*=6.9 Hz, 12 H; CHMe₂), 0.67 (s, 9H; SiMe₃), 0.06 ppm (s, Me₃SiO); ¹⁹F NMR (CD₂Cl₂, 282 MHz, 23 °C): δ = -131.4 (brs, 8F; *o*-F), -161.9 (t, *J*=20.3 Hz, 4F; *p*-F), -165.8 ppm (t, *J*=18.2 Hz, 8F; *m*-F). Third, this regenerated catalyst **4** was used for the polymerization of MMA (9.35 mmol) with ^{Me}SKA (0.047 mmol) as initiator in CH₂Cl₂ (10 mL). A quantitative conversion of MMA was achieved in 30 min, showing similar activity to that of the originally generated catalyst.

X-ray crystallographic analysis of [Me₃Si--N(Me₂)Ph]⁺[B(C₆F_{5)₄]⁻ (5): Single crystals suitable for X-ray diffraction were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 °C under 10⁻⁶ Torr for 24 h) after the mother liquor was decanted and then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by the direct method and refined by using the Bruker SHELXTL program library by full-matrix least-squares on F^2 for all reflections.^[37] All non-hydrogen atoms were located by difference Fourier synthesis and refined with anisotropic displacement parameters, whereas all hydrogen atoms were included geometrically with U_{iso} tied to the U_{iso} of the parent atoms and refined isotropically. CCDC-773064 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.}

X-ray crystal structural data for silylium complex **5**: $C_{35}H_{20}BF_{20}NSi$, $M_r = 873.42$, T = 123(2) K, $\lambda = 0.71073$ Å, crystal dimensions $0.509 \times 0.365 \times 0.132$ mm³, monoclinic, P21/c, a = 13.6097 (3) Å, b = 14.1254(3) Å, c = 18.6174(4) Å, $\beta = 99.2180(10)^{\circ}$, V = 3532.83(13) Å³, Z = 4, $\rho_{calcd} = 1.642$ Mg⁻³, θ range for data collection = 1.82–30.70°, 43.253 reflections collected, 10.953 unique ($R_{int} = 0.0289$), goodness-of-fit on $F^2 = 1.022$, final $R_1 = 0.0381$ and $wR_2 = 0.1029$ with $I > 2\sigma(I)$, and residual electron density extremes = 0.396 and -0.279 e Å⁻³.

General polymerization procedures: Polymerizations were performed either in 30 mL oven-dried glass reactors inside the glove box for ambient-temperature (≈ 25 °C) runs or in 25 mL oven- and flame-dried Schlenk flasks interfaced to the dual-manifold Schlenk line for runs at nonambient temperatures. Two different polymerization procedures were employed for comparative studies. In method A (preactivation) procedures, SKA and an acid (1, 2, or 3) were premixed in CH₂Cl₂ or toluene and stirred for 5 min (to cleanly generate the silylium catalyst in situ), followed by addition of monomer to start the polymerization. In method B (in-reactor activation), SKA and monomer were premixed and the polymerization was started by addition of the acid. In both procedures, after the measured time interval, the polymerization was quenched by addition of 5% HCl-acidified methanol (5 mL). For MMA and BMA homo- and copolymerizations, the quenched mixture was precipitated into methanol (100 mL), stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. For nBA polymerizations, the polymer was isolated by evaporation of the solvent and dried in a vacuum oven at room temperature to a constant weight. For DMAA polymerizations, the polymer was precipitated into diethyl ether (100 mL), stirred for 1 h, filtered, washed with diethyl ether, and dried in a vacuum oven at 50 °C overnight to a constant weight.

A specific polymerization example: In an argon-filled glove box, a 30 mL oven-dried glass reactor was charged with 1 (3.9 mg, 4.7 μ mol) in CH₂Cl₂ (5 mL). In a 20 mL glass vial, ^{Me}SKA (9.0 mg, 51.5 μ mol) and MMA (1.00 mL, 9.35 mmol) were mixed in CH₂Cl₂ (5 mL). The mixture in the vial was rapidly poured into the reactor to start the polymerization at ambient temperature. The [MMA]/[^{Me}SKA]/[1] ratio in this selected example was 400:2.2:0.2, and the actual [M]/[1] ratio was 200 (as the acid consumes 0.2 equiv of ^{Me}SKA to form the equal amount of the Me₃Si⁺ catalyst). The reaction mixture was stirred at ambient temperature for 40 min, after which an aliquot (0.2 mL) was withdrawn from the reaction mixture by using a syringe and quickly quenched into a 1 mL vial that contains undried "wet" CDCl₃ (0.6 mL) stabilized with of BHT-H (250 ppm). The reactor was immediately taken out of the glove box, and the reaction was quenched by addition of 5% HCl-acidified methanol

(5 mL). The quenched mixture was precipitated into methanol (100 mL), stirred for 1h, filtered, washed with methanol, and dried in a vacuum oven at 50 °C overnight to a constant weight. The quenched aliquot was analyzed by ¹H NMR spectroscopy to show 100% monomer conversion. The isolated and dried polymer was analyzed by gel permeation chromatography (GPC), showing M_n of 2.21×10^4 gmol⁻¹ and PDI of 1.08, relative to PMMA standards. The dried polymer was also analyzed by ¹H NMR for tacticity measurement. ¹H NMR (CDCl₃, 300 MHz, 23 °C): δ = 3.60 (s, OMe), 2.05 (d, *J*=13.6 Hz, *CH*₂), 1.96–1.90 (m, CH₂), 1.82 (s, CH₂), 1.44 (d, *J*=13.6 Hz, CH₂), 1.21 (s, Me, [*mm*]=1.9%), 1.02 (s, Me, [*mr*]=25.9%), 0.86 ppm (s, Me, [*rr*]=72.2%).

Polymerization kinetics: Kinetic experiments were carried out in a stirred glass reactor at ambient temperature (\approx 25 °C) inside the glove box by using stock solutions of the reagents and the procedures described previously.^[3,38]

Polymer characterizations: Polymer M_n and PDI values were measured by GPC analyses carried out at 40°C and a flow rate of 1.0 mLmin⁻¹, with CHCl₃ as the eluent on a Waters University 1500 GPC instrument equipped with one PLgel 5 µm guard and three PLgel 5 µm mixed-C columns (Polymer Laboratories; linear range of molecular weight=200-2000000). The instrument was calibrated with ten PMMA standards, and chromatograms were processed with Waters Empower software (version 2002). Glass-transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) on a DSC 2920, TA Instrument. Samples, weighted (typically in a 7-10 mg range) and sealed in hermetic aluminum pans by using a DSC press, were first heated to 200 °C at 10°Cmin⁻¹, equilibrated at this temperature for 4 min, then cooled to 0°C (for methacrylate polymers) or -80°C (for nBA-containing polymers) at 10°Cmin⁻¹, held at this temperature for 4 min, and finally reheated to 200 °C at 10 °C min⁻¹. All T_g values were obtained from the second scan after removing the thermal history. ¹H NMR spectra for the analysis of PMMA and PBMA microstructures were recorded in CDCl₃ and analyzed according to the literature,^[39] whereas ¹³C NMR spectra of PDMAA were recorded in D2O at 80°C and analyzed by using literature procedures.[40]

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