EXPERIMENTAL INVESTIGATIONS OF AI-BASED INITIATIOR FOR (CO)POLYMERIZATION OF EPOXIDES AND EPISULFIDE AND APPLICATION TOWARD MEMBRANE SYNTHESIS

By

Niloofar Safaie Ashtiani

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemistry- Doctor of Philosophy

ABSTRACT

EXPERIMENTAL INVESTIGATIONS OF AI-BASED INITIATIOR FOR (CO)POLYMERIZATION OF EPOXIDES AND EPISULFIDE AND APPLICATION TOWARD MEMBRANE SYNTHESIS

By

Niloofar Safaie Ashtiani

We developed a novel aluminum-based initiator for epoxide polymerization which facilitated polymerization of various epoxides (epichlorohydrin, propylene oxide, *etc.*) and episulfide up to molecular weights of 100 kg/mol while maintaining relatively narrow polydispersity (D < 1.3). The initiator was simply synthesized through the reaction of a thiol ligand and trialkyl aluminum, with the thiol ligand choice enabling polymer end group control. Copolymerization of epichlorohydrin and propylene oxide and copolymerization of different epoxides with episulfide demonstrated the ability of this method to control polymer architecture. We further investigated the effect of catalyst concentration and initiator structure on the kinetics of epoxide polymerizations through ¹H NMR spectroscopy.

Finally, we combined our method of polymerization with another facile method, reversible addition fragmentation with chain transfer (RAFT) polymerization, to synthesize block-co-polymers made from vinyl and epoxide monomers. To do this, we made a macroinitiator from polystyrene (PS) and poly(methyl methacrylate) (PMMA), synthesized by RAFT polymerization, and further polymerized epoxide from it. Therefore, this new synthetic tool allows for the facile and controlled polymerization of epoxides into well-defined, functional, polyether materials. Furthermore, the introduced innovative and reliable methodology for the synthesis of SAI initiators enabled us to tune the polymer architecture to readily access more complex structure of polyepisulifides. We synthesized di-functional (d-H) and tetra-functional (tH) SAl initiators to produce ABA and star-(co)polymers consisting of propylene sulfide and PO or ECH. Finally, polyethylene glycol (PEG) was used as a macroinitiator to create PEG-*b*-PPS block copolymers and characterized by ¹H, ¹³C NMR spectroscopy, DOSY, DSC, and SEC.

Motivated by the result, we prepared the star shape cross linked membrane from t-H initiator. The composition was controlled through the monomer feed ratio of propylene oxide (PO) and epichlorohydrin (ECH) for synthesis of PPO-PECH membrane in the presence of poly(ethylene oxide)-diglycidyl ether as a cross linker and the most optimized PPO-PECH with the ratio of 90:10 resulted optically clear and flexible film. We further modified the membrane with a range of amines like trimethylamine (TEA), dimethylamine (DMA), triethylamine (TEA), and diethylamine (DEA) by membrane dipping method. The chemical, physical, and mechanical properties of resultant secondary amine grafted and quartenized membranes were characterized as a candidate for CO₂ transport.

Moreover, we designed the facilitated transport membranes of crosslinked ether-based PPO-PECH membranes with the range of hindered and unhindered primary amines using previously reported mono(µ-alkoxo)- bis(alkylaluminum) (MOB). The physical and chemical properties of the membranes investigated by FT-IR spectroscopy, DSC, TGA, and rheology. This method demonstrated a simple and robust strategy to prepare copolymers cross linked membranes containing amines for CO₂ transport. This enables us to compare the effect of different amines in the structure of facilitated transport membranes.

In this thesis research we seek to develop a SAl initiator as a platform that is both simple to use and can synthesize new polymeric materials. This methodology is simple and tunable to produce robust crosslinked membranes for molecular transport.

Copyright by NILOOFAR SAFAIE ASHTIANI 2022 To my parents, my husband, and my sister

ACKNOWLEDGMENTS

I had a great time with my advisor Prof. Ferrier It was impossible to complete my Ph. D. without him. He truly guided me not only in science but also in my life.

Also, I would like to thank all my committee members (Prof. Gary Blanchard, Prof. Ramani Narayan, and Prof. Shiwang Cheng) for their valuable inputs during my presentations. Furthermore, I would like to thank all my lab mates (Geetanjali Shukla, Shayylyn Crum, Gouree Kumbhar, Danielle DeJonge, and Mayson Wipple) for all their help and support on my research.

Also, I like to say special thanks to my family and friends for their constructive support and help throughout my life. Last but not least, I wanted to thank Mohammad wo stood by me in bad and good days of life during PhD.

