THESIS

LEWIS ACID-MEDIATED CONTROLLED ANIONIC POLYMERIZATION AT HIGH TEMPERATURE

Submitted by

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ABSTRACT

LEWIS ACID-MEDIATED CONTROLLED ANIONIC POLYMERIZATION AT HIGH TEMPERATURE

Lewis acid-mediated controlled anionic polymerization under industrially desired conditions (ambient or higher temperature) is described in this thesis. The central theme focuses on the utilization of Lewis acids, primarily trialkylaluminum tris(pentafluorophenyl)alane and isoelectronic silylium cation, in three different anionic polymerization systems to mediate, or act as catalyst, for the controlled anionic polymerization of (meth)acrylic monomers or the anionic coordination ring opening polymerization of bio-derived cyclic monomers ε-caprolactone and *meso*-lactide. The first system uses potassium hydride as an anionic initiator, activated with aluminum Lewis acids of varied acidity, sterics and equivalents, for the controlled polymerization of methyl methacrylate (MMA) and block copolymerization of MMA with other alkyl methacrylates such as *n*-butyl methacrylate and 2-ethylhexyl methacrylate. The second system involves the synthesis of nonpolar-polar block copolymer of poly(styrene-*b*-methacrylate) in aliphatic solvents at high temperature. Aluminum Lewis acids or non-polymerizable monomers such as *N*,*N*-dimethyl methacrylamide are added between blocks to control the propagation crossover from the styrenic block to the methacrylate

block. The third system utilizes silylium ions to catalyze anionic polymerization, focusing on the anionic coordination polymerization of cyclic esters and the development of new dinuclear catalysts exhibiting potential to new polymerization pathways that could promote faster polymerization under dilute conditions and enhanced polymerization stereochemical control.

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CHAPTER 1

Introduction

This thesis is written in a "journals-format" style that is accepted by the Graduate School at Colorado State University and is based on a section of one peer-reviewed publication that has appeared in *Journal of Polymer Science, Part A: Polymer Chemistry*, and some unpublished work. The principal theme of this thesis is to utilize Lewis acids, namely trialkylaluminum tris(pentafluorophenyl)alane and isoelectronic silylium cations, as catalysts for the controlled anionic polymerizations of (meth)acrylates and anionic ring opening polymerization of bio-derived cyclic esters. The author has studied three topics in controlled anionic polymerization and the formation of new silylium catalysts, which are discussed in detail in the proceeding chapters:

1) Lewis Acid-Mediated Anionic Polymerization of (Meth)acrylates by Potassium Hydride
2) Controlled Anionic Block Copolymerization of Styrene and (Meth)acrylates at High Temperature
3) Silylium Catalyzed Anionic Polymerization of Methacrylates and Cyclic Esters

In Chapter 2, the anionic polymerization of methyl methacrylate (MMA) was explored using potassium hydride as an initiator, activated by aluminum Lewis acids of varied acidity, sterics and equivalents; addition sequence was also explored for its effect

on polymerization control. *n*-Butyl acrylate was also successfully polymerized by this system, as well as bulkier methacrylate monomers in the block copolymer form following an initial block of PMMA.

In Chapter 3, the controlled, high temperature anionic block copolymerization of styrene and methacrylates was explored. The conventional synthesis of PS-*b*-PMMA is performed at -78 ˚C, in THF and with additives such as 1,1-diphenylethylene (DPE); this section outlines attempts to perform this synthesis at high temperatures in aliphatic solvents and without DPE. Aluminum Lewis acids were explored to control the methacrylate block formation, achieving limited success in controlling the crossover chemistry between the two blocks. In an attempt to control the crossover chemistry, it was hypothesized that a fluorinated methacrylate or a fluorinated alane would stabilize the initiating polymer chain end; however, 2,2,2-trifluoroethyl methacrylate was not polymerizable by this system and attempts at synthesizing hexane-soluble fluorophenyl and fluorophenoxy alanes were unsuccessful. However, the addition of *N*,*N*-dimethyl methacrylamide between polymer blocks was successful in reducing multimodal behavior in the resulting polymer product.

In Chapter 4, silylium cations were used to catalyze the anionic coordination ring opening polymerization of bio-derived cyclic esters. Also, new dinuclear catalysts exhibiting potential for new polymerization pathways to promote faster polymerization in dilute conditions and enhance polymerization stereocontrol were synthesized.

Chapter 5 contains a brief summary of the work presented herein. The majority of the work conducted by the author during the course of graduate studies has been included in this dissertation, but to maintain a level of consistency, some work that has been

published but not directly pertaining to the central theme of this thesis has been excluded. For reference, a list of all the work that has resulted in a publication during the course of this dissertation can be found in Appendix I.

CHAPTER 2

Lewis Acid-Mediated Anionic Polymerization of (Meth)acrylates by Potassium Hydride

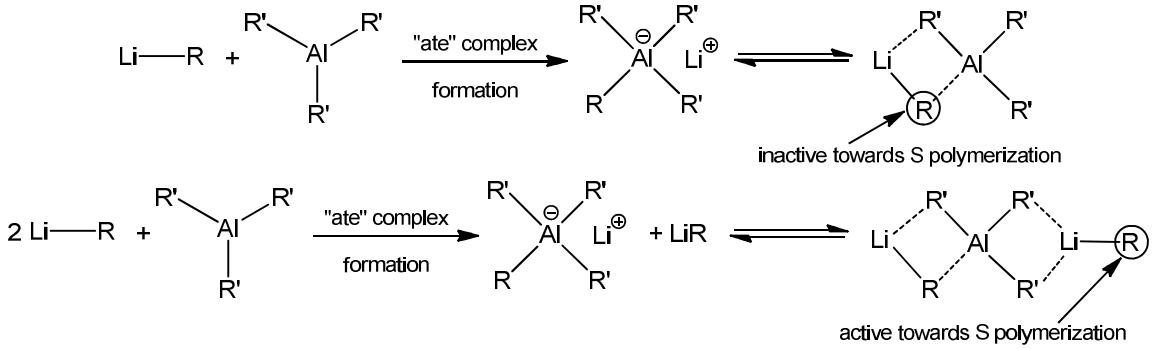
Abstract

Potassium hydride (KH), in combination with aluminum Lewis acids, was explored as a catalyst for the polymerization of methyl methacrylate (MMA). The amount and acidity of the alanes used greatly affected polymer control; the strongest acid alane, $Al(C_6F_5)_3$, was the most effective catalyst when used in 2 equivalents, while the weakest Lewis acid, triisobutylaluminum (TIBA), was the least effective alane. Interestingly, the analogous $B(C_6F_5)_3$ does not allow for any polymerization due to the strong B-H bond in the resulting "ate" complex. A crystal structure for the preformed "ate" complex $K^+[HAl(C_6F_5)_3]^-$ has been obtained, and the complex tested for polymerization activity. $K^+[HAl(C_6F_5)_3]^-$ by itself is only modestly active for MMA polymerization, but adding a second equivalent of $Al(C_6F_5)_3$ promotes rapid polymerization of MMA, behaving similarly to the in situ formed catalyst. KH/AlR_3 is also active towards polymerizing *n*-butyl acrylate (^{n}BA), but not *n*-butyl methacrylate (^{n}BMA), *t*-butyl methacrylate (^{t}BMA) or 2-ethylhexyl methacrylate (EHM) due to steric reasons.

Introduction

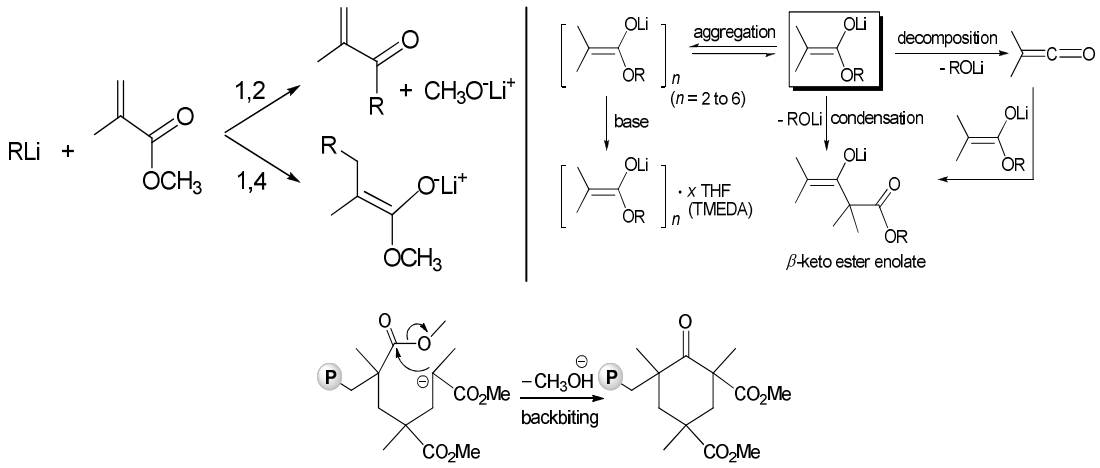
The living anionic polymerization of non-polar vinyl monomers such as styrene by organolithium (RLi) reagents is a facile process, even at temperatures up to 100 ˚C.[1] Polymerization proceeds without chain transfer or spontaneous termination until a protic source is added. On a large industrial scale, however, the speed of the reaction can generate too much heat, which can lead to side reactions. Deffieux and coworkers developed a method to control styrene polymerization called retarded anionic polymerization (RAP)[2], where a sub-stoichiometric amount of organoaluminum is added to the reaction mixture to form a reversible "ate" complex with the initiator, which slows polymerization enough to prevent excess heat generation (Scheme 1). They showed that only H^- was necessary to initiate polymerization, and had success with using metal hydrides in RAP[2a,b].

