Anionic Polymerization of MMA and Renewable Methylene Butyrolactones by Resorbable Potassium Salts

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Received 21 January 2011; accepted 8 February 2011
DOI: 10.1002/pola.24628

ABSTRACT: Three resorbable potassium salts of hydride (K[H]), enolate $Me_2C{=}C(O^iPr)OK$ (K[E]), and allyl $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ (K[A]) have been investigated for controlled anionic polymerization of methyl methacrylate (MMA) and its cyclic analogs, naturally renewable methylene butyrolactones including α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL). When used alone at ambient temperature in toluene, these salts exhibit no (K[H]) to low (K[A]) to modest (K[E]) polymerization activity. Mixing of K[H] and $Al(C_6F_5)_3$ leads to the formation of an "ate" complex, $K^+[HAl(C_6F_5)_3]^-$, which has been structurally characterized by X-ray diffraction; this complex has a high polymerization activity producing atactic PMMA, but addition of another equiv of $Al(C_6F_5)_3$ further enhances both the rate and the efficiency of the polymerization, now producing syndiotactic PMMA with a narrow molecular weight (MW) distribution of 1.04. The K[H]/$2Al(C_6F_5)_3$ system also exhibits high activity for polymerization of (M)MBL. In sharp contrast, addition of $Al(C_6F_5)_3$ to K[A] shuts down the polymerization at various temperatures. The most active, controlled, and syndioselective polymerization system in this series is K[E]/$2Al(C_6F_5)_3$. Accordingly, the polymerization control and kinetics of this most effective system have been examined in more detail. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 2008–2017, 2011

KEYWORDS: anionic polymerization; catalysis; methylene butyrolactone; organometallic catalysts; potassium initiator; renewable monomer

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INTRODUCTION Calling for gradually replacing existing petroleum-based polymeric materials with those derived from naturally occurring, renewable resources in a technologically and economically competitive fashion has stimulated increasing attention to sustainability-related research directed at examining the possibility of replacing petroleum-based raw materials by renewable feedstocks for the production of polymeric materials in large commodity and specialty chemicals markets.[1] In this context, naturally renewable methylene butyrolactones, α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL), are of particular interest in exploring the prospects of substituting the petroleum-based methacrylate monomers for specialty chemicals production.[2] MBL, or tulipalin A, is a natural substance found in tulips, and the MBL ring is an integral building block of many (~10% known) natural products,[3] whereas its γ-methyl derivative, MMBL, is readily prepared via a two-step process from the cellulosic biomass-derived levulinic acid.[4] As the cyclic analog of MMA (Scheme 1), MBL exhibits greater reactivity in free radical polymerization[5] than MMA, attributable to the presence of both the nearly planar five-membered lactone ring (which provides resonance stabilization for the active radical species) and the higher energy exocyclic C=C double bond (as a result of the ring strain and the fixed *s*-cis conformation).[6] The cyclic ring in MBL also imparts significant enhancements in the materials properties of the resulting PMBL, due to the conformational rigidity of the polymer chain through incorporation of the butyrolactone moiety. For example, the glass-transition temperature (T_g) of PMBL produced by the radical polymerization is 195 °C,[7] which is about 90 °C higher than that of atactic PMMA. Additionally, compared to PMMA, PMBL exhibits increased optical properties and resistance to solvent, heat, and scratch.[8]

Polymerization of MBL has been investigated predominately using various free radical polymerization mechanisms,[5,6,7,9] but several other types of mechanisms, including group-transfer polymerization,[10] anionic polymerization,[7] and coordination polymerization by metallocene complexes (*vide infra*) have also been explored. MBL has been copolymerized with various comonomers[5] such as MMA,[11] styrene,[9(d),12] methoxystyrene,[13] and vinyl thiophenes.[14] In comparison, the polymerization of MMBL has been studied to a much lesser extent. Nevertheless, MMBL has also been free radically copolymerized with styrene and MMA,[15] polymerized by free radical emulsion polymerization,[16,17] and polymerized by free-radical, anionic, and group-transfer polymerization methods, which required long reaction times (2 to 44 h), often at low temperatures, achieving low to high, but

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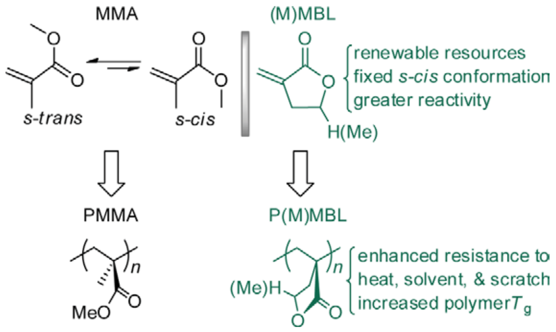
Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 2008–2017 (2011) © 2011 Wiley Periodicals, Inc.



SCHEME 1 Renewable methylene butyrolactones (M)MBL as cyclic analogs of MMA and comparisons between their derived polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

never complete conversions, with unknown polymerization and polymer molecular weight (MW) characteristics.[18]

Building-off of our extensive work on the metal-mediated coordination polymerization of polar vinyl monomers such as (meth)acrylates and (meth)acrylamides,[19] we have recently developed the rapid and controlled coordination–addition polymerization of (M)MBL by metallocene complexes with high activity and other new types of polymerization processes for (M)MBL. For example, the coordination polymerization of (M)MBL in dimethylformamide (DMF) by the divalent Cp^*_2 Sm(THF, tetrahydrofuran)$_2$ catalyst is fast, with TOF (turn-over frequency = mol of monomer consumed per mol catalyst or initiator per h) approaching 3000 h^{-1}, efficient (initiator efficiency, I^*, approaching 100%), and controlled, leading to P(M)MBL with relatively narrow MW distributions (MWDs) and their diblock copolymers with MMA or with each other.[20] Half-sandwich dialkyl rare-earth metal complexes incorporating a disilylated indenyl ligand, $(1,3\text{-}(SiMe_3)_2C_9H_5)M(CH_2SiMe_3)_2(THF)$ (M = Sc, Y, Dy, Lu), are even more (10 times) active for polymerization of MMBL in DMF, achieving quantitative monomer conversion in <1 min with a 0.2 mol % catalyst loading, which gives a high TOF of >30,000 h^{-1}, and producing PMMBL with MW ranging from a medium M_n of 1.89×10^4 Da to a high M_n of 1.63×10^5 Da.[21] We also reported the high-speed and living polymerization of (M)MBL catalyzed by silylium ions R_3Si^+.[22] Atactic PMMBL produced exhibits a T_g of 225 °C, representing a T_g enhancement of ~120 °C over the T_g of the typical atactic PMMA with a comparable MW. Most recently, we developed an extremely active (M)MBL polymerization system, based on classical or frustrated Lewis pairs consisting of a bulky phosphine (e.g., $^tBu_3P$) or bulky *N*-heterocyclic carbene base and the strong acid $Al(C_6F_5)_3$, exhibiting an exceptional TOF of >48,000 h^{-1}.[23]

