4902 *Macromolecules* **2010**, *43*, 4902–4908
DOI: 10.1021/ma100615t

Macromolecules
ARTICLE

Living Polymerization of Naturally Renewable Butyrolactone-Based Vinylidene Monomers by Ambiphilic Silicon Propagators

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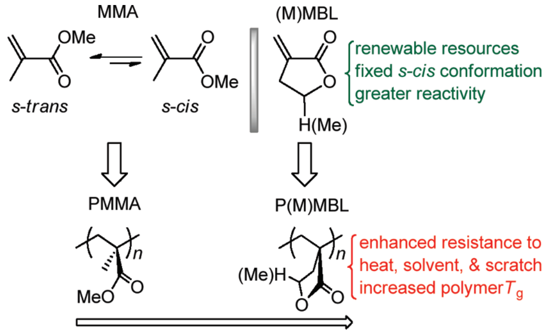
Received March 21, 2010; Revised Manuscript Received April 29, 2010

ABSTRACT: Naturally renewable butyrolactone-based vinylidene monomers, α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL), have been successfully polymerized in a rapid and living fashion, using ambiphilic silicon propagating species consisting of both the nucleophilic silyl ketene acetal (SKA) initiating moiety and the electrophilic silylium catalyst. Uniquely, the R_3Si^+ catalyst is derived directly from the SKA initiator upon *in situ* oxidative activation with a catalytic amount of the trityl borate activator. Investigations into effects of SKA (thus the resulting R_3Si^+ catalyst) and activator (thus the resulting counteranion) structures have revealed that the $Me_2C{=}C(OMe)OSi^iBu_3/Ph_3CB(C_6F_5)_4$ combination is the most active *and* controlled system for (M)MBL polymerizations. Thus, under ambient conditions and with a low catalyst loading (0.05 mol % relative to monomer), this polymerization system rapidly (within 10 min) and completely converts MMBL to PMMBL with controlled low to high (M_n = 5.43 × 10^5 kg/mol) MW's and narrow MW distributions (1.01−1.06). Well-defined block copolymers of MBL and MMBL with MMA as well as block and statistical copolymers of MBL with MMBL have also been readily synthesized. Atactic homopolymers, PMBL and PMMBL, produced herein exhibit high glass transition temperatures (T_g's) of 194 and 225 °C, respectively, representing T_g enhancements of ∼90 °C (for PMBL) and ∼120 °C (for PMMBL) over the T_g of the typical atactic PMMA. The critical MW of PMMBL has been estimated to be ∼47 kg/mol.

Introduction

As petroleum resources continue to be depleted, polymer chemists face the challenge of gradually replacing existing petroleum-based polymeric materials with those derived from naturally occurring, renewable resources in a technologically and economically competitive fashion.[1−5] In this context, renewable butyrolactone-based vinylidene monomers, such as MBL (α-methylene-γ-butyrolactone) and MMBL (γ-methyl-α-methylene-γ-butyrolactone), are of particular interest in exploring the prospects of substituting the petroleum-based methacrylate monomers for specialty chemicals production.[6] 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,[7] while its γ-methyl derivative MMBL can be readily prepared via a two-step process from the biomass-derived levulinic acid.[8,9] Structurally, MBL can be described as the cyclic analogue of MMA (methyl methacrylate) (Chart 1); however, it exhibits greater reactivity in free radical polymerization[10] than typical methacrylate monomers such as MMA due to the presence of both the nearly planar five-membered lactone ring, which provides a high degree of 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.[11] The cyclic ring in MBL also imparts significant enhancements in the materials properties of the resulting PMBL (Chart 1), as compared to PMMA, thanks to the conformational rigidity of the polymer chain through incorporation of the butyrolactone moiety. Thus, the T_g (glass-transition temperature) of PMBL produced by the radical polymerization is 195 °C,[12] which is about 90 °C higher than that of atactic PMMA. Additionally, PMBL has increased optical properties as well as resistance to solvent (as evidenced by its insolubility in common organic solvents such as $CHCl_3$ and THF), heat, and scratch.[13−15] Some of these materials property enhancements have also been observed for PMMBL.[16]

Chart 1. Renewable Butyrolactone-Based Vinylidene Monomers (M)MBL and Polymers P(M)MBL vs MMA and PMMA



Several types of polymerization processes have been employed to polymerize MBL to low to high MW (molecular weight) polymers, including various radical polymerization mechanisms,[10−12,17−20] group-transfer polymerization,[21] anionic polymerization,[12] and coordination polymerization by metallocene complexes.[16] MBL has been copolymerized with various comonomers[10] such as MMA,[22] styrene,[19,23] methoxystyrene,[24] and vinylthiophenes.[25] While the polymerization of MMBL has been studied to a much lesser extent, it has also been polymerized by free-radical emulsion polymerization[26,27] as well as by radical, anionic, and group-transfer polymerization methods which required long reaction times (2−44 h), often at low temperatures, achieving low to high, but never complete, conversions, with unknown polymerization and polymer MW characteristics.[28] Most recently, we found that the coordination polymerization of MBL and MMBL in DMF by the divalent decamethylsamarocene catalyst is fast (with TOF, turnover frequency, > 3000 h^{-1}), efficient (with I^*, initiator