Scheme 1. Formation of the reversible "ate" complex for the retarded anionic polymerization of styrene[2d].



The living anionic polymerization of *polar* vinyl monomers such as methyl methacrylate (MMA) by RLi reagents alone at high temperatures, however, poses some issues[3]. The initiator can undergo either the preferred 1,4-addition, or the undesired 1,2-addition that generates a new monomer and a new initiator. The preformed first addition product, lithium enolate, can also undergo several side reactions, including condensation, aggregation and decomposition, which generate new initiators and new monomer. Also, the initiating end of the growing polymer chain can attack an earlier carbonyl carbon in the polymer chain; this back-biting mechanism creates cyclic oligomers and new polymerization initiators. The resulting polymer is ill-defined with broad polydispersity[4].

Scheme 2. Side reactions present in the anionic polymerization of MMA by RLi[4].



The addition of a strong Lewis acid to the system affords a living anionic polymerization at high temperature[4,5]. The Lewis acid works in a two-fold fashion: first, it forms an "ate" complex with the initiator to prevent side reactions with itself, and also to prevent the back-biting mechanism; second, it activates the monomer by coordinating with the carbonyl oxygen, which makes the activated monomer preferred for addition in the 1,4-addition pathway only.

In this work, we investigated (meth)acrylate polymerization by the metal hydride/Lewis acid system. We chose KH as our metal hydride because there is no prior literature on using KH as an initiator for MMA polymerization and also because potassium salts are less toxic because of the natural occurrence of K^+ in the body. Since this system is successful at polymerizing styrene, we also envisioned that success with MMA polymerization by KH could also make the KH system ideal for styrene/MMA block copolymerization.

Experimental Section

General Methods. All air-sensitive reactions and manipulations were performed using standard Schlenk techniques on a dual-manifold Schlenk line or in an argon- or nitrogen-filled glovebox. HPLC grade toluene was sparged extensively with nitrogen and dried over Q-5 supported copper catalyst, while ACS grade cyclohexane (CyH) was degassed and dried over CaH. These solvents were further dried over sodium/potassium alloy (NaK). Benzene-d_6 was degassed and dried over NaK; $CDCl_3$ was degassed and dried over Davidson 4Å molecular sieves. ^{1}H NMR data were recorded on a Varian 300 or Varian 400, with ^{1}H referenced to tetramethylsilane.

Reagents. Methyl methacrylate (MMA), *n*-butyl acrylate (^{n}BA), *n*-butyl methacrylate (^{n}BMA) and *t*-butyl methacrylate (^{t}BMA) were purchased from Sigma Aldrich, while 2-ethylhexyl methacrylate (EHM) and styrene (S) were purchased from TCI America. The above monomers were purified by degassing and drying over calcium hydride overnight, followed by vacuum distillation. MMA was further purified by titrating with *n*-octylaluminum to a yellow point[6] and a second vacuum distillation. All

monomers were stored in brown glass bottles at -30 ˚C and, except in the case of styrene, over Davidson 4Å molecular sieves. Potassium hydride (oil dispersion) was washed repeatedly with hexanes and extensively dried. Butylated hydroxytoluene (2,6-Di-*tert*-butyl-4-methylphenyl benzene, BHT) was recrystallized from hexanes prior to use. Methanol, triisobutylaluminum (TIBA) and trimethylaluminum were used as purchased. $MeAl(BHT)_2$[7], $Al(C_6F_5)_3$[8] and $K^+[HAl(C_6F_5)]^-$[9] were prepared according to literature procedure.

General Polymerization Procedures. Polymerizations were performed in 30 mL reactors inside the glovebox at ambient temperatures (*ca*. 25 ˚C). In a typical polymerization, the potassium initiator was stirred for 5 minutes in 5 or 10 mL of solvent with the appropriate Lewis acid before the addition of monomer. In the case of reverse addition polymerization, the Lewis acid was premixed with the monomer and approximately 1 mL of solvent; this mixture was quickly added to the stirring suspension of potassium initiator in the remaining solvent. For block copolymerizations, MMA was allowed to polymerize in the typical manner for 20 minutes, followed by the addition of second monomer. At the completion of the polymerizations, a 0.2 mL aliquot was injected into 0.6 mL of "wet" $CDCl_3$ stabilized by BHT, and conversion was determined via NMR. Polymerization was terminated by the addition of 5 mL of a 5% HCl by volume solution in methanol. Except in the case of P^{n}BA, which was isolated by removing volatiles, the polymer was isolated by precipitation into 100 mL of methanol and filtering. All polymers were dried in a vacuum oven at 50 ˚C overnight to a constant weight prior to ^{1}H NMR and GPC analysis.

Polymer Characterization. Polymer molecular weights and polydispersities were determined by gel permeation chromatography (GPC). Analyses were carried out on a Waters University 1500 GPC instrument at 40 °C, at a flow rate of 1.0 mL/min and with $CHCl_3$ as the eluent. The instrument was calibrated with 10 PMMA standards and chromatograms were processed with Waters Empower software. The microstructure for MMA polymers was determined by ^1H NMR in $CDCl_3$ according to literature[10].

Results and Discussion

Polymerization of MMA. Because metal hydrides were successful catalysts for styrene polymerization, we wanted to explore the activity of KH towards MMA to see if the system was a viable option for polar/non-polar block copolymerization. KH itself is not soluble in toluene, and its suspension in toluene was not active to MMA polymerization. With the addition of Lewis acid, the initiator becomes toluene-soluble and active to MMA polymerization; homogeneity was tested by filtering the initiator after the initial reaction time but before the addition of monomer (Table 1, Run 11), exhibiting similar results to non-filtered runs. Both the amount and the relative acidity of the Lewis acid used greatly affect polymerization control and conversion. Unlike the case for non-polar vinyl monomers, a substoichiometric amount of added alane is not sufficient to control polymerization, as when only 0.5-1 equivalents of alane are used, PDI values are generally broader and complete monomer conversion in most cases cannot be achieved. However, adding 2 equivalents of alane affords the greatest control. Polymerization runs 5-7 in Table 1 best illustrate this effect. When only 0.5 equivalents of $MeAl(BHT)_2$ are added to KH, modest conversion is afforded with very broad polydispersity, but when 2

equivalents are added, complete conversion and a narrow polydispersity of 1.13 are achieved. Also, stronger Lewis acidity affords greater control. When the strongest alane $Al(C_6F_5)_3$ is used, complete conversion and narrow polydispersity is afforded even at 0.5 equivalents, whereas TIBA, the weakest Lewis acid in this series, does not afford complete conversion even at 2 equivalents and the resulting polymer has a much broader PDI in comparison. Interestingly, the analogous $B(C_6F_5)_3$ completely shuts down the system; this is because when KH reacts with $B(C_6F_5)_3$, the B-H bond in the resulting "ate" complex is too strong to make H^- available for polymerization. The reverse addition sequence, where the monomer is pre-activated with Lewis acid and added to KH suspended in toluene, was also explored. This method also affords complete conversion but causes a slight increase in polydispersity (Table 1, runs 9 and 10), suggesting that propagation is faster than the activation of KH.

Table 1. MMA polymerization by KH (23.4 μmol) and alanes in 5 mL of toluene at ambient temperatures for 2 h.