It becomes readily apparent that reports on the anionic polymerization of renewable (M)MBL monomers are scarce. There were two reports that mentioned the anionic polymerization, one of which used C_6H_5MgBr and 9-fluorenyllithium to polymerize MBL in a low monomer-to-initiator ratio of 43 at typically −78 °C for 6 h,[7] whereas the other used ^nBuLi to polymerize MMBL in a low monomer-to-initiator ratio of 60 at −78 °C for 2 h,[18] but neither report gave MW and MWD characteristics of the resulting polymers. On the other hand, anionic polymerization by organolithium initiators has become the most widely adopted methodology to polymerize polar vinyl monomers, especially conjugated acrylic monomers, to technologically important polar-functionalized vinyl polymers.[24] An important challenge in anionic polymerization using such initiators has been the extensive and continued quests for effective additives or catalysts that can render these multiple-site anionic active species to exhibit high polymerization activities and degrees of polymerization control preferably at ambient temperature or above.[25] In this context, we showed that bulky strong Lewis acids such as $MeAl(BHT)_2$ (BHT = 2,6-di-*tert*-butyl-4-methylphenolate) can convert the hexameric isopropyl α-lithioisobutyrate initiator into the monomeric lithium ester enolaluminate propagating species, $Li^+[Me_2C{=}C(O^iPr)OAlMe(BHT)_2]^-$, thereby, effecting the single-site anionic polymerization with a high degree of polymerization control at ambient temperature.[26] Accordingly, the central objective of this study was to examine the characteristics of anionic polymerization of (M)MBL monomers, along with MMA, using three potassium salts of hydride (K[H]), enolate $Me_2C{=}C(O^iPr)OK$ (K[E]), and allyl $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ (K[A]), as well as their combinations with strong and bulky aluminum Lewis acids, $MeAl(BHT)_2$ and $Al(C_6F_5)_3$. The reasons for choosing the potassium-based initiators for this study are threefold. First, potassium-based initiators have received much less attention as initiators for anionic polymerization in general[25] and never been investigated for polymerizations of renewable (M)MBL monomers, the focus of the current work. Second, potassium-based initiators may possess some advantages over analogous organolithium initiators because the larger potassium cation should change ion-pairing and solvation dynamics of the anionic propagating species and its counterion, thus impacting propagation rates and even polymerization stereochemistry.[25,27] Third, unlike lithium salts, potassium salts are typically nontoxic (resorbable) as the potassium ion belongs to the human metabolism.

EXPERIMENTAL

Materials 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, a high-vacuum line, or in an argon or nitrogen-filled glovebox. HPLC-grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir 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. HPLC-grade DMF was degassed, dried over CaH_2 overnight, followed by vacuum transfer (not by distillation). NMR solvents $CDCl_3$ and DMSO-d_6 were dried over activated Davison 4-Å molecular sieves, and NMR spectra were recorded on a Varian Inova 300 MHz, a Varian Inova 400 MHz, or an Inova

500 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 tetramethylsilane.

Monomers MBL and MMBL were purchased from TCI America, whereas methyl methacrylate (MMA), *n*-butyl acrylate (*n*-BA), potassium hydride, potassium bis(trimethylsilyl)amide, and methyl isobutyrate were purchased from Aldrich. The liquid chemicals were degassed, dried over CaH_2 overnight, followed by vacuum distillation, whereas MMA was further purified by titration with neat tri(*n*-octyl)aluminum (Strem Chemical) to a yellow end point,[28] followed by vacuum distillation. The purified monomers were stored in brown glass bottles over activated Davison 4 Å molecular sieves (for *n*-BA) in a −30 °C freezer inside the glovebox. Butylated hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol) was purchased from Aldrich and was recrystallized from hexanes before use. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was obtained as a research gift from Boulder Scientific Co. and was further purified by recrystallization from hexanes at −30 °C. Tris(pentafluorophenyl)alane, $Al(C_6F_5)_3$, as a 0.5·toluene adduct based on the elemental analysis for the vacuum-dried sample, was prepared from the exchange reaction of $B(C_6F_5)_3$ and $AlMe_3$ in a 1:3 toluene/hexanes solvent mixture in quantitative yield according to a literature procedure.[29] Literature procedures were used to prepare $MeAl(BHT)_2$[30] and potassium 1,3-bis(trimethylsilyl)allyl $K[1,3\text{-}(SiMe_3)_2C_3H_3]$ (K[A]).[31] Potassium isopropyl isobutyrate $Me_2C{=}C(O^iPr)OK$ (K[E]) was freshly prepared, following typical procedures established for the preparation of alkali metal isobutyrate ester enolates,[32] from the reaction of isopropyl isobutyrate and potassium bis(trimethylsilyl)amide (0.5 M in toluene) at 0 °C and isolated as a solid after filtering, washing with hexanes, and drying *in vacuo*. ^{1}H NMR (C_6D_6, 23 °C): δ 4.11 (sept, J = 6.3 Hz, 1H, OC*H*Me$_2$), 1.91 (s, 3H, =C*Me*$_2$), 1.71 (s, 3H, =C*Me*$_2$), 1.18 (d, 6H, J = 6.3 Hz, CH*Me*$_2$).