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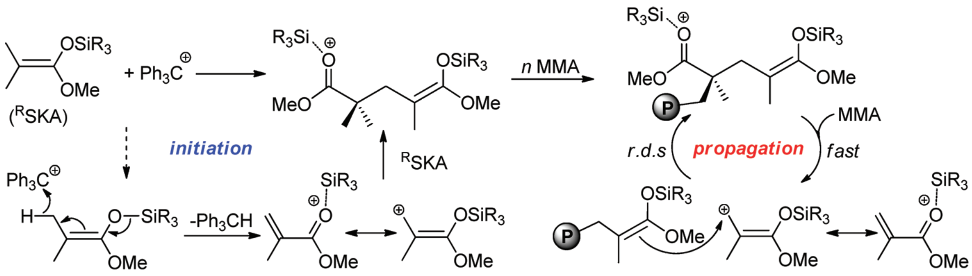
Scheme 1. Living/Controlled (Meth)acrylate Polymerization Catalyzed by R_3Si^+[30,31]



efficiency, approaching 100%), and controlled, leading to PMBL and PMMBL with relatively narrow MWD's (molecular weight distributions) as well as their well-defined block copolymers with MMA or with each other.[16] The resulting atactic PMBL and PMMBL have high T_g's of 194 and 227 °C, respectively.

Metal catalysts/initiators have been extensively utilized to effect stereochemically or architecturally controlled coordination polymerization of polar vinyl and vinylidene monomers such as (meth)acrylates and (meth)acrylamides under ambient conditions.[29] We recently developed a highly active, efficient, and living/controlled (meth)acrylate polymerization system catalyzed by *metalloid* silylium ions, R_3Si^+, at room temperature.[30] The highly active, *ambiphilic* propagating species contains both the nucleophilic SKA (silyl ketene acetal) moiety and the electrophilic silylium ion (or silyl cation) sites (Scheme 1). This propagator is generated by a unique "*monomer-less*" initiation involving oxidative activation of ^{R}SKA (trialkylsilyl methyl dimethylketene acetal) by a catalytic amount of TTPB [trityl tetrakis(pentafluorophenyl)borate, $Ph_3CB(C_6F_5)_4$], leading to the R_3Si^+-activated MMA derived from vinylogous *hydride abstraction* of ^{R}SKA with Ph_3C^+ (i.e., the monomer is generated from the initiator), followed by subsequent Michael addition of ^{R}SKA to the activated MMA (or silylated MMA) (Scheme 1). A propagation "catalysis" cycle consists of a fast step of recapturing the silylium catalyst from the ester group of the growing polymer chain by the incoming MMA, followed by a rate determining step (r.d.s.) of the C−C bond coupling via intermolecular Michael addition of the polymeric SKA to the silylated MMA (see the propagation manifold, Scheme 1). This novel polymerization system can produce high molecular weight ($M_n > 10^5$ g/mol) and well-defined (M_w/M_n = 1.04−1.12) homo- and copolymers with a high silylium catalyst TOF (up to 1500 h^{-1} for methacrylates) to an exceptionally high TOF (up to 120 000 h^{-1} for acrylates) at 25 °C.[31] Recently, strong Brønsted acid trifluoromethanesulfonimide ($HNTf_2$) was also utilized to activate SKA, leading to living polymerization of MMA, through the same silylium-catalyzed propagation process.[32] Intriguingly, earlier fast "group transfer polymerization" systems using SKA as initiator and additionally employing different combinations of a Lewis acid and a Me_3Si-containing reagent, such as $Me_3SiOTf/B(C_6F_5)_3$,[33] Me_3SiI/HgI_2,[34] or $Me_3SiI/RAl(OAr)_2$,[35] may also involve the silylium-catalyzed process as demonstrated in the SKA/TTPB system.[30,31] Considering the high activity and living nature, as well as potentially a broad implication of the silylium-catalyzed polymerization process for (meth)acrylates, we reasoned that the SKA/TTPB system could be an excellent system for the polymerization of renewable monomers (M)MBL because the reactivity of (M)MBL lies somewhere between methacrylates and acrylates. Accordingly, the central objective of this study was to examine the characteristics of (M)MBL polymerizations using the unique ambiphilic silicon propagator derived from the activation of SKA with TTPB.