TABLE OF CONTENTS

LIST OF	TABLES	X
LIST OF	FIGURES	xi
LIST OF	SCHEMES	XXV
Chapter 1	. Introduction	1
1.1 Ba	ckground	1
BIBLIOG	RAPHY	. 10
Chapter 2	Aluminum-based Initiators from Thiols for Epoxide Polymerization	. 15
2.1 Int	roduction	15
2.2 EX	Characterization	/ 1
2.2.1	Synthesis of trimethylaluminum and triathylamina adduct (NA1) ²⁶	10
2.2.2	General procedure for synthesis of initiators	10
2.2.3	General procedure for synthesis and purification of polymers	20
2.2.4	Procedure for synthesis and reactivity ratio measurement of P(PO-orad-ECH)	20
2.2.6	General procedure for synthesis of P(PO-b-ECH)	
2.2.7	Polymerization procedure for synthesis of P(MMA-b-ECH)	23
2.2.8	Detailed purification procedure for synthesized polymers	25
2.2.9	Kinetic study for different concentrations of NAI by ¹ H NMR spectroscopy at	
specifie	d time points	25
2.2.10	Kinetic study for different initiators by ¹ H NMR spectroscopy specified time	25
2.2.11	Polymerization procedure for synthesis of poly(styrene-block-epichlorohydrin))
(P(styer	me-b-ECH))	26
2.3 Re	sults and discussion	27
2.4 Su	pporting information	44
BIBLIOG	RAPHY	81
Chapter 3	. Investigation of Aluminum-based initiators for Propylene Sulfide	
(Co)Polyme	rization with Compositional and Architectural Control	. 87
3.1 Int	roduction	87
3.2 Ex	perimental section	89
3.2.1	Materials	89
3.2.2		90
3.2.3	Synthesis of trimethylaluminum and triethylamine Adduct (NAI)	91
5.2.4 (h =	Synthesis of (Benzylthio)dimethylaluminum (BhSAlWe2),	
(benzyl	(Directly) and dimethyl(propylthio)aluminum	02
(FISAI) 3 2 5	Synthesis of di-functional initiator (d-H)	ے لار 02
3.2.5	Synthesis of tetra-functional initiator (t-H)	<u>۲</u> و
5.2.0		

3.2.7	Procedure for synthesis of poly(propylene sulfide) and its purification using	
BnsAll	Me ₂ or BnOAlMe ₂	93
3.2.8	Procedure for one-pot synthesis of poly(ECH-stat-PS) using	
BnSAL	Me ₂ as an initiator	94
3.2.9	Procedure for one-pot synthesis of poly(PO-stat-PS) using	0.5
BnSAL	Me ₂ as an initiator	95
3.2.10	Procedure for synthesis of poly(ECH-b-PS) using BnSAlMe ₂ as an initiator.	95
3.2.11	Procedure for synthesis of poly(PO-b-PS) using BnSAlMe ₂ as an initiator	96
3.2.12	Procedure for synthesis of poly(PS-b-PO) by d-H initiator	97
3.2.13	Procedure for synthesis of poly(PS-b-PO) by t-H initiator	98
3.2.14	Procedure for control experiments by kinetics Studies using ¹ H NMR	
spectro	scopy of BnSAlMe2 and NAl, only NAl, and only BnSAlMe2 or PS polymeriza	tion:
With o	nly BnSAlMe ₂	98
3.2.15	Procedure for Kinetics Studies by ¹ H NMR spectroscopy of d-H initiator and	t oo
PrSAIN	Ae ₂ for PS polymerization	99
3.2.16	Procedure for synthesis of poly(EG-b-PS)	99
3.3 R	esults and discussion	100
3.4 Si	ipporting information	116
BIBLIOC	ЭКАРНҮ	133
	A True stars Colored Free Courth and Mothed for Dree and the official stars	J
Chapter 4	4. I wo-steps Solvent Free Synthesis Method for Preparation of Star-snape	u 127
	traduction	I 37
4.1 III 4.2 E ₁	uoducuon	137
4.2 E2	Matoriala	139
4.2.1	Synthesis of Trimothylaluminum and Triothylamina Adduct (NIA1)	139
4.2.2	Synthesis of Tatra handed Initiator (t H)	140
4.2.3	Membrane Propagation	140
4.2.4	Functionalization of the Membranes	1/1
4.2.3	Functionalization of the Memoranes	1/1
4.2.0	Thermal Characterization	1/1
4.2.7	Water Untake and Swalling Datio	141
4.2.8	Pagister of Characterization	142
4.2.9	Resistance Characterization	142
4.2.10	Allealing stability	143
4.2.11	Alkaline stability	143
4.5 K	Synthesis and Characterization of Madified Cross linked Manhannes	143
4.3.1	Synthesis and Characterization of Modified Cross-linked Membranes	140
4.3.2	Structural characterization	14/
4.3.3	I nermal characterization	148
4.3.4	water uptake and swelling ratio	149
4.3.5		150
4.3.6	Kheology	151
4.4 Sı	ipporting information	153
DIT = = = = = = =		155

Chapter	5. Development and Characterization of Crosslinked Amine Modifi	ied
Membrane	es for CO ₂ separation and capture	
5.1 II	ntroduction	
5.2 E	Experimental section	
5.2.1	Material	
5.2.2	Synthesis of Bis(µ-oxo)alkylaluminum [(CH ₃) ₂ NCH ₂ CH ₂ (µ ₂ -	
O)Al(CH ₃) ₂ ·Al(CH ₃) ₃](MOB)	
5.2.3	Synthesis of crosslinked membranes	
5.2.4	Crosslinked membrane functionalization	
5.2.5	Structure Characterization	
5.2.6	Thermal Characterization	
5.2.7	Rheology Characterization	
5.3 R	Results and discussion	
5.3.1	Chemical properties	
5.3.2	Thermal and Rheological Properties	
5.4 S	upporting information	
BILBIO	GRAPHY	
Chapter	6. Conclusion and Future Work	