Isolation of "Ate" Complex $K^+[HAl(C_6F_5)_3]^-$

A suspension containing $Al(C_6F_5)_3$·toluene (115 mg, 0.20 mmol), and KH (160 mg, 4.0 mmol) in precooled toluene (5 mL, −30 °C) was stirred for about 10 min. On filtration, the filtrate was kept at ambient temperature for 1 week after which colorless crystals suitable for X-ray diffraction studies were formed and isolated (80 mg, 70% yield). The *in situ* generated solution of KH and $Al(C_6F_5)_3$ is soluble in hydrocarbon solvents such as benzene, toluene, and cyclohexane. However, the slowly grown crystals of the titled complex have poor solubility in such solvents. ^{19}F NMR (C_6D_6, 23°C): δ −123.2 (d, 6F, *o*-F), −155.3 (t, 3F, *p*-F), −162.2 (m, 6F, *m*-F).

X-Ray Crystallographic Analysis of $K^+[HAl(C_6F_5)_3]^-$

Single crystals of the complex were quickly covered with a layer of Paratone-N oil (Exxon, dried, and degassed at 120 °C/10^{-6} Torr for 24 h) after decanting the mother liquor. A crystal was 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 direct methods and refined using the Bruker SHELXTL program library.[33] The structure was refined by full-matrix least squares on F^2 for all reflections. All atoms were located by difference Fourier synthesis and refined anisotropically except for one hydrogen atom, which was refined isotropically. Owing to the inclusion of potassium as a heavy atom in this ionic compound, the residual electronic density of 2.228 e Å^{-3} appeared a little high. CCDC-807949 contains the supplementary crystallographic data for this article. 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 $K^+[HAl(C_6F_5)_3]^-$: $C_{18}HAlF_{15}K$, $M_r = 568.27$, $T = 173(2)$ K, $\lambda = 0.71073$ Å, crystal dimensions $0.54 \times 0.39 \times 0.31$ mm^3, monoclinic, $C2/c$, $a = 21.2204\ (5)$ Å, $b = 12.1699(3)$ Å, $c = 15.7115(4)$ Å, $\beta = 109.5400(10)°$, $V = 3823.82(16)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.974$ Mg m^{-3}, θ range for data collection = 1.96–33.24°, 22,601 reflections collected, 7278 unique ($R_{int} = 0.0238$), zero restraints, goodness-of-fit on $F^2 = 1.099$, final $R_1 = 0.0803$ and $wR_2 = 0.2287$ with $I > 2\sigma(I)$, and residual electron density extremes = 2.228 and −0.483 eÅ^{-3}.

General Polymerization Procedures

Polymerizations were performed either in 25-mL flame-dried Schlenk flasks interfaced to the dual-manifold Schlenk line for runs using external temperature bath, or in 30-mL glass reactors inside the glovebox for ambient temperature (ca. 25 °C) runs. In a typical polymerization procedure, a predetermined amount of the potassium initiator (11.7 μmol for runs with a [MMA]/[K] ratio of 400, or 10.3 μmol for runs with a [(M)MBL]/[K] ratio of 400) was dissolved in a solvent (4.5 mL toluene or 3.0 mL DMF). With vigorous stirring, monomer (MMA, 0.50 mL, 4.68 mmol; MBL, 403 mg, 4.11 mmol; or MMBL, 461 mg, 4.11 mmol) was quickly added to the above initiator solution via syringe to start the polymerization. For polymerizations by the potassium initiator combined with aluminum Lewis acids, $Al(C_6F_5)_3$ or $MeAl(BHT)_2$ was premixed with the initiator in toluene for 5 min before addition of monomer. For (M)MBL polymerizations in DMF or dichloromethane (DCM), toluene (291 μL, 2.74 mmol) was added as an internal standard, to the reaction mixture. After the measured time interval, a 0.2-mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4-mL vial containing 0.6 mL of undried "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.

The ratio of $[MMA]_0/[MMA]_t$ at a given time 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 O*Me* signal) and PMMA (centered at 3.4 ppm for the O*Me* signals) according to $[MMA]_0/[MMA]_t = 2A_{3.4}/3A_{5.2+6.1}$, 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

TABLE 1 Selected Results of Polymerization of MMA by K[H] and K[H]/ER_3 (E = Al, B)[a]

Run No.	Initiator (I)	Conv[b] (%)	M_n[c] (kg mol^{-1})	MWD[c] (M_w/M_n)	I^*[d] (%)	[*rr*][b] (%)	[*mr*][b] (%)	[*mm*][b] (%)
1	K[H]	0	–	–	–	–	–	–
2	K[H]/1MeAl$(BHT)_2$	69	57.1	1.25	48	76.2	22.7	1.1
3	K[H]/2MeAl$(BHT)_2$	100	90.4	1.13	44	76.2	21.1	2.7
4	K[H]/1Al$(C_6F_5)_3$	100	67.0	1.04	60	74.2	23.0	2.8
5	K[H]/2Al$(C_6F_5)_3$	100	77.7	1.04	52	76.5	21.3	1.2
6	K[HAl$(C_6F_5)_3$]	79	21.3	1.44	148	26.6	51.7	21.7
7	K[HAl$(C_6F_5)_3$]/Al$(C_6F_5)_3$	100	50.3	1.04	80	69.5	26.5	4.0
8	K[H]/1B$(C_6F_5)_3$	0	–	–	–	–	–	–
9	K[H]/2B$(C_6F_5)_3$	0	–	–	–	–	–	–

[a] Carried out in toluene at ambient temperature in a [MMA]/[I] ratio of 400 for 2 h.

[b] Monomer conversion and polymer tacticity measured by ^1H or ^{13}C NMR.

[c] Determined by GPC relative to PMMA standards.

[d] Initiator efficiency (I^*) = M_n(calcd)/M_n(exptl), where M_n(calcd) = M_W(monomer) × [monomer]/[initiator] × conversion% + MW of chain-end groups.

integrals for both peaks at 5.2 and 6.1 ppm. For (M)MBL polymerizations, monomer percent conversions were calculated by comparing the integration of the vinyl protons of the unreacted monomer to the methyl protons of toluene added as internal standard.