Run no.	Initiator system	Conversion (%)	$10^4 M_n$ (g/mol)	PDI (M_w/M_n)
1	KH	<1	--	--
2	KH/0.5 $Al(C_6F_5)_3$	100	12.3	1.08
3	KH/1 $Al(C_6F_5)_3$	100	6.70	1.04
4	KH/2 $Al(C_6F_5)_3$	100	7.77	1.04
5	KH/0.5 $MeAl(BHT)_2$	27	4.19	3.39
6	KH/1 $MeAl(BHT)_2$	69	5.71	1.25
7	KH/2$MeAl(BHT)_2$	100	9.04	1.13
8	KH/2 Al^iBu_3	56	7.18	1.39
9	2 $Al(C_6F_5)_3$ to KH	100	28.9	1.28
10	2 $MeAl(BHT)_2$ to KH	100	9.04	1.13
11	KH/2 $Al(C_6F_5)_3$, filtered	100		
15	KH/1 $B(C_6F_5)_3$	0	--	--
16	KH/2 $B(C_6F_5)_3$	0	--	--

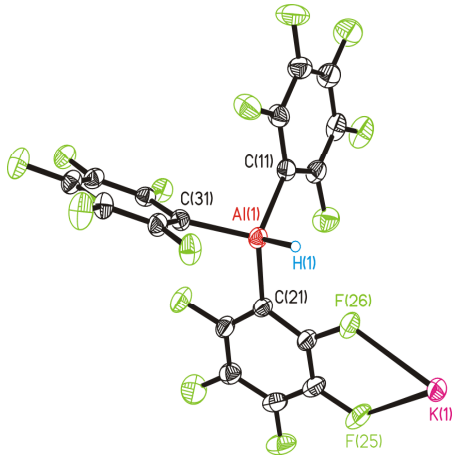
In an effort to isolate the active species, KH and $Al(C_6F_5)_3$ were reacted together to form "ate" complex $K^+[Al(C_6F_5)_3]^-$ (Fig. 1). The pre-formed catalyst was able to polymerize MMA but only to a moderate conversion, although it is interesting to note that the resulting polymer is nearly atactic (Table 2, run 17), and both broader polydispersity and high initiator efficiency indicate that there is significantly less polymerization control. However, when 1 equivalent of $Al(C_6F_5)_3$ is premixed with $K^+[Al(C_6F_5)_3]^-$ (Table 2, run 18) in order to return the ratio of Al and H^- to 2:1, polymerization once again is similar to the in situ reaction.

Table 2. MMA polymerization by "ate" complex $K^+[Al(C_6F_5)_3]^-$ in 5 mL of toluene at ambient temperatures; polymerization time: 2 h.

Run No.	Initiator[a]	Conv[b] (%)	PDI[c] (M_w/M_n)	I^*[d] (%)	[*rr*][b] (%)	[*mr*][b] (%)	[*mm*][b]
17	$K^+[HAl(C_6F_5)_3]^-$	79	1.44	148	26.6	51.7	21.7
18	$K^+[HAl(C_6F_5)_3]^-$ + 1 $Al(C_6F_5)_3$	100	1.04	79.6	69.5	26.5	4.0

[a] [M]/[I] ratio of 400. [b] Conversion and tacticity measured by ^{1}H NMR [c] Determined by GPC relative to PMMA standards. [d] $I^* = M_{calc}/M_n$; M_{calc} = (equiv. monomer)(MW monomer)(% conv) + (MW end groups).

a)



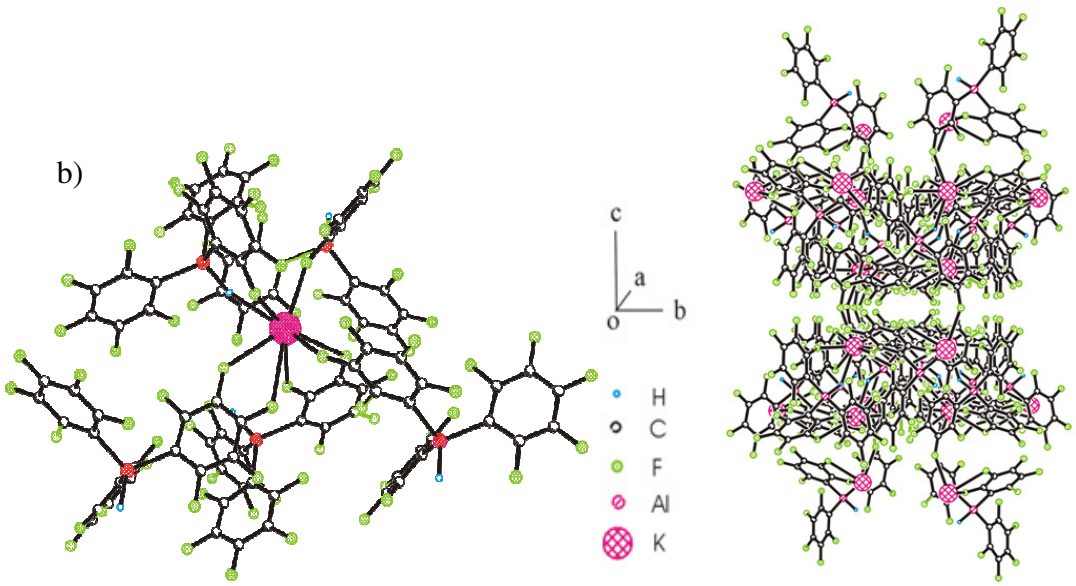


Figure 1. X-ray crystal structure of "ate" complex $K^+[Al(C_6F_5)_3]^-$: a) single ion pair structure with thermal ellipsoids at 50%; b) molecular structure with isotropic ellipsoids drawn at ARAD of 0.6 for the adjusted radius of the K ion for clarity. The left picture highlights the coordination of K^+ cation, while the picture on the right shows ion interactions in a 3-D structure.[12]

Homopolymerization and block copolymerization of other monomers. Since styrene polymerization is optimized in aliphatic solvents and MMA polymerization is uncontrolled in aliphatic solvents due to the insolubility of PMMA, we explored other polar vinyl monomers whose polymers do have sufficient solubility in aliphatic solvents in order to find a suitable (meth)acrylate monomer for non-polar/polar block copolymerization. Table 3 outlines the polymerization of ^{n}BA in both toluene and CyH with both $MeAl(BHT)_2$ and $Al(C_6F_5)_3$. KH itself again is inactive for polymerization but is active when Lewis acid is added. It is interesting to note that in this case that $MeAl(BHT)_2$ is more active than $Al(C_6F_5)_3$ even though it is the weaker Lewis acid.

CyH also seems to help polymerization control; in the case of both Lewis acids, polydispersity was improved in CyH over toluene as a solvent choice.

Table 3. ^{n}BA polymerization by KH and alanes in 5 mL solvent at ambient temperatures for 2h.

Run no.	Initiator system	Solvent	Conv. (%)	M_n 10^4 (g/mol)	PDI (M_w/M_n)
19	KH	tol	0	--	--
20	KH/2 $Al(C_6F_5)_3$	tol	77.6	13.5	2.19
21	KH/2 $Al(C_6F_5)_3$	CyH	43.2	8.50	1.74
22	KH/2 $MeAl(BHT)_2$	tol	100	37.4	1.87
23	KH/2 $MeAl(BHT)_2$	CyH	100	71.3	1.68

We also explored the polymerization of other methacrylates whose polymers are CyH-soluble: ^{n}BMA, ^{t}BMA and EHM. KH, however, was inactive for homopolymerization of these monomers with or without an added Lewis acid. To determine whether these monomers were too sterically incumbered to be initiated by H^- with alane or if these monomers were truly not polymerizable by the KH system, and to confirm if this system was indeed living, we first polymerized a block of MMA and then polymerized the second monomer to form the block copolymer. For both ^{n}BMA and EHM, this method successfully formed block copolymers in toluene with both $Al(C_6F_5)_3$ and $MeAl(BHT)_2$, but ^{t}BMA proved too sterically hindered for block copolymer formation. Also, all attempts at triblock polymer formation were not successful due to the system's sensitivity to concentration and solution viscosity. Although this system was able to polymerize CyH-soluble (meth)acrylate polymers and form block copolymers, all attempts at forming a poly(styrene-*b*-(meth)acrylate) polymer were unsuccessful.

Conclusion

KH, while inactive on its own, is highly effective for polymerizing MMA to complete conversion when combined with a suitable aluminum Lewis acid. Both the amount and the acidity of the Lewis acid used greatly affects polymerization control, with the stronger acid $Al(C_6F_5)_3$ in 2 equivalents as the best catalyst. The analogous $B(C_6F_5)_3$, however, completely shut down polymerization because the strength of the B-H bond in the resulting "ate" complex did not allow H^- to be available for polymerization. "Ate" complex $K^+[HAl(C_6F_5)_3]^-$ was isolated and found to be modestly active for MMA polymerization, affording a nearly atactic polymer; with the addition of $Al(C_6F_5)_3$ the "ate" complex becomes highly active for MMA polymerization, behaving like the in situ formed catalyst. Homopolymerization of ^{n}BMA or EHM was not successful due to steric reasons, but block copolymerization was possible.