LIST OF TABLES

Table 2-1 Control experiment.	
Table 3-1 Polymerization and copolymerization char	acteristics102
Table 4-1 Characterization of t-H-Initiated Cross-link	ed Membranes145
Table 4-2 Characterization of amine modified t-H-Ini	tiated Cross-linked Membranes147
Table 5-1 Characterization of Amine Modified Cross	s-linked Membranes

LIST OF FIGURES

Figure 2-1 (top) Chemical reaction scheme for the synthesis of BnSAlMe ₂ . (bottom) Resultant chemical structure of the asymmetric structure determined by X-Ray crystallography. Thermal ellipsoids are shown at 50% probability level
Figure 2-2 Plot of normalized ECH concentration over time with BnSAlMe ₂ initiator and NAl catalyst. Monomer concentration was monitored via ¹ H NMR spectroscopy. The full conversion was achieved in <i>ca</i> . 10 hours with the combined catalyst and initiator system, with $k_{obs} = 7.38 \times 10^{-5} \pm 5.41 \times 10^{-6} \text{ s}^{-1}$, whereas no conversion is present with just catalyst and slow conversion is present with just BnSAlMe ₂ as initiator. The inset is a plot of the k_{obs} as a function of equivalents of NAl catalyst to BnSAlMe ₂ initiator, where a linear relationship was observed.
Figure 2-3 Plot of M_n (left axis, blue circles) and D (right axis, red triangles) as a function of ECH to initiator BnSAlMe ₂ ratio ([ECH]/[BnSAlMe ₂]). M_n increased linearly at increasing ratio of epichlorohydrin, while D remained consistently low ($D < 1.4$) suggesting a controlled chain growth polymerization of ECH
Figure 2-4 Resultant structure of cPenSAlMe ₂ (a) and ClBnSAlMe ₂ (b) formed from the reaction of cyclopentyl thiol and 4-chlorobenzenemethanethiol, respectively, with trimethyl aluminum determined by X-Ray crystallography. cPenSAlMe2 forms a dimer (shown) consisting of a four membered thio-aluminum ring while the ClBnSAlMe ₂ forms a chain of initiator units connected via dative bonds to aluminum and sulfur atoms of adjacent initiators, like BnSAlMe ₂ (<i>cf.</i> , Figure 1). Thermal ellipsoids are shown at 50% probability level.
Figure 2-5 ¹ H NMR Spectra of PECH initiated by PrSAlMe ₂ (a), cPenSAlMe ₂ (b), BnSAlMe ₂ (c), and ClBnSAlMe ₂ (d) in CD ₂ Cl ₂ (c, d) or CDCl ₃ (a, b). The peaks corresponding to the various end groups are clearly visible in each of the spectra and are marked with letters 'a' through 'c' and their chemical shift and multiplicity is consistent with expectations. Peaks marked with 'x' correspond to CD ₂ Cl ₂ and peaks marked with 'y' correspond to water impurity in CDCl ₃ . Intensity increased to accentuate peaks corresponding to end groups36
Figure 2-6 Plot of the $-\ln([ECH]/[ECH]_0)$ as a function of time for the polymerization of ECH with SAl initiators PrSAlMe ₂ (red squares), BnSAlMe ₂ (blue circles), ClBnSAlMe ₂ (purple triangles), and cPenSAlMe ₂ (green diamonds). Monomer conversion was monitored via ¹ H NMR spectroscopy for 2.5 hours by taking aliquots from the reaction vessel and an observed rate constant (k _{obs}) was determined to be $k_{obs} = (3.83 \pm 0.15) \times 10^{-4} \text{ s}^{-1}$ (PrSAlMe ₂), $(1.86 \pm 0.08) \times 10^{-4} \text{ s}^{-1}$ (BnSAlMe ₂), $(1.34 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$ (ClBnSAlMe ₂), and $(0.21 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$ (cPenSAlMe ₂)
Figure 2-7 ¹ H and ¹³ C NMR spectra and labeled chemical structures for PECH-grad-PPO (a and

b, respectively) and PECH-*b*-PPO (c and d, respectively) in CDCl₃. The ¹³C NMR spectrum