Experimental Section

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, on 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 and 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 (FT 300 MHz, ^1H; 75 MHz, ^{13}C), a Varian Inova 400 MHz, or an Inova 500 MHz spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane.

Monomers α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL) were purchased from TCI America, while methyl methacrylate (MMA), dimethylketene methyl trimethylsilyl acetal (^{Me}SKA), chlorotriisobutylsilane, diisopropylamine, and methyl isobutyrate were purchased from Aldrich. These chemicals were degassed and dried over CaH_2 overnight, followed by vacuum distillation, while MMA was further purified by titration with neat tri(*n*-octyl)aluminum (Strem Chemical) to a yellow end point,[36] followed by vacuum distillation. Butylated hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol) was purchased from Aldrich and was recrystallized from hexanes prior to use. Activator $Ph_3CB(C_6F_5)_4$ (TTPB)[37] was obtained as a research gift from Boulder Scientific Co. and used as received. Modified literature procedures were employed to prepare the following compounds: dimethylketene methyl triisobutylsilyl acetal $Me_2C{=}C(OMe)OSi(^iBu)_3$ (^{iBu}SKA),[31] $H(Et_2O)_2B(C_6F_5)_4$,[38] and trityl [tris(tetrachlorobenzenediolato)phosphate(V)] $[Ph_3C]$[*rac*-TRISPHAT].[39]

General Polymerization Procedures. Polymerizations were performed in 30 mL oven-dried glass reactors inside the glovebox at ambient temperature (∼25 °C). In a typical polymerization procedure (which is the same as established for MMA polymerization[30,31]), predetermined amounts of the appropriate SKA initiator and MBL (0.500 mL, 6.07 mmol) or MMBL (0.648 mL, 6.07 mmol) were premixed in a flask with 4 mL of CH_2Cl_2, and with vigorous stirring, TTPB (1.00 mL, 3.03 mM in CH_2Cl_2, 3.03 μmol) was added to start the polymerization. Polymerizations were quenched at the time specified in the tables with 5 mL of 5% HCl in methanol, and the polymer was precipitated into 50 mL of methanol and collected by filtration and centrifugation, before being washed extensively with methanol to remove any catalyst residue or unreacted monomer. Polymers were then dried at 50 °C overnight in a vacuum oven to a constant weight. ^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, CH), 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

Table 1. Selected Results of Polymerization of (M)MBL by SKA + TTPB[a]

run no.	M	I	[M]/[I]	time (min)	conv[b] (yield)	M_w[c] (kg/mol)	MWD[c] (M_w/M_n)
1	MBL	^{Me}SKA	100	10	(31.6)	129, 25.6	1.13, 1.31
2	MBL	^{iBu}SKA	100	10	(>99)	427, 12.2	1.46, 1.21
3	MBL	^{iBu}SKA	200	10	(57.1)	169, 18.9	1.57, 1.08
4	MBL	^{iBu}SKA	400	10	(12.5)	374, 19.9	1.24, 1.04
5	MMBL	^{Me}SKA	200	10	64.2	50.3	1.22
6	MMBL	^{iBu}SKA	100	10	100	18.8	1.06
7	MMBL	^{iBu}SKA	200	10	100	31.0	1.02
8	MMBL	^{iBu}SKA	400	15	100	93.2	1.03
9	MMBL	^{iBu}SKA	600	30	100	176	1.01
10	MMBL	^{iBu}SKA	800	120	100	548	1.01

[a] Carried out in 5 mL of CH_2Cl_2 at ambient temperature (~25 °C). [b] Conversion, measured by ^{1}H NMR, or in parentheses, isolated yield. [c] Determined by light scattering.

(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.

Conversion data were performed by adding toluene (289 μL, 2.72 mmol), as an external standard, to the reaction mixture. At specified times 0.2 mL aliquots were withdrawn from the solution and quenched into septum sealed vials containing 0.7 mL of undried "wet" $CHCl_3$. Percent conversion was then calculated by comparing the integration of the vinyl protons of the unreacted monomer to the methyl protons of toluene.