Acknowledgements

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CHAPTER 3

Controlled Anionic Block Copolymerization of Styrene and Methacrylates at High Temperature

Abstract

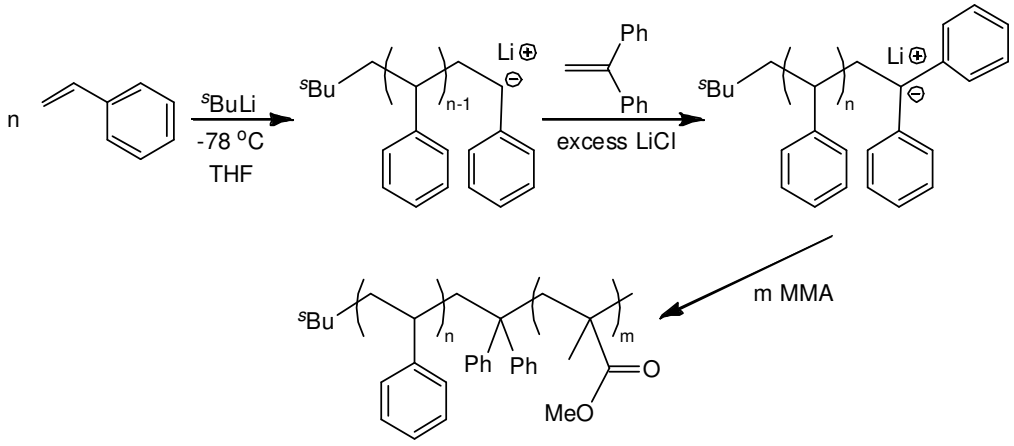
The conventional synthesis of the well-defined block copolymer PS-*b*-PMMA is done at -78 ˚C in THF with additives such as 1,1-diphenylethylene (DPE) and LiCl. On a large industrial scale, however, this is impractical. This contribution reports efforts to synthesize PS-*b*-poly(methacrylate) at high temperatures in aliphatic solvents without the use of DPE. The addition of $MeAl(BHT)_2$ during methacrylate block formation afforded a block copolymer with narrow polydispersity, but it is not unimodal. A block variation study that explored whether multimodal behavior was due to a mixture of homo- and block copolymer revealed that no PS homopolymer is present, and a Soxhlet extraction of PS-*b*-P^{t}BMA in MeOH showed no P^{t}BMA homopolymer present. It was hypothesized that the introduction of fluorine to the initiating polymer chain end would help modulate the crossover chemistry at the block junction. Fluorinated monomer or alane was thought to be the most effective way to do this; however, 2,2,2-trifluoroethyl methacrylate was not polymerizable by our system, and attempts at preparing cyclohexane-soluble fluorophenyl and fluorophenoxy alanes were unsuccessful. The addition of

nonpolymerizable *N*,*N*-dimethyl methacrylamide between polymer blocks was successful in reducing multimodal behavior.

Introduction

Poly(styrene-*b*-(methyl methacrylate)), PS-*b*-PMMA, synthesized by anionic means (Scheme 1), is conventionally formed at low temperatures (-78 ˚C) and in aprotic polar solvents such as THF[1]. In addition to this, 1,1-diphenylethylene (DPE), as well as an excess of LiCl, are both needed to stabilize the initiation of methacrylate polymerization due to the different polymerization mechanisms of polar and non-polar monomers, and also because PSLi is too active of an initiator to polymerize methacrylate

Scheme 1. Conventional synthesis of PS-*b*-PMMA by anionic polymerization[1].



in a living fashion. While this method of block copolymer formation is achievable in an academic setting, these necessary conditions make the production of PS-*b*-PMMA on a large industrial scale impractical for three main reasons: firstly and most importantly, maintaining sub-ambient temperatures requires a significant amount of costly energy;

secondly, THF is not a preferable solvent due to its toxicity; and thirdly, additives such as DPE are too expensive to make the process profitable.

In a more desired large-scale polymerization, temperatures would be ambient or higher, a less toxic solvent such as cyclohexane would be used, and expensive additives such as DPE would not be necessary. These conditions are possible for living anionic styrene polymerization, where tight ion pairing in aliphatic solvents is preferred. The reaction is so facile that on a large scale that excess amounts of heat are generated and sub-stoichiometric amounts of alane must be added to slow the reaction[2]. However, the polymerization of *polar* vinyl monomers like MMA is not living under these conditions. The mechanism for polymerization prefers loose ion pairing and therefore more polar solvents. Polystyryllithium (PSLi), the unterminated PS chain, is also too reactive an initiator for MMA polymerization as it is non-preferential to the site of addition. Alane is a necessary addition in a *super*-stoichiometric ratio to both stabilize the initiator and activate the monomer for preferential addition[3].

This work focuses on utilizing the addition of alane to create living anionic polymerization conditions for the block copolymerization of styrene with methacrylates and also on progress towards controlling the crossover chemistry between non-polar and polar monomer polymerization at the block junction.

Experimental Section

General Methods. All air-sensitive reactions and manipulations were performed using standard Schlenk techniques on a dual-manifold Schlenk line or in an argon- or nitrogen-filled glovebox. HPLC grade toluene was sparged extensively with nitrogen and

dried over Q-5 supported copper catalyst, while ACS grade cyclohexane (CyH) was degassed and dried over CaH. These solvents were further dried over sodium/potassium alloy (NaK). Benzene-d_6 was degassed and dried over NaK; and $CDCl_3$ was degassed and dried over Davidson 4Å molecular sieves. NMR data were recorded on a Varian 300 or Varian 400, with ^1H referenced to tetramethylsilane.

Reagents. Methyl methacrylate (MMA), *n*-butyl methacrylate (^{n}BMA), *t*-butyl methacrylate (^{t}BMA) and 2,2,2-trifluoroethyl methacrylate (TFM) were purchased from Sigma Aldrich, while styrene (S) and *N,N*-dimethyl methacrylate (DMMA) were purchased from TCI America. The above monomers were purified by degassing and drying over calcium hydride overnight, followed by vacuum distillation. MMA was further purified by titration with *n*-octylaluminum to a yellow point[4] and a second vacuum distillation. All monomers were stored in brown glass bottles at -30 ˚C and, except in the case of styrene, over Davidson 4Å molecular sieves.

Methanol, trimethylaluminum (TMA), triethylaluminum (TEA, 25 w/w % in hexanes), and *sec*-butyllithium (^{s}BuLi, 1.3M in CyH) were used as received or diluted prior to use. The following fluorinated benzenes and phenols were used as received: 1-chloro-2,4,6-trifluorobenzene (Sigma Aldrich); 1-chloro-3,5-difluorobenzene (Alpha Aesar); 1-chloro-4-fluorobenzene (Alpha Aesar); 4-chloro-(trifluoromethyl)benzene (Sigma Aldrich); 3,5-difluorophenol (Sigma Aldrich); p-fluorophenol (MP Biomedicals); pentafluorophenol (Sigma Aldrich); p-trifluoromethylphenol (Sigma Aldrich). Butylated hydroxytoluene (2,6-Di-*tert*-butyl-4-methylphenyl benzene, BHT) was recrystallized from hexanes prior to use. $MeAl(BHT)_2$[5] and $Al(C_6F_5)_3$[6] were prepared according to literature procedure. Attempted preparation of fluorophenyl[6] and fluorophenoxy[7] alanes

followed modified literature procedures, substituting the appropriate fluorobenzene or fluorophenol.

General polymerization procedure. In an argon-filled glovebox, a 25 mL Schlenk flask equipped with a glass-coated stir bar was charged with 10 mL of CyH, followed by the addition of ^{s}BuLi (usually 23.4 μmol, 0.65 M in CyH, 72.0 μL) and styrene. After sealing with a rubber septum, the Schlenk flask was interfaced to a Schlenk line and submerged in a 50 ˚C oil bath within 5 minutes of the addition of styrene. After 40 minutes total of styrene polymerization, the second monomer, premixed inside the glovebox with alane, was added via syringe and allowed to react for the appropriate amount of time. In the case of DMMA addition, 1.5 equivalents of DMMA were added via syringe to the PS reaction mixture and stirred for 5 minutes before the addition of the next monomer. In the case of the reverse addition polymerization, the PS reaction mixture was added via cannula to a second Schlenk flask containing DMMA, 2 mL of solvent and alane where applicable in a 0 ˚C ice bath. This reaction mixture stirred for 5 minutes before the addition of the next monomer.

Polymer Characterization. Polymer molecular weights and polydispersities were determined by gel permeation chromatography (GPC). Analyses were carried out on a Waters University 1500 GPC instrument at 40 °C, at a flow rate of 1.0 mL/min and with $CHCl_3$ or THF as the eluent. The instrument was calibrated with 10 PMMA standards and chromatograms were processed with Waters Empower software. Microstructure for MMA polymers was determined by ^{1}H NMR in $CDCl_3$ according to literature[8].