^1H NMR ($CDCl_3$, 300 MHz, 23 °C) for PMMA: δ 3.60 (s, O*Me*), 2.05 (d, CH_2), 1.99–1.90 (m, CH_2), 1.82 (s, CH_2), 1.48 (d, CH_2), 1.22 (s, CH_3, *mm*), 1.02 (s, CH_3, *mr*), 0.85 (s, CH_3, *rr*). ^1H NMR (DMSO-d_6, 300 MHz, 100 °C) for PMBL: δ 4.34 (b.s, 2H, OCH_2), 2.24-1.99 (m, 4H, CH_2, CH_2). ^{13}C NMR (DMSO-d_6, 125 MHz, 100 °C) for PMBL: δ 179 (C=O), 64.36 (OCH_2), 44.22, 43.90, 43.74 (quaternary carbon, *rr*, *mr*, *mm*), 41.89–40.58 (main-chain CH_2, unresolved tetrads), 30.47 (β-CH_2). ^1H NMR (DMSO-d_6, 300 MHz, 100 °C) for PMMBL: δ 4.64 (b.s, 1H, C*H*), 2.31 (b.s, 2H, CH_2), 1.99 (b.s, 2H, CH_2), 1.39 (b.s, 3H, CH_3). ^{13}C NMR (DMSO-d_6, 125 MHz, 100 °C) for PMMBL: δ 178 (C=O), 72.65 (OCH), 46.48, 46.15, 45.80 (quaternary carbon, *rr*, *mr*, *mm*), 43.05 (β-CH_2), 40.53, 39.19, 37.69 (main-chain CH_2, *rr*, *mr*, *mm*), 19.46 (CH_3). DEPT experiments were used to remove the DMSO signals in the ^{13}C NMR experiments.

Polymerization Kinetics

Kinetic experiments were carried out in a stirred glass reactor at ambient temperature (ca. 25 °C) inside the argon-filled glovebox using the procedure already described above and $[MMA]_0/[KE]_0$ ratios of 400:1, 800:1, 1200:1, and 1600:1, where $[MMA]_0$ = 0.936 M, $[KIPIB]_0$ = 2.34, 1.17, 0.78, and 0.585mM in 4.5 mL of toluene + MMA solutions. At appropriate time intervals, 0.2-mL aliquots were withdrawn from the reaction mixture using syringe and quickly quenched into 1-mL septum-sealed vials containing 0.6 mL of undried "wet" $CDCl_3$ mixed with 250 ppm BHT-H. The quenched aliquots were analyzed by ^1H NMR to obtain monomer conversions.

Polymer Characterizations

Polymer number-average MWs (M_n) and MW distributions (MWD = M_w/M_n) were measured by gel permeation chromatography (GPC) analyses carried out at 40 °C and a flow rate of 1.0 mL min^{-1}, with $CHCl_3$ as the eluent for PMMA or with DMF for PMBL and PMMBL, on a Waters University 1500 GPC instrument coupled with a Waters RI detector and equipped with four PLgel 5-μm mixed-C columns (Polymer Laboratories; linear range of MW = 200–2,000,000). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower software (version 2002). ^1H NMR spectra for the analysis of PMMA microstructures were recorded in $CDCl_3$ at 50 °C and analyzed according to the literature methods,[34] whereas tacticities of PMBL,[10] and PMMBL[18] were measured by ^{13}C NMR in DMSO-d_6 at 100 °C.

RESULTS AND DISCUSSION

Polymerization by K[H] and K[H]/AlR_3

Alkali metal (Li, Na, K) hydrides, in combination with common alkyl aluminum AlR_3, have been used as initiators for the so-called "retarded" anionic polymerization of styrene and conjugated dienes in toluene or cyclohexane.[35] We wondered if such hydrides could also initiate the anionic polymerization of MMA and (M)MBL. Potassium hydride K[H] is insoluble in toluene, and its suspension in this solvent exhibited no activity for MMA polymerization at ambient temperature (run 1, Table 1). On the other hand, premixing K[H] with 1 equiv of MeAl$(BHT)_2$ in toluene at ambient temperature generated a homogenous solution that is active for MMA polymerization, achieving 69% monomer conversion in 2 h with a [MMA]:[KH] ratio of 400; the PMMA produced had a modest syndiotacticity of 76.2% *rr* (run 2, Table 1). Increasing the amount of MeAl$(BHT)_2$ to 2 equiv relative to K[H] brought about a quantitative monomer conversion under the same conditions; the polymer tacticity remained the same, but the polymer MWD was narrower (1.13 for run 3 vs. 1.25 for run 2). However, both runs had <50% initiator efficiencies, presumably caused by K[H] weighing errors due to its rather small formula weight and insolubility in toluene

TABLE 2 Selected Results of Polymerization of (M)MBL by K[H] and K[H] + AlR_3[a]

Run No.	Monomer (M)	Initiator (I)	Time (h)	Conv[b] (%)	TOF (h^{-1})	M_n[c] (kg/mol)	MWD[c] (M_w/M_n)
10	MBL	K[H]	24	0	0	–	–
11	MBL	K[H]/2MeAl$(BHT)_2$	24	8.4	1.4	88.0	1.33 [d]
12	MBL	K[H]/2Al$(C_6F_5)_3$	4	100	100	52.0	1.87
13	MMBL	K[H]	24	0	0	–	–
14	MMBL	K[H]/2MeAl$(BHT)_2$	24	12.2	2.0	63.0	1.68
15	MMBL	K[H]/2Al$(C_6F_5)_3$	0.83	100	482	209[e]	1.56

[a] Carried out in DMF at ambient temperature (~25 °C) in a [M]/[I] ratio of 400.

[b] Conversion measured by ^{1}H NMR.

[c] Determined by GPC relative to PMMA standards.

[d] A clear bimodal MWD; for a lower MW peak, $M_n = 4.90$ kg/mol, $M_w/M_n = 1.22$.