Polymer Characterizations. Gel permeation chromatography (GPC) and light scattering (LS) analyses of the polymers were carried out at 40 °C and a flow rate of 1.0 mL/min, with DMF as the eluent, on a Waters University 1500 GPC instrument coupled with a Waters RI detector and a Wyatt miniDAWN Treos LS detector equipped with four 5 μm PL gel columns (Polymer Laboratories). Chromatograms were processed with Waters Empower software (version 2002); number-average molecular weight (M_n) and polydispersity (M_w/M_n) of polymers were given relative to PMMA standards. Weight-average molecular weight (M_w) was obtained from the analysis of the LS data which were processed with Wyatt Astra Software (version 5.3.2.15), and d*n*/d*c* values were determined assuming 100% mass recovery of polymers with known concentrations. Tacticities of PMBL[10,21] and PMMBL[28] were measured by ^{13}C NMR in DMSO-d_6 at 100 °C. Decomposition onset temperatures (T_{onset}) of the polymers were measured by thermal gravimetric analysis (TGA) on a TGA 2950 thermogravimetric analyzer, TA Instruments. Polymer samples were heated from ambient temperature to 600 °C at a rate of 20 °C/min. Values for $T_{10\%}$ and T_{onset} (initial and end temperatures) were obtained from wt % vs temperature (°C) plots. Glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) on a DSC 2920, TA Instruments. Polymer samples were first heated to 150 at 20 °C/min, equilibrated at this temperature for 4 min, then cooled to 30 at 20 °C/min, held at this temperature for 4 min, and reheated to 300 at 10 °C/min. All T_g values were obtained from the second scan, after removing the thermal history.

Results and Discussion

Homopolymerization Characteristics. Table 1 summarizes the selected results of polymerizations of MBL and MMBL by the SKA/TTPB (0.05 mol % relative to monomer) system (where M = monomer, MBL or MMBL, and I = initiator ^{Me}SKA or ^{iBu}SKA). Given the unique initiation mechanism by which the SKA/TTPB system operates (cf. Scheme 1), a polymerization with an $x[M]_0/y[SKA]_0/z[TTPB]_0$ ratio will have the *total* equivalency of the propagating SKA = $y - 2z + z = y - z$, thereby giving a [M]/[I] ratio of $x/(y - z)$.[30] Thus, a MBL polymerization with ^{Me}SKA being the initiator and [MBL] = 1.10 M, [^{Me}SKA] = 11.6 mM, and [TTPB] = 0.551 mM (i.e., 400:4.2:0.2) gives the calculated [M]/[I] ratio of 100. This polymerization in CH_2Cl_2 became heterogeneous instantaneously upon addition of the TTPB activator (due to the insolubility of PMBL in CH_2Cl_2) and afforded a low isolated polymer yield of only 31.6% in 10 min of reaction (run 1, Table 1). Under the same conditions, but utilizing ^{iBu}SKA, a quantitative polymer yield was achieved (run 2), despite the heterogeneous polymerization. However, increasing the MBL to ^{iBu}SKA feed ratios to 200 and 400 significantly reduced the polymer yields to modest 57.1% (run 3) and low 12.5% (run 4). Furthermore, the heterogeneity of the MBL polymerization in CH_2Cl_2 resulted in bimodal MWD's of the polymers (runs 1−4), with the high MW fraction comprising of ≈10−15% of the polymer sample. Nevertheless, the polymerization by the SKA + TTPB system is free of any ring-opening of the butyrolactone ring, and the PMBL produced by ^{iBu}SKA is essentially atactic, with a triad distribution of 39.3% *rr*, 37.3% *mr*, 23.4% *mm* (run 3). Polar, donor solvents such as DMF (in which PMBL is soluble) deactivate the silylium catalyst through adduct formation, thus shutting down the polymerization.

Similarly to MBL, the polymerization of MMBL is more rapid when utilizing ^{iBu}SKA as the initiator (thus the $^iBu_3Si^+$ catalyst) as compared to ^{Me}SKA (thus the Me_3Si^+ catalyst). Specifically, when MMBL in a [M]/[I] ratio of 200 was polymerized by ^{Me}SKA + TTPB and ^{iBu}SKA + TTPB, after 10 min, 64.2% and 100% monomer conversions were observed, respectively (runs 5 and 7). Not only is the polymerization of MMBL by ^{iBu}SKA more rapid (TOF up to 12 000 h^{-1}) than that by ^{Me}SKA (TOF = 7680 h^{-1}), it is also more *efficient and controlled* as shown by the following two levels of evidence. First, the M_w (determined by LS) of the polymer produced by ^{Me}SKA was 50.3 kg/mol (M_n = 41.2 kg/mol), while the polymer produced by ^{iBu}SKA had a M_w of 31.0 kg/mol (M_n = 30.4 kg/mol), giving initiator efficiencies (*I**) of 34.9% and 73.8%, respectively. Second, the MWD of the polymer produced by ^{Me}SKA was relatively broad (1.22), but the polymer by ^{iBu}SKA has an extremely narrow MWD of 1.02. Also noteworthy is the high activity of the MMBL polymerization of this system that achieves a complete monomer conversion in 10 min at ambient temperature, as compared to the MMBL polymerization by conventional mechanisms, including radical, anionic, and group-transfer polymerization methods, which required 2−44 h, often at low temperatures, achieving low to high, but never complete, conversions.[28] The PMMBL produced by ^{iBu}SKA and TTPB is syndio-biased atactic, with a triad distribution of 45.8% *rr*, 39.9% *mr*, 14.3% *mm* (run 8).