Results and Discussion

As the polymerization of styrene by ^{s}BuLi is living at 50 ˚C in CyH and the formation of the methacrylate block is not, we directed our focus to controlling the second block formation and the chemistry at the block junction. Our first step was to activate the methacrylate monomer and simultaneously stabilize the initiating polymer chain end PSLi with aluminum Lewis acid. In this case we chose $MeAl(BHT)_2$ over the stronger Lewis acid $Al(C_6F_5)_3$ because $MeAl(BHT)_2$ is CyH-soluble ($Al(C_6F_5)_3$ is not) and a comparable but less expensive alternative. We found that the addition of alane afforded polymer with narrow polydispersity and complete monomer conversions, but upon examination by GPC (Fig. 1), the polymer traces exhibited multimodal behavior similar to the polymerization without the addition of alane.

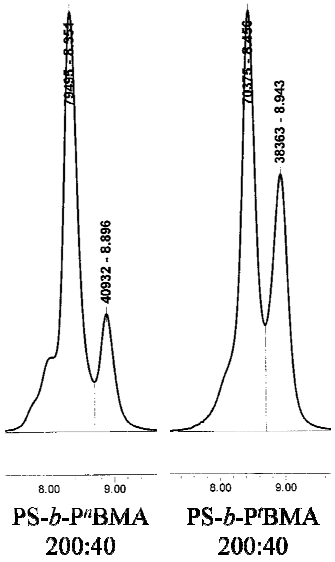


Figure 1. GPC traces of PS-*b*-P^{n}BMA and –P^{t}BMA polymerized by ^{s}BuLi and and $MeAl(BHT)_2$. Ratio of styrene to $^{n/t}$BMA to initiator is 200:40:1.

When PS-*b*-P^{n}BMA is synthesized in CyH at 50 ˚C *without* the addition of an aluminum Lewis acid, both the homopolymer and the block copolymer are present in the final polymer product; we were curious if this was still happening even though alane had been added. In a GPC experiment, PS-*b*-P^{n}BMA was synthesized with varying PS and P^{n}BMA block lengths. Fig. 2 shows the GPC traces of the block copolymers where the ^{n}BMA block was varied in size from 50-150 equivalents and the styrene block was kept constant at 200 equivalents. As the size of the ^{n}BMA block increases, a "convergent" behavior occurs in the traces, that is, there is no growing separation between the block copolymer from the PS homopolymer in the GPC traces that would be seen if the multimodal behavior was due to a mixture of the homopolymer and the block copolymer. A UV detector trace set to detect only PS collected at the same time as the RI detector supports this hypothesis, as the RI and UV detector traces are nearly identical, meaning that the P^{n}BMA is mostly uniformly attached to PS. A Soxhlet extraction of PS-*b*-P^{t}BMA in refluxing MeOH also confirms there is no P^{t}BMA homopolymer present; all PBMA homopolymer is attached to PS. Narrow polydispersity implies that once the second block is initiated, the alane still aids in controlling methacrylate polymerization; therefore, it is reasonable to assume that the multimodal behavior is due to the crossover chemistry at the block junction.

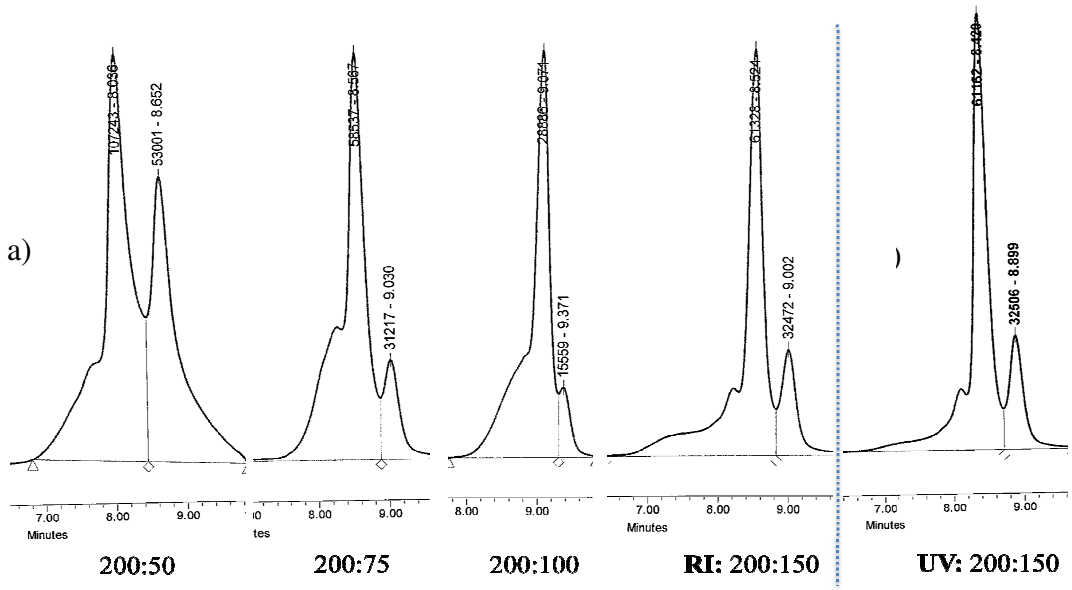


Figure 2. a) RI detector GPC traces of PS-*b*-P^{n}BMA with ratio of PS to P^{n}BMA at 200:50, 200:75, 200:100, 200:125, and 200:150. b) UV detector GPC trace of PS-*b*-P^{n}BMA with a ratio of PS to P^{n}BMA of 200:150.

Notably, previous anionic catalysts[3a,9,10] (Fig. 3) that have been used to polymerize MMA in a living fashion have an important fluorine or arene-M^+ (M = Li, K) interaction that aids in initiator stabilization; we thought that by utilizing this interaction we might be able to stabilize PSLi for further MMA polymerization.