of the PECH-grad-PPO (b) reveals additional cross-peaks compared with PECH-b-PPO (d).
Figure 2-8 PMMA-block-PECH synthetic route
Figure 2-9 SEC traces (RI) of RAFT synthesized PMMA (right, red curve) and P(MMA- <i>b</i> -ECH) (left, blue curve). The M _n and Đ was determined to be 6.3 kg/mol and 1.13 (PMMA) and 18.4 kg/mol and 1.05 (P(MMA- <i>b</i> -ECH))
Figure 2-10. ¹ H NMR spectra in CDCl ₃ of RAFT synthesized PMMA (c), thiol-end terminated PMMA (b), and P(MMA- <i>b</i> -ECH) (a). The peak associated with the benzyl end group from the RAFT agent (<i>cf.</i> , c) disappears after the aminolysis step (<i>cf.</i> , b), which reveals a free thiol
Figure 2-11 ¹ H NMR spectroscopy of BnSAlMe ₂ . ¹ H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.21 (m, 5H, PhCH ₂ S-Al(CH ₃) ₂), 3.91 (s, 2H, PhCH ₂ S-Al(CH ₃) ₂), -0.43 (s, 6H, PhCH ₂ S-Al(CH ₃) ₂)
Figure 2-12 ¹³ C NMR spectrum of BnSAlMe ₂ . ¹³ C NMR(126 MHz, CD ₂ Cl ₂) δ 141.46, 128.56, 127.97, 126.89 PhCH ₂ S-Al(CH ₃) ₂ , 32.00 PhCH ₂ S-Al(CH ₃) ₂ , 28.78 PhCH ₂ S-Al(CH ₃) ₂ 45
Figure 2-13 Carbon labeling scheme for BnSAlMe ₂ . There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1 for BnSAlMe ₂
Figure 2-14 The Unit structure of dimethyl aluminum bound to benzyl thiolate, consistent with trimethyl aluminum reacting with the benzyl mercaptan. This unit, we propose, defines our initiator for epoxide polymerizations. The entire crystal structure reveals these individual units to be datively bound to adjacent units in a linear chain
Figure 2-15 Plot of the $-\ln([ECH]/[ECH]0)$ over time for the polymerization of ECH with BnSAI and 1 eq of NAI showing a linear slope consistent with a living polymerization. $r^2 = 0.9646$
Figure 2-16 ¹ H NMR spectroscopy for ECH polymerizations with just NAl after 7 days which shows no conversion to PECH. ¹ H NMR (500 MHz, Chloroform-d) δ 3.62 – 3.50 (m, 2H, ECH OCH ₂ CH(CH ₂ Cl)), 3.22 (dddd, 1H, ECH OCH ₂ CH(CH ₂ Cl)), 2.88 (ddd, 1H, ECH OCH ₂ CH(CH ₂ Cl)), 2.67 (dd, 1H, ECH OCH ₂ CH(CH ₂ Cl))
 Figure 2-17 ¹H NMR spectroscopy for ECH polymerizations with just BnSAlMe₂ after 7 days which shows slow conversion (ca. 10% after 7 day). ¹H NMR (500 MHz, Chloroform-d) δ 3.77- 3.49 (bm, PECH, -OCH₂CH(CH₂Cl)O-), 3.62 – 3.49 (m, 2H, ECH OCH₂CH(CH₂Cl)), 3.22 (ddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.88 (ddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.67 (dd, 1H, ECH OCH₂CH(CH₂Cl))
Figure 2-18 ¹ H NMR spectroscopy for ECH polymerizations with benzyl mercaptan (ligand) and NAl after 7 days which shows no conversion to PECH. ¹ H NMR (500 MHz, Chloroform- d3.62 – 3.50 (m, 2H, ECH OCH ₂ CH(CH ₂ Cl)), 3.22 (dddd, 1H, ECH OCH ₂ CH(CH ₂ Cl)), 2.88 (ddd, 1H, ECH OCH ₂ CH(CH ₂ Cl)), 2.67 (dd, 1H, ECH OCH ₂ CH(CH ₂ Cl))

Figure 2-19 RI trace of targeted 30k PECH synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 30.7 with $D = 1.17$
Figure 2-20 DSC analysis of targeted 30k PECH with BnSAlMe2. The data from the second heating curve were collected which reveals one Tg at -26 °C
 Figure 2-21 ¹H NMR spectroscopy of 30K PECH treated with 1 M HCl in MeOH. This is magnified ¹H NMR to verify benzyl signal loss. ¹H NMR (500 MHz, Chloroform-d) δ 3.83-3.39 (bm, -OCH₂CH(CH₂Cl)O-)
Figure 2-22 Plot of normalized ECH concentration over time with BnSAlMe ₂ initiator and 0.25 eq. of NAl catalyst. Monomer concentration was monitored via ¹ H NMR spectroscopy and the rate of reaction calculated based on it ($k_{obs} = 5.06 \times 10^{-6} \pm 5.54 \times 10^{-7} \text{ s}^{-1}$). Sigmoidal shape of conversion curve for 0.25 eq. of NAl can be seen in this figure which is related to induction period. The k_{obs} is calculated using the data collected after the induction period, where conversion is first order in monomer
Figure 2-23 Plot of normalized ECH concentration over time with BnSAlMe ₂ initiator and 0.5 eq. of NAL catalyst. Monomer concentration was monitored via ¹ H NMR spectroscopy, and the rate of reaction calculated based on it ($k_{obs} = 2.34 \times 10^{-5} \pm 2.21 \times 10^{-6} \text{ s}^{-1}$). Sigmoidal shape of conversion curve for 0.5 eq. of NAl can be seen in this figure which is related to induction period. The k_{obs} is calculated using the data collected after the induction period, where conversion is first order in monomer
Figure 2-24 Plot of normalized ECH concentration over time with BnSAlMe ₂ initiator and 2 eq. of NAl. Monomer concentration was monitored via ¹ H NMR spectroscopy. Full conversion was achieved in <i>ca</i> . 10 hours with the combined catalyst and initiator system, with $k_{obs} = 1.91 \times 10^{-4} \pm 5.79 \times 10^{-6} s^{-1}$
Figure 2-25 Plot of the $-\ln([ECH]/[ECH]_0)$ over time for the polymerization of ECH with BnSAl and 2 equivalents of catalyst showing a linear slope consistent with a living polymerization. $r^2 = 0.96$
Figure 2-26 RI trace of targeted 15k PECH synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 17.7 with $D = 1.37$
Figure 2-27 RI trace of targeted 50k PECH synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 49.4 with $D = 1.28$
Figure 2-28 RI trace of targeted 70k PECH synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 75.7 with $D = 1.25$
Figure 2-29 RI trace of targeted 100k PECH synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 94.6 with $D = 1.28$
Figure 2-30 RI trace of targeted 30k PBO synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 23.6 with $D = 1.16$