Monitoring the polymerization in a [MMBL]/[I] of 600 (run 9) reveals living characteristics of the polymerization by ^{iBu}SKA + TTPB, in that there is a linear increase in MW with increasing monomer conversion, while MWD remains nearly constant during the course of polymerization (Figures 1 and 2). This polymerization was further examined over the [MMBL]/[I] ratios from 200 to 800 (runs 7−10,

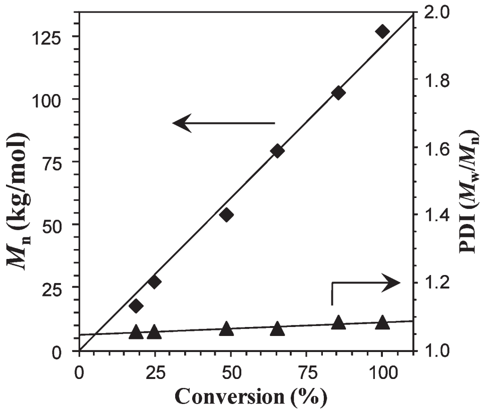


Figure 1. Plot of M_n (obtained by GPC against PMMA standard) and PDI of PMMBL vs monomer conversion for the polymerization of MMBL by ^{iBu}SKA + TTPB (run 9, Table 1).

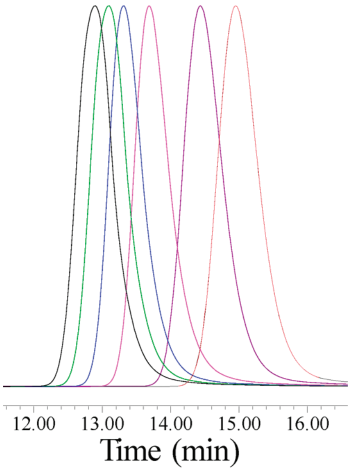


Figure 2. Overlay of GPC traces of aliquots taken during the polymerization plotted in Figure 1. M_n (kg/mol) and PDI (M_w/M_n) for traces from right (low MW) to left (high MW) are 17.6, 1.06; 27.2, 1.06; 53.9, 1.07; 79.4, 1.07; 103, 1.09; and 127, 1.09.

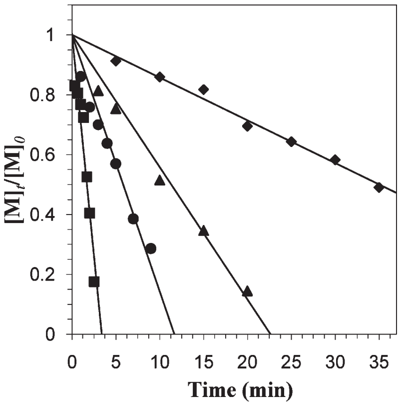


Figure 3. Zero-order kinetic plots of $[M]_t/[M]_0$ vs time for the polymerization of MMBL by ^{iBu}SKA + TTPB in CH_2Cl_2 at ambient temperature (~25 °C). Conditions: [MMBL] = 1.074 M; [TTPB] = 0.537 mM; [^{iBu}SKA] = 5.91 (■), 3.22 (●), 2.33 (▲), and 1.88 mM (◆).

Table 1). In all cases, the polymerization follows zero-order dependence on monomer concentration (Figure 3), thus proceeding through the same mechanism that has been established previously for the polymerization of MMA (cf. Scheme 1).[30,31] Specifically, the r.d.s. of a propagation "catalysis" cycle is the C−C bond coupling via Michael addition of the polymeric SKA to the silylated monomer, while recapturing the silylium catalyst coordinated to the growing polymer chain by the incoming monomer is relatively fast, thereby giving rise to the zero-order dependence on monomer concentration. Quantitative monomer conversions can be achieved for all runs, and the resulting polymers exhibit narrow MWD's ($\leq$1.03), but the MW's for the high [M]/[I] ratio runs are much higher than the calculated ones, typically a consequence of sacrificial consumption of the highly active catalysts like silylium ions as a scavenger (the effect of which is especially magnified at low catalyst loadings under high [M]/[I] ratios). Remarkably, a high MW PMMBL with a M_w of 548 kg/mol and an extremely narrow MWD of 1.01 (M_n = 543 kg/mol) was produced with a [M]:[I] ratio of only 800:1.