[e] There exists a small amount of a lower MW tail ($M_n = 12.0$ kg/mol, $M_w/M_n = 1.10$).

(so that a stock solution could not be made for a more accurate handling of this reagent in very small quantities).

Replacing MeAl$(BHT)_2$ with a more strongly Lewis acidic Al$(C_6F_5)_3$ further enhances the polymerization activity (run 4 vs. run 2) and improves the polymerization control (MWD = 1.04 for runs 4 and 5) while keeping the PMMA syndiotacticity largely unchanged. The polymerization with the isolated "ate" complex $K^+[HAl(C_6F_5)_3]^-$, derived from the reaction of K[H] and Al$(C_6F_5)_3$ in toluene (see Experimental), was also examined (run 6). This polymerization was also effective but, interestingly, the resulting PMMA is now essentially atactic (51.7% *mr*); when an additional equiv of Al$(C_6F_5)_3$ was added, the expected syndiotactic PMMA was produced (69.5% *rr*, run 7).

Other two aspects of the polymerization by K[H] are worth mentioning. First, substituting the alane with the borane congener, B$(C_6F_5)_3$ (1 or 2 equiv) completely shuts down the polymerization (runs 8 and 9). This observation is consistent with the polymerization behavior of other classical organolithium initiators, such as ^{t}BuLi and $Me_2C{=}C(O^iPr)OLi$, when combined with the alane and borane Lewis acids;[36] the remarkable differences, in terms of the observed high activity and control with the alane additive versus the inactivity with the borane additive, were attributed to the inability of the lithium enolborate/borane pair to effect the bimolecular, activated-monomer anionic polymerization as does the lithium enolaluminate/alane pair.[19] Second, the K[H]/2AlR_3 initiator system is also effective for polymerization of *n*-butyl acrylate in toluene or even in cyclohexane. For example, the polymerization by K[H]/2MeAl$(BHT)_2$ achieved quantitative monomer conversions at ambient temperature in 2 h, producing high MW P(*n*-BA), M_n = 374 kg mol^{-1} (MWD = 1.87), and 713 kg mol^{-1} (MWD = 1.68), in toluene and cyclohexane, respectively.

Having established the effectiveness of the K[H]/2AlR_3 initiator system for MMA polymerization at ambient temperature, we turned our attention to the polymerization of renewable (M)MBL, the results of which were summarized in Table 2. Consistent with the above findings, no activity was observed for polymerizations up to 24 h using K[H] alone (runs 10 and 13). Addition of 2 equiv of MeAl$(BHT)_2$ brought about some activity: TOF = 1.4 h^{-1} for MBL polymerization (run 11) and 2.0 h^{-1} for MMBL polymerization (run 14). Significantly, the K[H]/2Al$(C_6F_5)_3$ system is far more active, with TOF approaching 100 h^{-1} for MBL polymerization (run 12). The MMBL polymerization by K[H]/2Al$(C_6F_5)_3$ was even more impressive and achieved a high TOF of 482 h^{-1} (run 15), producing high MW, atactic PMMBL (M_n = 209 kg mol^{-1}; MWD = 1.56; *mr* = 49.9%, *mm* = 10.7%, *rr* = 39.4%).

Given the fact that $K^+[HAl(C_6F_5)_3]^-$ itself is active for polymerization, presumably with the hydride being the initiating moiety, and that the presence of excess of Al$(C_6F_5)_3$ drastically accelerates the polymerization, the current polymerization by K[H]/2AlR_3 can be reasonably proposed to proceed through an activated-monomer anionic polymerization mechanism.[26]

In light of the high activity of K[H] when combined with Al$(C_6F_5)_3$, we examined the fundamental reaction and determined the product to be the anticipated "ate" complex $K^+[HAl(C_6F_5)_3]^-$, the structure of which has been confirmed by X-ray diffraction analysis (see Experimental). Figure 1 highlights the geometry of the hydridoaluminate anion, featuring a slightly distorted tetrahedron with a sum of C—Al—C angles of 336.66°, whereas Figure 2 depicts the coordination environment of the potassium cation and a 3-D molecular packing structure formed on the basis of the ionic interactions. As in the case of zirconocenium–hydridoborate $[Cp^*_2ZrH]^+[HB(C_6F_5)_3]^-$ ion pair in that two F atoms, rather than the H atom, of the borate anion are coordinated to the cation,[37] the K cation in $K^+[HAl(C_6F_5)_3]^-$ is coordinated to eight aryl F atoms and one H atom of the anion, thus giving rise to a total coordination number of 9 for K^+ (Fig. 2). The K—F bonds span from the shortest K—F26 distance of 2.670(2) Å to the longest K—F34 distance of 3.116(2) Å, and the K—H contact has a distance of 2.688(2) Å.

Polymerization by K[E] and K[E]/AlR_3

We first examined MMA polymerization in toluene by potassium enolate $Me_2C{=}C(O^iPr)OK$ (K[E]), which showed a