Figure 2-31 RI trace of targeted 100k PBO synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 80.2 with $D = 1.02$
Figure 2-32 RI trace of targeted 30k PPO synthesized by PrSAlMe ₂ initiator. The M_n is determined to be 23.5 with $D = 1.17$
Figure 2-33 RI trace of targeted 30k PPO synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 38.9 with $D = 1.04$
Figure 2-34 RI trace of targeted 100k PPO synthesized by BnSAlMe ₂ initiator. The M_n is determined to be 80.1 with $D = 1.02$
Figure 2-35 DSC analysis of targeted 30k PPO with BnSAlMe ₂ . The data from the second heating curve were collected which reveals one T _g at -70 °C56
Figure 2-36 DSC analysis of targeted 30k PBO with BnSAlMe ₂ . The data from the second heating curve were collected which reveals one T _g at -73 °C57
Figure 2-37 ¹ H NMR spectroscopy of targeted 30K poly(allyl glycidyl ether) (PAGE) with BnSAlMe ₂ . ¹ H NMR (500 MHz, Chloroform-d) δ 5.88 (m, –O–CH ₂ –CH=CH ₂), 5.27-5.14 (doublet of doublets, –O–CH ₂ –CH=CH ₂), 3.98 (d, –O–CH ₂ –CH=CH ₂), 3.75-3.42 (bm, –O– CH ₂ –CH(CH ₂ –O–CH ₂ –CH=CH ₂)–O–).
Figure 2-38 ¹³ C NMR spectroscopy of targeted 30K poly(allyl glycidyl ether) (PAGE) with BnSAlMe ₂ . ¹³ C NMR (126 MHz, Chloroform-d) δ 134.93 (-O-CH ₂ -CH=CH ₂), 116.74 (- O-CH ₂ -CH=CH ₂), 78.89 (-O-CH ₂ -CH(CH ₂ -O-CH ₂ -CH=CH ₂)-O-), 72.26 (-O-CH ₂ - CH=CH ₂), 70.25-69.84 (-O-CH ₂ -CH(CH ₂ -O-CH ₂ -CH=CH ₂)-O-, m), 69.74 (-O-CH ₂ - CH(CH ₂ -O-CH ₂ -CH=CH ₂)-O-, rrm or mrr)
Figure 2-39 DSC analysis of Targeted 30k PAGE with compound BnSAlMe ₂ . The data from the second heating curve were collected which reveals one T_g at -76 °C
Figure 2-40 RI trace of targeted 30k PAGE synthesized with BnSAlMe ₂ . The M_n is determined to be 29.6 Kg/mol with $D = 1.45$. The first modal peak is due to aggregation of polymer in presence of Al trace
Figure 2-41 ¹ H NMR spectrum of PrSAlMe ₂ . ¹ H NMR (500 MHz, Chloroform-d) δ 2.62 (m, 2H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 1.65 (dq, 2H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 1.04-0.95 (m, 3H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), -0.49 (S, 6H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂)
Figure 2-42 ¹³ C NMR spectrum of PrSAlMe ₂ ¹³ C NMR (126 MHz, Chloroform-d) δ 30.33 CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂ , 25.97 CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂ , 13.15 CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂ , - 9.21 CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂
Figure 2-43 ¹ H NMR spectrum of cPenSAlMe ₂ . ¹ H NMR (500 MHz, Chloroform-d) δ 3.39 – 3.33 (m, 1H, cyclopentane -CH-), 2.10 – 1.99 (m, 2H, cyclopentane -CH ₂ -CH ₂ -), 1.83 – 1.73 (m, 2H, cyclopentane -CH ₂ -CH ₂ -), 1.62–1.53 (m, 4H, cyclopentane -CH ₂ -CH ₂ -), -0.49 (s, 6H, cyclopentane-S-Al(CH ₃) ₂)