Effects of Initiator and Activator. Focusing on the homogeneous polymerization of MMBL in CH_2Cl_2, we further investigated the effects of the SKA initiator ($Me_2C{=}C(OMe)OSiR_3$, thus the effect of the structure of the resulting R_3Si^+ catalyst) and the activator (thus the effects of the initiation process and the structure of the resulting counteranions). We have previously shown that there is a remarkable selectivity of SKA on monomer structure for the polymerization of (meth)acrylates by SKA + TTPB.[31] Specifically, the Me_3Si^+ catalyst derived from ^{Me}SKA bearing a small silyl group is highly active and efficient for the polymerization of MMA but inefficient for the polymerization of the sterically less demanding *n*-butyl acrylate (^{n}BA). In contrast, the $^{i}Bu_3Si^+$ catalyst derived from ^{iBu}SKA bearing the bulky silyl group exhibits low activity in the polymerization of MMA but exceptional activity, efficiency, and control for the polymerization of ^{n}BA.[31] In the context of (M)MBL, in forming the cyclic butyrolactone ring, they can be considered to be sterically smaller than MMA. Indeed, our initial results discussed above demonstrated that the polymerization of MMBL by $^{i}Bu_3Si^+$ is more rapid, efficient, and controlled than that by Me_3Si^+.

Table 2 compiles more complete data to illustrate the effects of initiator and activator structures. Using TTPB (0.05 mol % relative to monomer) as activator in a fixed [MMBL]:[SKA] ratio of 200:1, the polymerizations using ^{Me}SKA and ^{iBu}SKA gave apparent rate constants (derived from the zero-order plot of $[M]_t/[M]_0$ vs time) of 0.114 mol/L min^{-1} (run 11, Table 2) and 0.295 mol/L min^{-1} (run 14, Table 2), respectively, thus indicating a 2.6-fold activity enhancement by $^{i}Bu_3Si^+$ over Me_3Si^+. When replacing TTPB with the Brønsted acid activator $H(Et_2O)_2B(C_6F_5)_4$, coupled with either ^{Me}SKA or ^{iBu}SKA, the apparent rate constant was reduced by either 22% (run 12) or 38% (run 15), accordingly. Lastly, when substituting TTPB with $[Ph_3C]$[*rac*-TRISPHAT] containing the racemic, hexacoordinate bulky chiral phosphate anion, the rate of the polymerization was increased by 63% (run 13 vs run 11) when coupled with ^{Me}SKA but decreased by 25% (run 16 vs run 14) when coupled with ^{iBu}SKA. These results suggest the importance of the cation−anion steric interplay (ion-pairing) on polymerization activity, where the bulky TRISPHAT anion enhances the activity of the small Me_3Si^+ cation while decreasing the activity of the large $^{i}Bu_3Si^+$ cation, as compared with the pairing $[B(C_6F_5)_4]^-$ counteranion. On the other hand, the racemic chiral phosphate anion did not noticeably impact the tacticity (45.7% *rr*, 43.0% *mr*, 11.3% *mm*) of the resulting polymer (run 16, Table 2). Regardless of the activators (thus counteranions) utilized, polymerizations employing ^{Me}SKA never achieved quantitative monomer conversion, even with extended reaction times (up to 24 h), while all runs with ^{iBu}SKA achieved quantitative monomer conversion within 10 min. Overall,

Table 2. Results of Polymerization of MMBL with Varied Initiator and Activators[a]

run no.	M	I	activator	time (min)	conv[b] (%)	M_w[c] (kg/mol)	MWD[c] (M_w/M_n)	k_{app}[d] (mol/L min^{-1})
11	MMBL	^{Me}SKA	TTPB	10	64.2	50.3	1.22	0.114
12	MMBL	^{Me}SKA	$HB(C_6F_5)_4$	10	71.2	40.2	1.27	0.089
13	MMBL	^{Me}SKA	TRISPHAT	10	81.2	48.7	1.32	0.186
14	MMBL	^{iBu}SKA	TTPB	10	100	31.0	1.02	0.295
15	MMBL	^{iBu}SKA	$HB(C_6F_5)_4$	10	100	40.0	1.07	0.182
16	MMBL	^{iBu}SKA	TRISPHAT	10	100	36.2	1.01	0.222

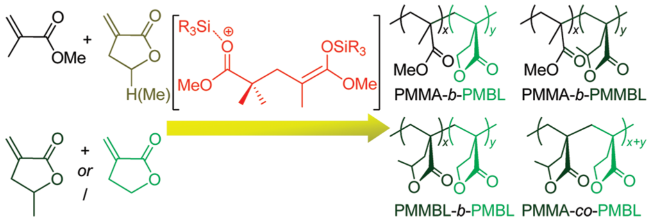
[a] Carried out in 5 mL of CH_2Cl_2 at ambient temperature in a fixed [MMBL]:[SKA] ratio of 200:1. [b] Conversion, measured by ^{1}H NMR. [c] Determined by light scattering. [d] Determined from the slope of the best-fit line from the zero-order kinetic plots.