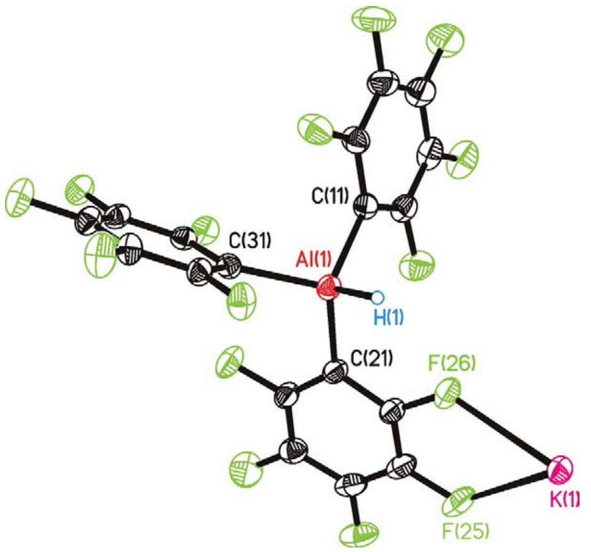


FIGURE 1 X-ray crystal structure of "ate" complex $K^+[HAl(C_6F_5)_3]^-$, with thermal ellipsoids drawn at the 50% probability. Selected bond lengths [Å] and angels [°]: Al(1)—H(1) 1.59(5), Al(1)—C(11) 2.016(3), Al(1)—C(21) 2.024(3), Al(1)—C(31) 2.015(3), K(1)—F(25) 3.039(3), K(1)—F(26) 2.670(2); C(11)—Al(1)—C(21) 111.70(12), C(11)—Al(1)—C(31) 107.55(11), C(21)—Al(1)—C(31) 111.41(12), C(11)—Al(1)—H(1) 106.7(17), C(21)—Al(1)—H(1) 108.9(16), C(31)—Al(1)—H(1) 110.5(17), F(25)—K(1)—F(26) 55.13(6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modest activity for MMA polymerization at ambient temperature with a TOF of 15.4 h^{-1} (i.e., 92.4% conversion in 24 h) and produced essentially atactic (52.5% *mr*) PMMA with a broad MWD of 3.21 (run 16, Table 3). Interestingly, this tacticity is substantially different from the isotacticity observed for the MMA polymerization in toluene by the enolate with the much smaller lithium counterion.[36(b)] Addition of 2 equiv of $MeAl(BHT)_2$ significantly enhanced the rate of the polymerization, now reaching a TOF of 80 h^{-1} and also produced syndiotactic PMMA with $rr = 72\%$ (run 17). The rate enhancement was even more dramatic by $Al(C_6F_5)_3$; thus, the $K[E]/2Al(C_6F_5)_3$ system gave a high TOF of 1600 h^{-1}, producing high MW, syndiotactic PMMA ($M_n = 100$ kg mol^{-1}; MWD = 1.23; $rr = 79.3\%$; run 18). In comparison, polymerizations of MBL (runs 19 and 20) and MMBL (runs 21 and 22) are slower but, nonetheless, the $K[E]/2Al(C_6F_5)_3$ initiator system can achieve quantitative monomer conversion in 24 h for MBL polymerization (run 20) or 4 h for MMBL polymerization (run 22). Noteworthy is the loss of tacticity control over the polymerizations of MBL and MMBL.

We also investigated the degree of control of the MMA polymerization over polymer MW by percentage monomer conversion and by the [MMA]/ [K] ratio. As can be seen from Figure 3, the M_n of the resulting PMMA increased linearly with the MMA conversion ($R^2 = 0.997$) for the MMA polymerization by $K[E]/2Al(C_6F_5)_3$ in toluene at 25 °C with a [MMA]:[K] ratio of 800:1, while MWD varies narrowly from 1.10 to 1.15 for the entire conversion range. Polymerizations with other [MMA]/[K] ratios exhibited similarly linear plots. The ability of the current initiator system to control the polymer MW was reaffirmed by the experiments varying the [MMA]/[K] ratio. Hence, a plot of M_n of PMMA versus the [MMA]/[K] ratio (400–1600) also gave a straight line (Fig. 4), demonstrating the control over M_n by adjusting the monomer-to-initiator ratio.

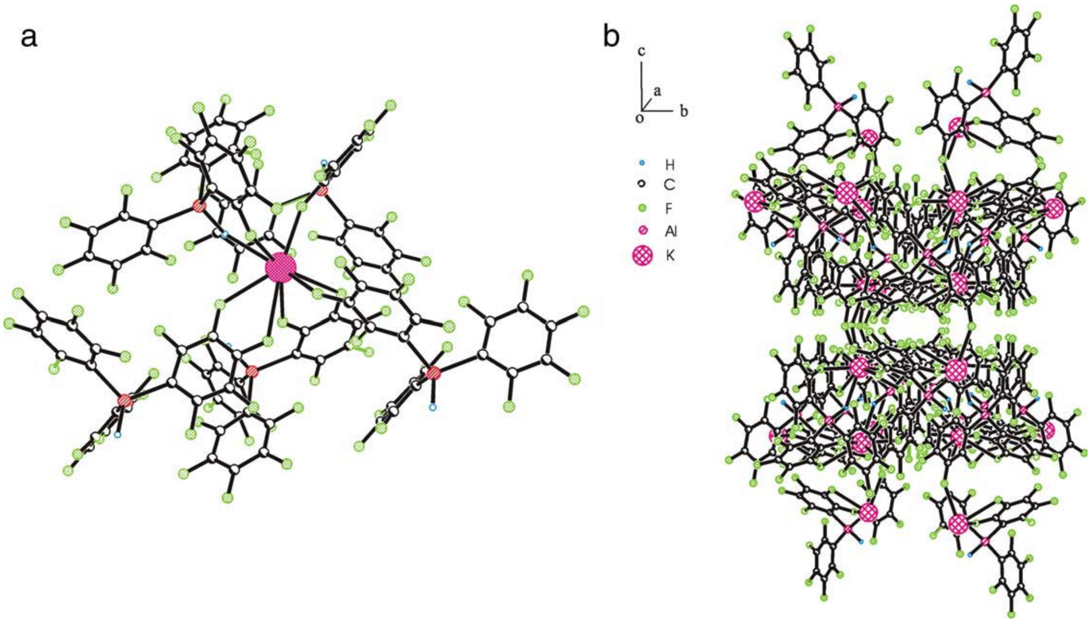


FIGURE 2 Molecular structure of $K^+[HAl(C_6F_5)_3]^-$, with isotropic ellipsoids drawn at ARAD of 0.6 for the adjusted the radius of K^+ for clarity. The left picture highlights the coordination environment of K^+, whereas the picture on the right shows a 3-D molecular packing structure.