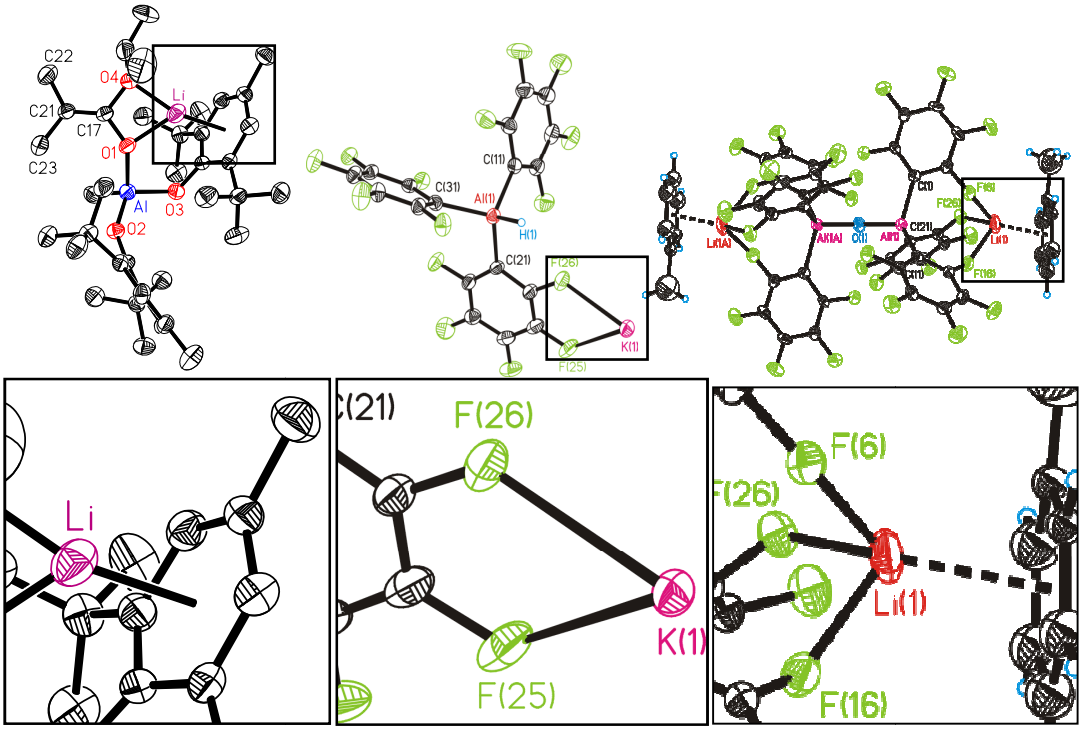


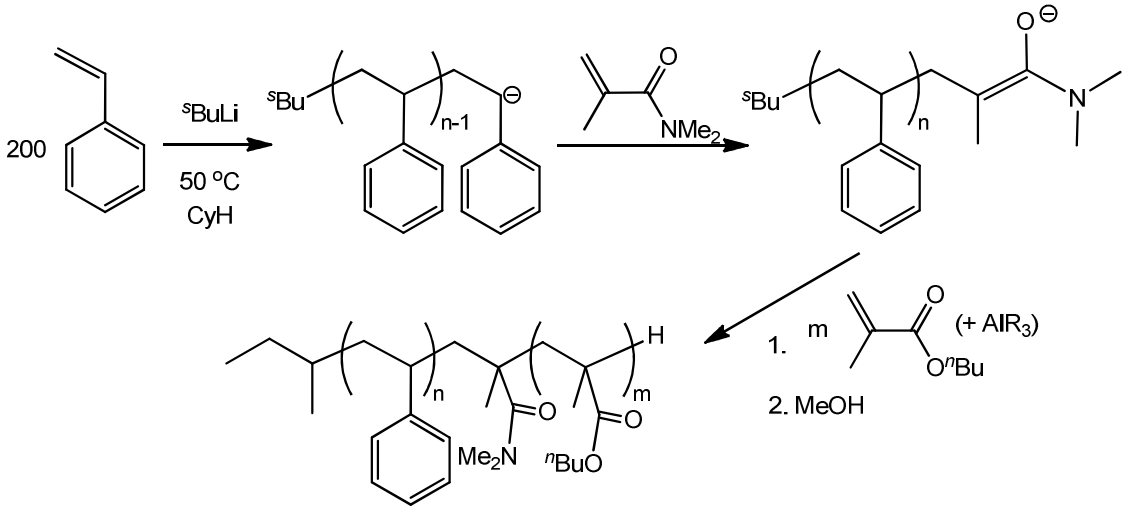
Figure 2. a) RI detector GPC traces of PS-*b*-P^{n}BMA with ratio of PS to P^{n}BMA at 200:50, 200:75, 200:100, 200:125, and 200:150. b) UV detector GPC trace of PS-*b*-P^{n}BMA with a ratio of PS to P^{n}BMA of 200:150.

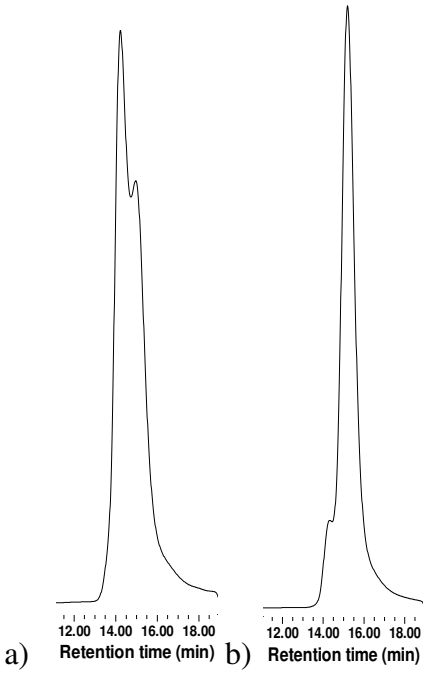
First, we looked at polymerizing 2,2,2-trifluoroethyl methacrylate (TFEM), as the fluorines would form a relatively stable 7-membered ring in the lithium enolate form and also withdraw more electron density from the vinyl carbon to make it more facile to polymerize. However, TFEM was not polymerizable by our system. Another method to introduce an arene- or fluorine-M^+ interaction was to add a fluorophenyl or fluorophenol alanes during second block formation. $Al(C_6F_5)_3$ and $Al(OC_6F_5)_3$, while strong, fluorinated Lewis acids that have shown an ability to aid in the polymerization of olefins[11], have limited solubility in CyH, so analogous fluorophenyl and –phenol alanes that are soluble in aliphatic solvents were needed. However, the synthesis of phenyl and

phenol organoaluminum compounds in the absence of polar coordinating solvents is by no means trivial; attempts at synthesizing both the analogs of $Al(C_6F_5)_3$ and $Al(OC_6F_5)_3$ resulted in a mixture of products and insoluble solid, respectively.

Our next approach was to find a compound that could reduce the activity of PSLi, much like DPE, but would allow for controlled MMA polymerization at high temperatures. *N*,*N*-Dimethyl methacrylamide (DMMA) was a suitable option for this purpose (Scheme 2). DMMA is not polymerizable by anionic means because the enolate form is in a twisted conformation due to a steric interaction between the *N*-methyl groups and the β-methyl group or the vinyl protons, making it unstable for the addition of further monomer[11]. However, initiated DMMA does allow for further MMA polymerization[12]. To add DMMA to PSLi, we used a reverse-addition process, where PSLi was added to a stirring mixture of DMMA and 2 equivalents $MeAl(BHT)_2$ to ensure full capping of the PSLi chains, followed by the addition of ^{n}BMA. In comparison to the same method of polymerization without DMMA, the resulting polymer with DMMA exhibited less shouldering characteristics by GPC trace (Fig. 4), indicating that DMMA does aid in partially controlling the crossover chemistry between polymer blocks (Scheme 2).

Scheme 2. Synthesis of PS-*b*-P^{n}BMA with the addition of DMMA between copolymer blocks.





a) b)

Figure 4. GPC traces of PS-*b*-P^{n}BMA formed by the reverse-addition process a) without DMMA between blocks and b) with DMMA between blocks.

Conclusion

Advances were made towards the controlled anionic polymerization of styrene with butyl methacrylates at 50 ˚C in CyH. While the addition of aluminum Lewis acid to aid the second block polymerization did not fully control formation of the block copolymer, it did still aid in second block polymerization. A GPC study of varying block lengths showed us that the multimodal behavior observed in the GPC traces is most likely not due to a mixture of terminated PS and block copolymer, but rather because of the crossover chemistry at the block junction. The addition of DMMA at the block junction supports this hypothesis, as it increases the degree of control over block copolymerization.

Acknowledgements

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CHAPTER 4

Silylium Catalyzed Anionic Polymerization of Methacrylates and Cyclic Esters

Abstract

Methyl trimethylsilyl dimethylketene acetal (^{Me}SKA), when oxidatively activated by trityl tetrakis(pentafluorophenyl)borane (TTPB), is an effective catalyst for the well-controlled polymerization of (meth)acrylate monomers. To expand this system, polymerization of other types of monomers and the development of new catalysts were explored. ^{Me}SKA/TTPB was examined for its effectiveness in the anionic coordination ring opening polymerization the bio-derived monomers ε-caprolatone (CL) and *meso*-lactide (LA). CL was successfully polymerized by ^{Me}SKA in both toluene and CH_2Cl_2, and PMMA-*b*-P(CL) was also successfully produced. LA, however, was not polymerizable by this system due to the stable 6-membered ring structure. Two dinuclear catalyst precursors, 1,2-Bis([(1-methoxy-2-methyl-1-propenyl)oxy](dimethyl)silyl)ethane and 1,3-bis([(1-methoxy-2-methyl-1-propenyl)oxy])-1,1,3,3-tetramethyldisiloxane (ethyl- and siloxy-bridged bis(^{Me}SKA), respectively) have been prepared. In the bis(^{Me}SKA) catalyst precursors, two equivalents of ^{Me}SKA are tethered together by the silyl groups, making subsequent polymerization by bis(^{Me}SKA) an intramolecular process and introducing the possibility for modulation of the silyl methyl groups to introduce chirality

and subsequently control polymer stereochemistry. Bis(^{Me}SKA) was found to be active towards MMA polymerization.

Introduction

Tris(pentafluorophenyl)alane, $Al(C_6F_5)_3$, is a strong Lewis acid that can be used to create living conditions for the high-temperature anionic polymerization of methyl methacrylate (MMA)[1]. When formed in the presence of toluene, the formula by elemental analysis is $Al(C_6F_5)_3 \cdot 0.5\ C_7H_8$, where the aluminum center is coordinated to the *para* carbon of toluene (Fig. 1a)[2]. The isoelectronic triethyl silylium ion, Et_3Si^+, when paired with $B(C_6F_5)_4^-$, also coordinates toluene at the *para* carbon, but at a closer distance (0.24 Å versus 0.30 Å longer than covalent radius), Fig. 1b[3]. Therefore, it is reasonable to assume that R_3Si^+ will be a good alternative for living anionic polymerization of MMA.