Figure 2-44 ¹ H ¹³ C NMR spectrum of cPenSAlMe ₂ ¹³ C NMR (126 MHz, Chloroform-d) δ 30.33 (cyclopentane -CH-), 25.97 (cyclopentane -CH ₂ -CH ₂ -), 13.15 (cyclopentane -CH ₂ -CH ₂ -), - 9.21 (cyclopentane-S-Al(CH ₃) ₂)
Figure 2-45 ¹ H NMR spectrum of ClBnSAlMe ₂ . ¹ H NMR (500 MHz, Chloroform-d) δ 7.34 – 7.22 (m, 4H, (Cl)PhCH ₂ S-Al(CH ₃) ₂), 3.89 (s, 2H, (Cl)PhCH ₂ S-Al(CH ₃) ₂), -0.45 (s, 6H, (Cl)PhCH ₂ S-Al(CH ₃) ₂)
Figure 2-46 ¹³ C NMR spectrum of ClBnSAlMe ₂ . ¹³ C NMR (126 MHz, Chloroform-d) δ 127.50, 126.84 (Cl)PhCH ₂ S-Al(CH ₃) ₂ , 51.18 (Cl)PhCH ₂ S-Al(CH ₃) ₂ , 26.37 (Cl)PhCH ₂ S-Al(CH ₃) ₂ .
Figure 2-47 RI trace of targeted 30k PECH synthesized by $PrSAlMe_2$ initiator. The M_n is determined to be 30.2 with $D = 1.24$
Figure 2-48 RI trace of targeted 30k PECH synthesized by cPenSAlMe ₂ initiator. The M_n is determined to be 29.3 with $D = 1.25$
Figure 2-49 RI trace of targeted 30k PECH synthesized by ClBnSAlMe ₂ initiator. The M_n is determined to be 30.9 with $D = 1.28$
Figure 2-50 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The triply charged ion with m/z 1610.5194 [M+(NH ₄) ₃] ³⁺ corresponds to a neutral mass of 4777.4568 (1610.5194 * $3 - 3 * 18.0338$) which is consistent with a molecule containing 81 total propylene oxide units and a propylthiol end group (expected mass = 4777.426, 6.4 ppm mass error). The next abundant signal at m/z 1629.8662 corresponds to a neutral mass of 4835.4972, which is 58 Da heavier and represents one additional propylene oxide repeating unit
Figure 2-51 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The doubly charged ion with m/z 1386.0093 $[M+(NH_4)_2]^{2+}$ corresponds to a neutral mass of 2735.951 (1386.0093 * 2 – 2 * 18.0338) which is consistent with a molecule containing 45 total propylene oxide units and a BnS end group (expected mass = 2735.919, 11.7 ppm mass error). The next abundant signal at m/z 1415.0305 corresponds to a neutral mass of 2793.9934, which is 58 Da heavier and represents one additional propylene oxide repeating unit

Figure 2-52 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of

 Figure 2-59 600 MHz 2D DOSY NMR spectra obtained at 298 K in Chloroform-d solution of the PMMA-b-PECH. ¹H NMR (600 MHz, Chloroform-d) δ 3.99–3.62 (bm, - OCH₂CH(CH₂Cl)O-), 3.63-3.56 (bm,-CH₂C(CH₃)(COOCH₃)-), 2.19-1.66 (bm, - CH₂C(CH₃)(COOCH₃)-)
 Figure 2-60 ¹H NMR spectroscopy of thiol end-terminated PMMA without AlMe₃, in the presence of ECH and NAl, at 50°C after 7 days. 1H NMR (500 MHz, Chloroform-d) δ 3.52-3.48 (bm-CH₂-C(CH₃)(COOCH₃)-), 3.47–3.42 (d, J = 5.4 Hz, 2H, ECH, OCH₂CH(CH₂Cl)), 3.22 (tdd, J = 5.4, 3.9, 2.5 Hz, 1H, ECH, OCH₂CH(CH₂Cl)), 2.88 (dd, J = 4.8, 3.9 Hz, 1H, ECH, OCH₂CH(CH₂Cl)), 2.03-1.59 (bm,-CH₂-C(CH₃)(COOCH₃)-), 1.31-0.72 (bm -CH₂-C(CH₃)(COOCH₃)-). The only NAl peaks correspond to Me groups on Al below zero but Et groups are overlapping with other peaks and cannot be specified
Figure 2-61 DSC analysis of P(MMA-b-ECH). The data from the second heating curve were collected which reveals a broad T _g centered at 0 °C71
Figure 2-62 ¹³ C NMR spectroscopy of P(styrene- <i>b</i> -ECH) which is consistent with a regioregular PECH block. ¹³ C NMR (126 MHz, cdcl ₃) δ 145.21(-CH ₂ -CH(Ph, C)-) 128.00-127.11 (-CH ₂ -CH(Ph, CH)-), 125.68-125.25 (-CH ₂ -CH(Ph, CH)-), 78.97 (-O-CH ₂ -CH(CH ₂ Cl)-O-), 69.33(-O-CH ₂ -CH(CH ₂ Cl)-O-), 43.57 (-O-CH ₂ -CH(CH ₂ Cl)-O-), 44.46(-CH ₂ -CH(Ph)-), 40.21(-CH ₂ -CH(Ph)-) 29.59(-CH ₂ -Cl)
Figure 2-63 DSC analysis of P(styrene-b-ECH). The data from the second heating curve were collected which reveals two T _g , one at –27 °C corresponding to the PECH block and one at 74 °C corresponding to the PS block
 Figure 2-64 600 MHz 2D DOSY NMR spectra obtained at 298 K in Chloroform-d solution of the PS-b-PECH. ¹H NMR (600 MHz, Chloroform-d) δ 7.25- 6.30 (bm, -CH₂-CH(Ph)-), 3.77- 3.49 (broad m, -OCH₂CH(CH₂Cl)O-), 2.07-1.10 (bm, -CH₂-CH(Ph)-)73
Figure 2-65 ¹ H NMR spectroscopy of (P(styrene- <i>b</i> -ECH). ¹ H NMR (500 MHz, cdcl ₃) δ 7.25-6.30 (bm, -CH ₂ -CH(Ph)-), 3.77- 3.49 (bm, -OCH ₂ CH(CH ₂ Cl)O-), 2.07-1.10 (bm, -CH ₂ -CH(Ph)-)
Figure 2-66 ¹ H NMR spectroscopy of targeted 30K PECH with BnSAlMe ₂ initiator. ¹ H NMR (500 MHz, Chloroform-d) δ 3.83-3.39 (bm, -OCH ₂ CH(CH ₂ Cl)O-)
Figure 2-67 ¹³ C NMR spectroscopy of targeted 30K PECH with BnSAlMe ₂ . ¹³ C NMR (126 MHz, cdcl3) δ 79.18-79.09 (-O-CH ₂ -CH(CH ₂ -Cl)-O-), 69.80 (-O-CH ₂ -CH(CH ₂ -Cl)-O-m), 69.50 (-O-CH ₂ -CH(CH ₂ -Cl)-O- rrm or mrr)), 43.80 (-CH ₂ -Cl)
Figure 2-68 ¹ H NMR spectroscopy of targeted 30K PPO with BnSAlMe ₂ initiator. ¹ H NMR (500 MHz, Chloroform-d) δ 3.80 – 3.17 (bm, –O–CH ₂ –CH(CH ₃)–O–), 1.12 (m, -CH ₃)
Figure 2-69 ¹³ C NMR spectroscopy of targeted 30K PPO with BnSAlMe ₂ initiator. ¹³ C NMR