TABLE 3 Selected Results of Polymerization of MMA and (M)MBL by K[E] and K[E] + AlR_3[a]

Run No.	Monomer (M)	Initiator (I)	Time (h)	Conv[b] (%)	TOF (h^{-1})	M_n[c] (kg/mol)	MWD[c] (M_w/M_n)	[*rr*][b] (%)	[*mr*][b] (%)	[*mm*][b] (%)
16	MMA	K[E]	24	92.4	15	39.0	3.21	25.1	52.5	22.4
17	MMA	K[E]/2MeAl$(BHT)_2$	5	100	80	85.0	1.36	72.0	26.3	1.7
18	MMA	K[E]/2Al$(C_6F_5)_3$	0.25	100	1,600	100	1.23	79.3	19.1	1.6
19	MBL	K[E]	24	23.2	4	5.60	1.32	n.d.	n.d.	n.d.
20	MBL	K[E]/2Al$(C_6F_5)_3$	24	100	17	28.0	1.84	34.7	30.9	34.4
21	MMBL	K[E]	24	72.2	12	37.0	1.76	n.d.	n.d.	n.d.
22	MMBL	K[E]/2Al$(C_6F_5)_3$	4	100	100	28.0	1.79	47.1	43.4	9.5

[a] Carried out in toluene (MMA) or DMF (MBL and MMBL) at ambient temperature (~25 °C) in a [M]/[I] ratio of 400; n.d. = not determined.

[b] Monomer conversion and polymer tacticity measured by ^1H or ^{13}C NMR.

[c] Determined by GPC relative to PMMA standards.

Kinetic experiments that used the $[MMA]_0/[K]_0$ ratio ranging from 200 to 1600 revealed that the MMA polymerization by K[E]/2Al$(C_6F_5)_3$ in toluene at 25 °C follows zero-order kinetics in [MMA] for all the [MMA]/[K] ratios investigated (Fig. 5). A zero-order dependence on monomer concentration in this activated-monomer polymerization suggests that the rate determining step is the conjugate Michael addition of the monomer activated by the alane into the polymer chain (i.e., the C—C bond forming step), whereas the recapture of the aluminum catalyst coordinated to the penultimate polymer chain end by the incoming monomer is relatively fast (Scheme 2). This mechanism resembles that of the bimolecular, activated-monomer anionic polymerization by the lithium enolaluminate/alane pair,[36(a),19,38] or by nonbridged group 4 metallocene/metallocenium pair.[39]

Polymerization by K[A] and K[A]/Al$(C_6F_5)_3$

Although potassium allyl species K[1,3-$(SiMe_3)_2C_3H_3$] (K[A]) was reported to be highly active for MMA polymerization in toluene at 0 °C,[31] it showed no activity for polymerization of MBL in DMF (in which the polymer is soluble) at either 25 °C and 0 °C (runs 23 and 24, Table 4) or in combination with 2 equiv of Al$(C_6F_5)_3$ (run 25). On the other hand, K[A] was found to be active for polymerization of MMBL at 25 °C (run 26) and more active at 0 °C, achieving a quantitative monomer conversion (run 27) and producing atactic PMMBL (15.4% *mm*, 50.5% *mr*, 34.1% *rr*). Interestingly, unlike other potassium or lithium-based anionic initiators, addition of 2 equiv of Al$(C_6F_5)_3$ to K[A] completely shut down the polymerization at 25 °C (run 28), 0 °C, or −78 °C. This phenomenon could be attributed to the irreversible formation of an "ate" complex K[AAl$(C_6F_5)_3$], as shown by ^{19}F NMR (C_6D_6, 23°C) chemical shifts at δ −121.1, −123.0 (m, 6F, *o*-F), −157.7 (t, 3F, *p*-F) and −163.5 (m, 6F, *m*-F) for the aluminate formation,[26,36] which inhibits the allyl anion to function as an effective initiator. Consistent with this hypothesis, addition of only 0.5 equiv of Al$(C_6F_5)_3$ rendered an active system for polymerization of MMBL at ambient temperature, achieving 75% monomer conversion in 24 h.

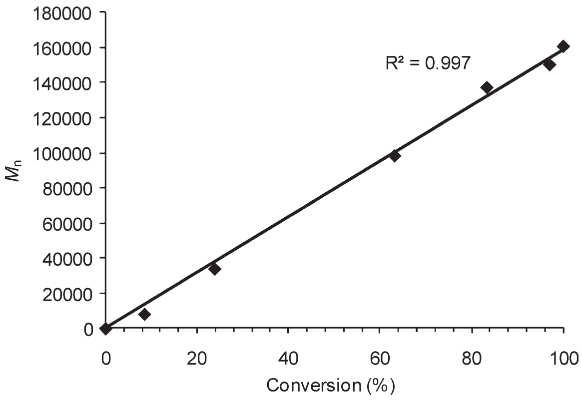


FIGURE 3 Plot of M_n of PMMA vs monomer conversion for the polymerization of MMA by K[E]/2Al$(C_6F_5)_3$ in toluene at 25 °C with a [MMA]:[K] of 800:1. MWD = 1.10 to 1.15 for the entire conversion range.

CONCLUSIONS

This study has investigated the characteristics of anionic polymerization of MMA and renewable (M)MBL monomers using three resorbable potassium salts of hydride K[H], enolate K[E], and allyl K[A], as well as their combinations

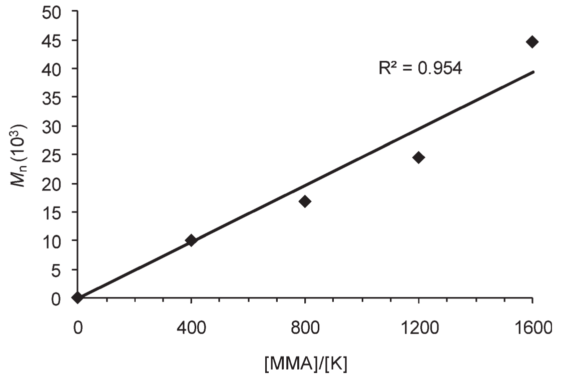


FIGURE 4 Plot of M_n of PMMA versus the [MMA]/[K] ratio for the polymerization of MMA by the K[E]/2Al$(C_6F_5)_3$ in toluene at 25 °C, achieving quantitative monomer conversion for all runs.