Table 3. Results of Copolymerizations of MBL, MMBL, and MMA by $^i Bu_3Si^+$[a]

run no.	M1 + M2 (block) M1/M2 (random)	[M1]:[M2]:[I]	time (h)	yield (%)	M_w[b] (kg/mol)	MWD[b] (M_w/M_n)
17	MMA + MBL	300:300:1	1:3	80.8	68.4	1.01
18	MMA + MMBL	300:300:1	1:3	80.7	68.1	1.03
19	MMBL + MBL	300:300:1	0.17:1	93.6	117	1.02
20	MMBL/MBL	300:300:1	1.17	91.3	123	1.01

[a] Carried out in 5 mL of CH_2Cl_2 at ambient temperature. [b] Determined by light scattering.

Scheme 2. Copolymerization of (M)MBL with MMA and with Each Other



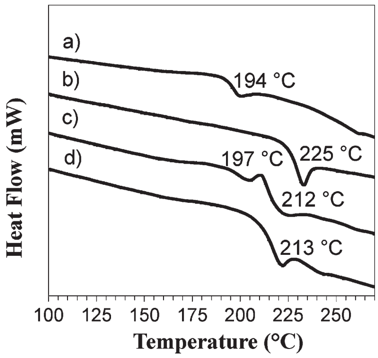


Figure 4. DSC of (a) PMBL (run 3, Table 1), (b) PMMBL (run 9, Table 1), (c) PMMBL-*b*-PMBL (run 19, Table 3), and (d) PMMBL-*co*-PMBL (run 20, Table 3).

these results show that the reactivity of MMBL lies between MMA and ^{n}BA, but the selectivity of MMBL for the silylium R_3Si^+ catalyst structure is much like that of ^{n}BA examined previously.[31]

Copolymerization Characteristics. The copolymerization studies outlined in Scheme 2 were aimed at further testing the living nature of the MMBL polymerization by the ^{iBu}SKA + TTPB system and also exploring the synthesis of unimodal polymers comprised of MBL. While the synthesis of the well-defined PMBL was not achieved by the current system through the homopolymerization approach (due to the insolubility of PMBL in the polymerization medium, *vide supra*), we found that copolymerization of MMA (300 equiv, which was polymerized first) with equimolar MBL successfully afforded the CH_2Cl_2-soluble, well-defined block copolymer with a very narrow MWD of 1.01 (run 17, Table 3). The measured M_n of 67.7 kg/mol is compared with the calculated M_n of 48.2 kg/mol, thus giving a good I^* of 72%. The block copolymerization of MMA with MMBL proceeded in a similar manner, also affording the well-defined diblock copolymer with a narrow MWD of 1.03 and a good $I^*$of 78% (run 18, Table 3). Not surprisingly, switching the order in which the monomers were added for both cases (i.e., polymerizing (M)MBL prior to MMA) resulted in the formation of only homopolymers P(M)MBL; this observation mirrors what has been observed in the block copolymerization of MMA (which must be polymerized first) and ^{n}BA (the more reactive monomer).[30]

We also examined block and statistical copolymerizations of MBL and MMBL by ^{iBu}SKA + TTPB in CH_2Cl_2 at ambient temperature. By polymerizing MMBL first in the block copolymerization or polymerizing MMBL and MBL simultaneously in the statistical copolymerization, well-defined diblock copolymer PMMBL-*b*-PMBL (M_w = 117 kg/mol, MWD = 1.02, run 19, Table 3) and statistical copolymer PMMBL-*co*-PMBL (M_w = 123 kg/mol, MWD = 1.01, run 20, Table 3) were successfully synthesized. Overall, the copolymerization approach not only confirmed the living nature of the MMBL polymerization catalyzed by $^i Bu_3Si^+$, it also solved the insolubility and bimodality issue of PMBL, thus successfully leading to the well-defined MBL-containing copolymers.

Thermal Properties of Polymers. We reported earlier that the atactic PMBL ($M_n = 5.98 \times 10^4$) and atactic PMMBL ($M_n = 5.48 \times 10^4$) produced by the decamethylsamarocene catalyst show narrow, one-step decomposition windows, with the initial (T_{ini}) and end (T_{end}) onset temperatures of PMMBL (T_{ini} = 356 °C, T_{end} = 441 °C) being 12 and 25 °C higher than those of PMBL (T_{ini} = 344 °C, T_{end} = 406 °C), both of which are higher than the onset decomposition temperatures (T_{ini} = 340 °C, T_{end} = 399 °C) of the atactic PMMA with comparable MW.[16] Even more dramatically, the T_g's of the resulting atactic PMBL and PMMBL are 194 and 227 °C, respectively, which are ~90 and ~120 °C higher than the T_g (105 °C) of the typical atactic PMMA with comparable MW.[16] Consistent with these findings, the DSC analysis showed that the atactic PMBL (run 3, Table 1) and PMMBL (run 9, Table 1) produced by the current SKA + TTPB system also exhibit high T_g's of 194 and 225 °C, respectively (Figure 4). As anticipated, the block copolymer PMMBL-*b*-PMBL displays two T_g's of 212 and 197 °C, corresponding to the PMMBL and PMBL blocks, respectively, while the statistical copolymer PMMBL-*co*-PMBL shows only one T_g at 213 °C (Figure 4).