(126 MHz, cdcl₃) δ 75.89 (-O-CH₂-CH(CH₃)-O-, mm), 75.68 (-O-CH₂-CH(CH₃)-O-

, mr + rm), 75.48 (-O-CH ₂ -CH(CH ₃)-O-, rr), 73.71 (-O-CH ₂ -CH(CH ₃)-O-, m), 73.16 (- O-CH ₂ -CH(CH ₃)-O-, rrm or mrr), 17.81 (-CH ₃)
 Figure 2-70 ¹H NMR spectroscopy of targeted 30K PBO with BnSAlMe₂ initiator. ¹H NMR (500 MHz, Chloroform-d) δ 3.68 – 3.25 (bm, –O–CH₂–CH(CH₂–CH₃)–O–), 1.68 – 1.37 (m, CH₂–CH₃), 0.91 (t, –CH₂–CH₃)
Figure 2-71 ¹³ C NMR spectroscopy of targeted 30K PBO with BnSAlMe ₂ initiator. ¹³ C NMR (126 MHz, cdcl3) δ 80.84-80.42 (-O-CH ₂ -CH(CH ₂ -CH ₃)-O-), 72.37 (-O-CH ₂ -CH(CH ₂ -CH ₃)-O-, m), 71.53 (-O-CH ₂ -CH(CH ₂ -CH ₃)-O-, rrm or mrr)), 24.72 (-CH ₂ -CH ₃), 9.76 (-CH ₃).
Figure 2-72 ¹ H NMR spectroscopy of targeted 30K PECH with PrSAlMe ₂ initiator. ¹ H NMR (500 MHz, Methylene Chloride-d ₂) δ 3.80 – 3.51 (bm, -OCH ₂ CH(CH ₂ Cl)O-)
Figure 2-73 ¹ H NMR spectroscopy of targeted 30K PECH with ClBnSAlMe ₂ initiator. ¹ H NMR (500 MHz, Methylene Chloride-d ₂) δ 3.80 – 3.51 (bm, -OCH ₂ CH(CH ₂ Cl)O-)77
Figure 2-74 ¹ H NMR spectroscopy of targeted 30K PECH with cPenSAlMe ₂ initiator. ¹ H NMR (500 MHz, Methylene Chloride-d ₂) δ 3.80 – 3.51 (bm, -OCH ₂ CH(CH ₂ Cl)O-)78
Figure 2-75 ¹ H NMR spectroscopy of P(MMA- <i>b</i> -ECH). ¹ H NMR (500 MHz, Methylene Chloride-d ₂) δ 3.99–3.62 (bm, -OCH ₂ CH(CH ₂ Cl)O-), 3.63-3.56 (bm, -CH ₂ C(CH ₃)(COOCH ₃)-), 2.19-1.66 (bm, -CH ₂ C(CH ₃)(COOCH ₃)-), 1.67 – 0.58 (bm, -CH ₂ C(CH ₃)(COOCH ₃)-)
Figure 2-76 DSC analysis of P(PO-grad-ECH). The data from the second heating curve were collected which reveals one T _g , one at -41 °C
Figure 2-77 DSC analysis of P(ECH-b-PO). The data from the second heating curve were collected which reveals two T _g , one at -30 °C corresponding to the PECH block and one at -67 °C corresponding to the PO block
Figure 2-78 RI trace of targeted P(ECH-grad-PO). The M_n is determined to be 29.0 kg/mol with $D = 1.28$
Figure 2-79 RI trace of targeted P(ECH-b-PO). The M_n is determined to be 33.4 kg/mol with $D = 1.27$
Figure 3-1 a) Plot of M_n (left axis, blue circles) and D (right axis, red triangles) as a function of the PS to BnSAlMe ₂ ratio ([PS]/[BnSAlMe ₂]). M_n increased linearly at increasing ratio of propylene sulfide with $D < 1.4$. b) SEC traces for PPS with different targeted molecular weights. blue, for 15 kg/mol targeted PPS, the M_n is determined to be 14.8 kg/mol with D of 1.20. purple, for 30 kg/mol targeted PPS, the M_n is determined to be 33.7 kg/mol with D of 1.21. green, for 50 kg/mol targeted PPS, the M_n is determined to be 47.1 kg/mol with D of 1.32. pink, for 70 kg/mol targeted PPS, the M_n is determined to be 68.4 kg/mol with D of 1.35. red, for 100 kg/mol targeted PPS, the M_n is determined to be 98.2 kg/mol with D of 1.24