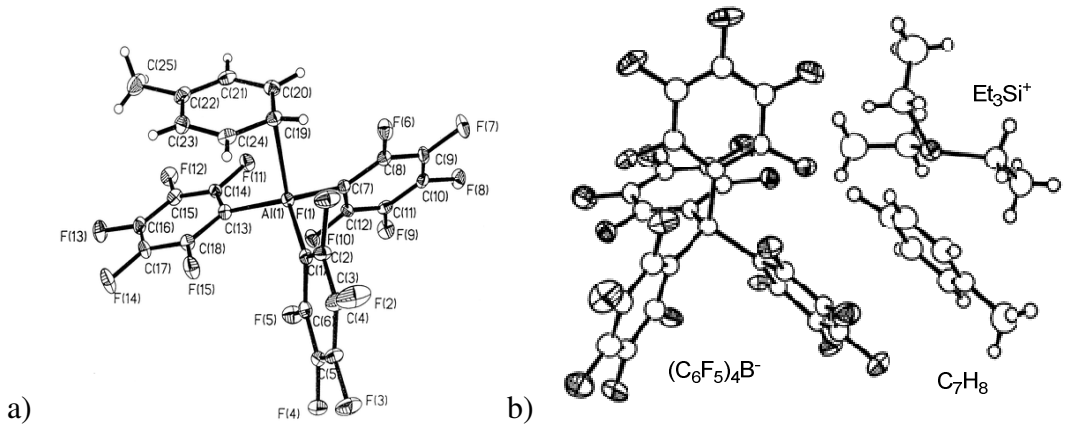
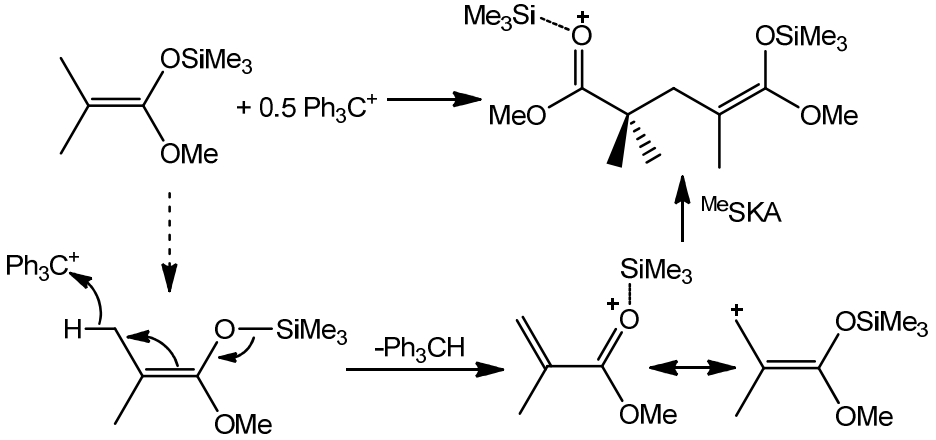


Figure 1. Crystal structures of a) $Al(C_6F_5)_3 \cdot C_7H_8$[2] and b) $[Et_3Si^+][B(C_6F_5)_4^-] \cdot C_7H_8$[3].

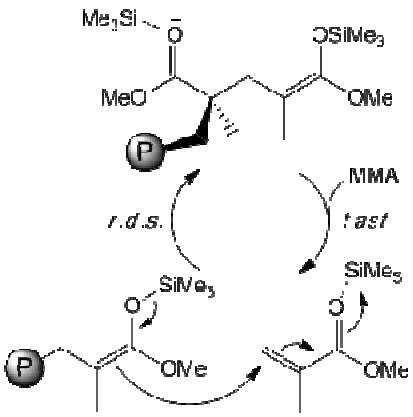
As previously reported by our research group[4], trimethylsilyl dimethylketene acetal (^{Me}SKA), when oxidatively activated by trityl tetrakis(pentafluorophenyl) borate

(TTPB), affords PMMA from low to high number average molecular weight (M_n, >10^5) with narrow polydispersity (polydispersity index, PDI = 1.04–1.12) with catalyst loading at 0.025 mol % based on monomer. ^{Me}SKA is activated by hydride abstraction by TTPB (Scheme 2), or in other words, undergoes a "monomer-less" initiation, forming silylium-activated MMA. ^{Me}SKA then undergoes Michael addition to the activated MMA, forming bifunctional active species **1**. In the propagation mechanism (Fig. 3), the activation of MMA by $SiMe_3^+$ occurs quickly, while the Michael addition step is the rate-determining step. Although ^{Me}SKA is a good initiator for methacrylate monomers, it is a poor initiator for *n*-butyl acrylate (^{n}BA), affording polymer with incomplete conversion and broad molecular weight distributions (MWD) even at 0 ˚C; however, the analogous ^{iBu}SKA is capable of polymerizing ^{n}BA in a living fashion at ambient temperatures with narrow PDI very rapidly, in less than one minute.

Scheme 1. Reaction of ^{Me}SKA with 0.5 equivalents of TTPB[4].

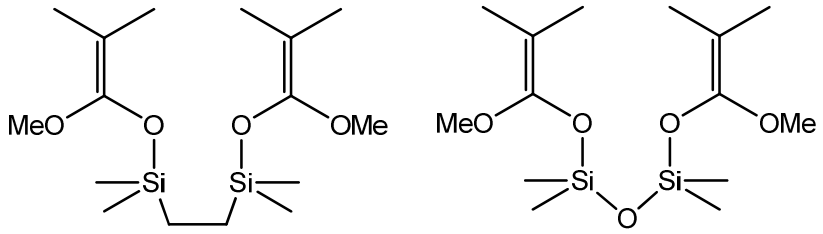


Scheme 2. Polymerization mechanism for PMMA by ^{Me}SKA/0.5 TTPB[4].



This contribution focuses on expanding this polymerization system in two ways. First, we wanted to expand the system to include other monomers, specifically the bio-derived cyclic esters ε-caprolactone (CL) and *meso*-lactide (LA). Both CL and LA produce technologically important biodegradable polymers[5] and are polymerized by anionic coordination ring opening polymerization. Secondly, we wanted to be able to control the stereochemistry of the resulting polymer. Polymer stereocontrol can be difficult to achieve with anionic polymerization because chirality introduced by the initiator becomes farther and farther removed from the site of monomer addition. However, since the ^{Me}SKA system is bifunctional, a bridge between the two Si sites (Scheme 3) will ensure that any chirality introduced by the initiator will be present at the monomer addition site.

Chart 1. Ethyl- and siloxy-bridged bis(^{Me}SKA).



Experimental Section

General Methods. All air-sensitive reactions and manipulations were performed using standard Schlenk techniques on a dual-manifold Schlenk line or in an argon- or nitrogen-filled glovebox. HPLC grade toluene and CH_2Cl_2 were sparged extensively with nitrogen and dried over activated alumina (THF and CH_2Cl_2) followed by passage over Q-5 supported copper catalyst (toluene). Toluene was further dried over sodium/potassium alloy (NaK). Benzene-d_6 was degassed and dried over NaK; $CDCl_3$ was degassed and dried over Davidson 4Å molecular sieves. NMR data were recorded on a Varian 300 or Varian 400, with ^{1}H referenced to tetramethylsilane.

Reagents. Methyl methacrylate (MMA), ε-caprolactone (CL) and *meso*-lactide (LA) were purchased from Sigma Aldrich. MMA and CL were purified by degassing and drying over calcium hydride overnight, followed by vacuum distillation. MMA was further purified by titration with *n*-octylaluminum[6] and a second vacuum distillation. LA was purified by sublimation. Methyl trimethylsilyl dimethylketene acetal, (^{Me}SKA) 1,2-bis(chlorodimethylsilyl)ethane, 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, methyl isopropyl isobutyrate, and *n*-butyllithium (^{n}BuLi) were purchased from Sigma Aldrich; all except nBuLi were degassed before use. Trityl tetra(pentafluorophenyl)borate (TTPB) was used as received.

Synthesis of 1,2-bis([(1-methoxy-2-methyl-1-propenyl)oxy](dimethyl)silyl) ethane and preparation of 1,3-bis([(1-methoxy-2-methyl-1-propenyl)oxy])-1,1,3,3-tetramethyldisiloxane[7] (bis(^{Me}SKA)). A modified literature procedure[4b] was used to synthesize bis(^{Me}SKA). In a nitrogen-filled glovebox, a 200 mL Schlenk flask equipped with a stir bar was charged with THF (100 mL) and diisopropylamine (5.00 mL, 3.61 g, 35.7 mmol). This flask was sealed with a rubber septum, removed from the glovebox, interfaced to a Schlenk line, and placed in a 0 °C ice-water bath. ^{n}BuLi (23.4 mL, 1.6 M in hexane, 37.5 mmol) was added dropwise via syringe to the flask. After being stirred at 0 °C for 30 min, methyl isobutyrate (4.09 mL, 3.64 g, 35.7 mmol) was added to this solution. The resulting mixture was stirred at this temperature for 30 min, after which 1,2-bis(chlorodimethylsilyl)ethane (3.85g, 17.9 mmol) or 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (3.64g, 3.50 mL, 17.9 mmol) was added. The mixture was allowed to warm slowly to room temperature and stirred for 3 h at this temperature, after which all volatiles were removed in vacuum. The resulting oil was heated at 90 ˚C under vacuum for 2 hours, redissolved in hexanes, and resulting precipitates were filtered off under an argon atmosphere and volatiles once again removed. The final product yielded 4.0g and 3.4g respectively, (64.4 and 56.8%) as a yellow oil. ^{1}H NMR data for ethyl-bridged bis(^{Me}SKA), $CDCl_3$: δ 0.20 (s, SiMe_2), 0.65 (s, SiCH_2), 1.52 (s, C=CMe_2), 1.58 (s, C=CMe_2), 3.51 (s, OMe); for siloxy-bridged bis(^{Me}SKA), $CDCl_3$: δ 0.25 (s, SiMe_2), 1.68 (s, C=CMe_2), 1.72 (s, C=CMe_2), 3.59 (s, OMe).