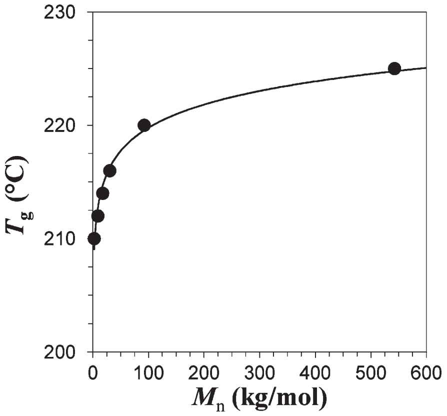


Figure 5. Plot of T_g vs M_n of atactic PMMBL.

With a series of MMBL homopolymers having a wide range of MW's on hand, we also investigated the effect of M_n on the T_g of PMMBL (Figure 5). Specifically, PMMBLs with M_n = 2.64, 8.99, 17.8, 30.4, 92.3, and 543 kg/mol exhibited T_g = 210, 212, 214, 216, 220, and 225 °C, respectively. These results suggest that the critical MW of PMMBL (estimated off of leveling of T_g values) is rather high, over 40 (~47) kg/mol.

Conclusions

Utilizing the recently developed unique polymerization system that employs the SKA + TTPB combination for *in situ* generation of the highly active *ambiphilic* propagating species containing both the nucleophilic SKA initiating moiety and the electrophilic silylium catalyst, this study has thoroughly investigated the characteristics of the polymerization of two naturally renewable butyrolactone-based vinylidene monomers, MBL and MMBL. Key findings of this study are summarized as follows.

First, while the polymerization of MBL in CH_2Cl_2 at ambient temperature is heterogeneous and achieves typically low yields of polymers that also exhibit bimodal MWD's, introduction of the γ-methyl group to the γ-butyrolactone ring (i.e., MMBL) enables a homogeneous reaction through completion in 10 min even with a low catalyst loading of 0.05 mol % (relative to monomer) and, more importantly, a rapid (up to 12 000 h^{-1} TOF) and living polymerization, thereby producing polymers with controlled low to high ($M_n = 5.43 \times 10^5$ kg/mol) MW and narrow MWD's (1.01−1.06). Besides the high degree of control, the activity of the MMBL polymerization by the current system is outstanding, typically achieving a complete monomer conversion within minutes of reaction at ambient temperature, as compared to the MMBL polymerization by conventional mechanisms, including radical, anionic, and group-transfer polymerization methods, which required many hours, often at low temperatures, achieving low to high, but never complete, conversions.

Second, through investigations into effects of SKA (thus the resulting R_3Si^+ catalyst) and activator (thus the resulting counteranion) structures, we have found that the $Me_2C{=}C(OMe)OSi^iBu_3/Ph_3CB(C_6F_5)_4$ combination is the most active *and* controlled system for (M)MBL polymerizations. The resulting large $^iBu_3Si^+$ cation (relative to the smaller Me_3Si^+ cation), when paired with the weakly coordinating anion $[B(C_6F_5)_4]^-$, exhibits exceptional activity and control toward polymerization of sterically less demanding monomers such as (M)MBL (and acrylates). These results further highlight the importance of the cation−anion pairing in catalysis and of the good match between the catalyst and monomer structures in polymerization.

Third, the living nature of the current polymerization system catalyzed by $^iBu_3Si^+$ has been further confirmed by the synthesis of well-defined block copolymers of MBL and MMBL with MMA as well as block and statistical copolymers of MBL with MMBL. All copolymers produced herein exhibit unimodal and narrow MWD's of ≤1.03. As anticipated, the block copolymer PMMBL-*b*-PMBL displays two T_g's corresponding to the PMBL and PMMBL blocks, while the statistical copolymer PMMBL-*co*-PMBL shows only one T_g.

Fourth, the current system produces essentially atactic polymers exhibiting high T_g's of 194 °C (PMBL) and 225 °C (PMMBL). These values represent T_g enhancements of ~90 °C (for PMBL) and ~120 °C (for PMMBL) over the T_g (105 °C) of the typical atactic PMMA. Also interestingly, the presence of the cyclic butyrolactone moiety in PMMBL considerably increases its estimated critical MW (~47 kg/mol) over that of PMMA (~28 kg/mol).

Acknowledgment. This work was supported by the National Science Foundation (NSF-0848845). We thank Boulder Scientific Co. for the research gift of $[Ph_3C][B(C_6F_5)_4]$.

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