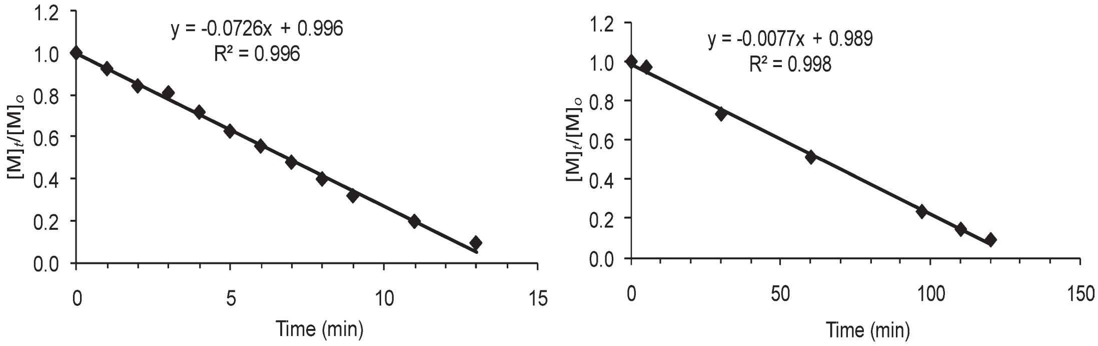
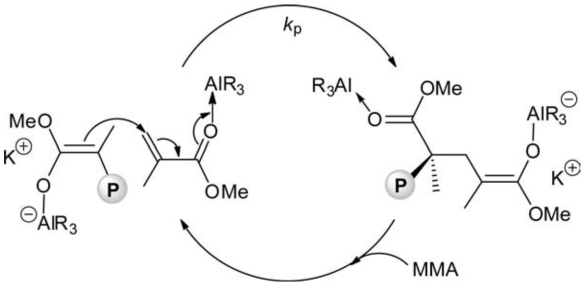


FIGURE 5 Zero-order kinetic plots of $[M]_t/[M]_0$ versus time for the polymerization of MMA by K[E]/2Al$(C_6F_5)_3$ in toluene at 25 °C. Left: [M]/[I] = 400/1; right: [M]/[I] = 1600/1.



SCHEME 2 Proposed propagation "catalysis" cycle for the polymerization by K[E]/2AlR$_3$.

with bulky and strong aluminum Lewis acids MeAl$(BHT)_2$ and Al$(C_6F_5)_3$. Key findings of this study are summarized as follows.

First, while K[H] itself is ineffective for polymerization of MMA and (M)MBL in toluene at ambient temperature, the K[H]/2AlR$_3$ system exhibits high activity for the activated-monomer polymerization of such monomers and even *n*-butyl acrylate. In particular, when combined with 1 equiv of Al$(C_6F_5)_3$, the "ate" complex $K^+[HAl(C_6F_5)_3]^-$, derived from the reaction of K[H] and Al$(C_6F_5)_3$ in toluene and structurally characterized by X-ray diffraction analysis, polymerizes MMA rapidly and efficiently, producing syndiotactic PMMA with a narrow MWD of 1.04. Similar polymerization characteristics can also be achieved by a simple mixing of K[H] with 2 equiv of Al$(C_6F_5)_3$. Significantly, the K[H]/2Al$(C_6F_5)_3$ system is also highly active for polymerizations of (M)MBL, achieving high TOF's of 100 h^{-1} and 482 h^{-1} for polymerizations of MBL and MMBL, respectively.

Second, the potassium enolate K[E] itself exhibits a modest activity for MMA polymerization in toluene at ambient temperature, producing atactic PMMA with a broad MWD of 3.2. Addition of 2 equiv of MeAl$(BHT)_2$ enhances the rate of the polymerization by five times and also produces syndiotactic PMMA (*rr* = 72%). More dramatic rate enhancement is observed for the K[E]/2Al$(C_6F_5)_3$ system that reaches a TOF of 1600 h^{-1}, representing a rate enhancement of over 100 times. This system produces syndiotactic PMMA (*rr* = 79.3%); the degree of polymerization control of this system has been demonstrated by linear relationships between polymer M_n and percentage monomer conversion while maintaining a narrow MWD range from 1.10 to 1.15 for the entire conversion range as well as between M_n and the [monomer]/[initiator] ratio. Kinetic experiments showed that the polymerization by K[E]/2Al$(C_6F_5)_3$ in toluene at 25 °C follows zero-order kinetics in [monomer], suggesting that the rate determining step of this activated-monomer polymerization is the conjugate Michael addition of the monomer activated by the alane into the polymer chain, whereas the recapture of the aluminum catalyst coordinated to the

TABLE 4 Selected Results of Polymerization of (M)MBL by K[A] and K[A] + Al$(C_6F_5)_3$[a]

Run No.	Monomer (M)	Initiator (I)	Temp (°C)	Time (h)	Conv.[b] (%)	M_n[c] (kg/mol)	MWD[c] (M_w/M_n)
23	MBL	K[A]	25	24	<1	–	–
24	MBL	K[A]	0	24	0	–	–
25	MBL	K[A]/2Al$(C_6F_5)_3$	25	24	0	–	–
26	MMBL	K[A]	25	24	52.8	27.0	1.49
27	MMBL	K[A]	0	24	>99	33.0	1.42
28	MMBL	K[A]/2Al$(C_6F_5)_3$	25	24	0	–	–

[a] Carried out in DMF in a [M]/[I] ratio of 400.
[b] Conversion measured by ^1H NMR.
[c] Determined by GPC relative to PMMA standards.

penultimate polymer chain end by the incoming monomer is relatively fast. Relative to the MMA polymerization, polymerizations of (M)MBL by this system are slower but can nonetheless achieve quantitative monomer conversion in several hours (4 h for MMBL).

Third, the potassium allyl species K[A] behaves differently from other anionic initiators in that K[A] itself is active for MMA and MMBL polymerizations but becomes inactive when combined with 2 equiv of $Al(C_6F_5)_3$ at various temperatures. This phenomenon was attributed to the irreversible formation of the "ate" complex that inhibits the ability of the allyl anion to function as an effective initiator.

This work was supported by the National Science Foundation (NSF-1012326). The authors thank Boulder Scientific Co. for the research gift of $B(C_6F_5)_3$.

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