General polymerization procedure. All polymerizations were performed in an argon-filled glovebox in a 30 mL reactor at ambient temperatures. In a typical polymerization, a mixture of SKA pre-catalyst and monomer in 5 mL of solvent was

rapidly added to a stirring solution of TTPB in 5 mL of solvent. The reaction mixture stirred for the appropriate amount of time, and aliquots were taken periodically to monitor conversion. In the case of block copolymerization, 200 equivalents of MMA were allowed to polymerize for 20 minutes before the addition of CL. For MMA polymerization, 5% HCl by volume in MeOH was added to terminate polymerization, and the resulting polymer was precipitated into MeOH and filtered. For CL and LA polymerization, MeOH was added to terminate polymerization and volatiles were removed.

Polymer Characterization. Polymer molecular weights and polydispersities were determined by gel permeation chromatography (GPC). Analyses were carried out on a Waters University 1500 GPC instrument at 40 °C, at a flow rate of 1.0 mL/min and with $CHCl_3$ as the eluent. The instrument was calibrated with 10 PMMA standards and chromatograms were processed with Waters Empower software. Microstructure for MMA polymers was determined by ^1H NMR in $CDCl_3$ according to literature[8].

Results and Discussion

Silylium catalyzed anionic-coordination ring opening polymerization of CL and LA. MeSKA/TTPB in a 2:1 ratio was found to be active for CL polymerization, although reaction times were significantly longer than for (meth)acrylate polymerization, with complete conversions achieved in days as opposed to minutes. Solvent also has an effect on reaction kinetics: CL polymerization in toluene achieves complete conversion in 1 day, whereas the same polymerization in CH_2Cl_2 only reaches 90% conversion, even after 4 days. LA is not polymerizable by this system, presumably because the initiator is

unable to open the stable six-membered ring. We were also able to form PMMA-*b*-P(CL) by first polymerizing MMA followed by CL, using a combination of anionic and anionic coordination ring opening polymerizations.

Preparation of bis(^{Me}SKA) and polymerization of MMA. Before introducing chirality to the Si at the propagating site, we wanted to ensure that the bis(MeSKA) precatalyst can be activated for MMA polymerization in a similar way to ^{Me}SKA. Synthesis of ethyl- and siloxy-bridged bis(^{Me}SKA) followed a modified literature procedure for the general formation of silyl ketene acetals; siloxy-bridged bis(^{Me}SKA), while already prepared in literature[7], had not been synthesized by this method previously. When reacted in a 1:1 ratio with TTPB, bis(^{Me}SKA) behaves similarly to ^{Me}SKA and TTPB in a 2:1 ratio[4]. The 1:1 and 1:0.5 ratios of bis(^{Me}SKA) to TTPB were active for MMA polymerization, making bis(^{Me}SKA) a viable option for modulation in order to introduce chirality to MMA polymerization.

Conclusion

In an effort to introduce bioderived monomers whose resulting polymers were biodegradable to the ^{Me}SKA/TTPB system, we attempted to polymerize both CL and LA, although only CL was active for polymerization. We were also able to form PMMA-*b*-P(CL), which involved a crossover from anionic to anionic coordination ring opening polymerization. Ethyl- and siloxy-bridged bis(^{Me}SKA) were successfully prepared and were active for MMA polymerization, making the introduction of chirality to bis(^{Me}SKA) a possible method of controlling PMMA stereochemistry.

Acknowledgement

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CHAPTER 5

Summary

This work has investigated Lewis acid mediated controlled anionic polymerization at high temperatures. Aluminum Lewis acids have been shown to aid in controlling the anionic polymerization of both polar and non-polar vinyl monomers, especially for bulk polymerizations where side reactions can make large scale reactions impractical. The addition of a Lewis acid makes the controlled production of technologically important polymers from monomers such as methacryates and styrene possible.

Potassium hydride (KH) was explored as a new catalyst for methyl methacrylate (MMA) polymerization; while KH by itself showed no activity, when combined with various alanes it exhibits high activity towards the controlled anionic polymerization of MMA. When stronger Lewis acids were used, better polymerization control was achieved; narrower molecular weight distributions (MWD) and better conversions were achieved with the addition of the most acidic alane used, $Al(C_6F_5)_3$, while the broadest MWDs and modest conversions were observed with the addition of the least acidic alane of the series, TIBA. The analogous $B(C_6F_5)_3$, however, was inactive towards polymerization, presumably due to the strong nature of the B-H bond in the KH/ $B(C_6F_5)_3$ "ate" complex. When alane was added with the monomer to KH suspended in solvent, slightly broader MWDs were observed, suggesting that monomer propagation was faster

than the reaction of KH with alane. The crystal structure for the preformed 1:1 "ate" complex $K^+[HAl(C_6F_5)_3]^-$ was obtained, and the "ate" complex was tested for polymerization activity. $K^+[HAl(C_6F_5)_3]^-$ was found to be active for MMA polymerization; conversions were modest and the resulting polymer was nearly atactic, although with the addition of a second equivalent of $Al(C_6F_5)_3$ the complex was highly active to the polymerization of MMA, much like the case of the in situ formed catalyst. ^{n}BA can also be polymerized by KH/AlR_3, although the system was only able to produce the polymer of bulkier methacrylates in the block copolymer form following an initial block of PMMA.

The addition of Lewis acids also aids in the anionic synthesis of polar/*non*-polar block copolymers, such as PS-*b*-PMMA. Conventionally, this well-defined block copolymer is prepared at -78 ˚C, in THF and with expensive additives such as 1,1-diphenylethylene (DPE); on a large scale this is impractical due to the high energy costs of cooling a reaction and the toxic nature of THF. However, the more desired situation of producing PS-*b*-PMMA at high temperatures in non-toxic cyclohexane without additives like DPE, while not difficult for the polymerization of styrene, proves to be problematic for the formation of the second polar methacrylate block, which can undergo many side reactions. The strong Lewis acid $MeAl(BHT)_2$ was added in an effort to control the polymerization of the second block; while low MWD was observed for the resulting polymer, a trace by gel permeation chromatography (GPC) revealed multimodal behavior. To determine this was not due to a mixture of homo- and block copolymer, a block length variation study was performed; due to the similarities in RI and UV detector traces, it was possible to see that the polymer present was true block copolymers. A

Soxhlet extraction of PS-*b*-P^{t}BMA also confirmed no P^{t}BMA homopolymer was present. This led to the conclusion that multimodal behavior was due to the crossover chemistry at the block junction. The introduction of fluorine by a fluorinated monomer or fluorinated alane to the initiating polymer chain end was hypothesized to aid in initiator stability. However, 2,2,2-trifluoroethyl methacrylate is not polymerized by the system used, and attempted syntheses of fluorophenyl- and fluorophenoxyalanes were unsuccessful. The addition of *N*,*N*-dimethyl methacrylamide, which is nonpolymerizable by anionic means, did lower multimodal behavior by GPC trace.

Towards the Lewis acid R_3Si^+ catalyzed anionic coordination ring opening polymerization of cyclic esters, CL was able to be polymerized by ^{Me}SKA/TTPB and even form a block copolymer with MMA. LA is not polymerizable by ^{Me}SKA/TTPB, presumably due to its stable 6-membered ring configuration. Two dinuclear bis(^{Me}SKA) precatalysts, where essentially two ^{Me}SKA catalysts are bridged together at the Si atom sites, were synthesized; these catalysts, active for MMA polymerization, undergo an intramolecular mechanism as opposed to the bimolecular mechanism of ^{Me}SKA, making it possible to introduce chirality through the catalyst in the future.

Appendix I

List of Publications by LOB

1) Hu, Y.; Gustafson, L. O.; Zhu, H.; Chen, E. Y.-X. "Anionic Polymerization of MMA and Renewable Methylene Butyrolactones by Resorbable Potassium Salts", *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2008-2017.
2) Ning, Y.; Caporaso, L.; Correa, A.; Gustafson, L. O.; Cavallo, L.; Chen, E. Y.-X. "Syndioselective MMA Polymerization by Group 4 Constrained Geometry Catalysts: A Combined Experimental and Theoretical Study", *Macromolecules* **2008**, *41*, 6910-6919.
3) Mariott, W. R.; Gustafson, L. O.; Chen, E. Y.-X. "Activation of Tantalocene(V) Alkyl and Alkylidene Complexes with Strong Organo-Lewis Acids and Application to Polymerization Catalysis", *Organometallics* **2006**, *25*, 3721-3729.