- Figure 3-4 DOSY NMR of statistical copolymers (a and b) and block copolymers (c and d). The DOSY spectra reveal that there is only one diffusing species for both the statistical and block copolymers, indicating that both monomers share a common backbone......108
- Figure 3-6 (top) Reaction scheme for the d-h or PrSAlMe₂ initiated polymerization of PS. (bottom) Plot of normalized PS concentration over time with PrSAlMe₂ initiator and NAl catalyst (red line) and plot of normalized PS concentration over time with d-H initiator and NAl catalyst (blue line). Monomer concentration was monitored via ¹H NMR spectroscopy, and the rate of reactions calculated. From the slope of the fit, the rate constant was calculated to be $k_{obs} = (7.11 \pm 0.59) \times 10^{-5} \text{ s}^{-1}$ (PrSAlMe₂) and (15.9 ± 0.86) × 10⁻⁵ s ⁻¹ (d-H). This experiment shows that the rate of polymerization is as twice as fast for d-H initiator in compare with PrSAlMe₂, proving that the initiation is happening from both heads of the initiator.
- Figure 3-7 DOSY NMR of (a) poly d-H (PS-b-PO) and (b) poly t-h (PS-b-PO). The results suggest both the epoxide and PS are in the same polymer chain......113
- Figure 3-8 a) Scheme for synthesis of PEG-*b*-PPS. b) DOSY NMR PEG-*b*-PPS c) SEC traces (LS) of PEG (right, blue curve) and PEG-*b*-PPS (left, red curve). The M_n and Đ were determined to be, respectively, 5.5 kg/mol and 1.24 (PEG) and 22.2 kg/mol and 1.18 PEG-*b*-PPS.

Figure 3-9 ¹ H NMR and ¹³ C NMR spectra of BnSPPS. a) ¹ H NMR (500 MHz, CDCl ₃) δ 2.91- 2.80 (m, -S-CH ₂ -CH(CH ₃)-S-), 2.65-2.58 (m, -S-CH ₂ -CH(CH ₃)-S-), 1.39 (m, -S-CH ₂ -CH(CH ₃)-S-). b) ¹³ C NMR (126 MHz, CDCl ₃) δ 41.14 (-S-CH ₂ -CH(CH ₃)-S), 38.18 (-S-CH ₂ -CH(CH ₃)-S), 20.63 (-S-CH ₂ -CH(CH ₃)-S-)
Figure 3-10 DSC analysis of targeted 30k PPS with BnSAlMe ₂ . The data from the second heating curve were collected which reveals one Tg at -41 °C116
Figure 3-11 EIS-MS characterization of the targeted 5kg/mol PPS117
Figure 3-12 DSC analysis of (a) poly(ECH- <i>stat</i> -PS) and (b) poly(PO- <i>stat</i> -PS). The data from the second heating curve were collected which reveals one Tg at -40 °C for poly(ECH- <i>stat</i> -PS) and one Tg at -46 °C for poly(PO- <i>stat</i> -PS)117
Figure 3-13 SEC traces of (a) poly(ECH- <i>stat</i> -PS) and (b) poly(PO- <i>stat</i> -PS). For poly(ECH-stat-PS), the M _n is determined to be 29.2 kg/mol with Đ of 1.56. And for or poly(PO-stat-PS), the M _n is determined to be 30.8 kg/mol with Đ of 1.21118
Figure 3-14 SEC traces of (a) P(ECH- <i>b</i> -PS) and (b) P(PO- <i>b</i> -PS). For poly(ECH- <i>b</i> -PS), the M _n is determined to be 29.9 kg/mol with Đ of 1.74. And for poly(PO- <i>b</i> -PS), the M _n is determined to be 29.6 kg/mol with Đ of 1.32118
Figure 3-15 DSC analysis of (a) poly(ECH- <i>b</i> -PS) and (b) poly(PO- <i>b</i> -PS). The data from the second heating curve were collected which reveals two Tg at -40 °C and -29 °C for PPS and PECH blocks, respectively. For poly(PO-b-PS) two T _g at -70 °C and -47 °C for PPO and PPS blocks, respectively
Figure 3-16 SAXS data for the synthesized copolymers. The block copolymer and statistical copolymer all have very weak phase separation as indicated by the broad shoulder peak at Q~0.02 Å - 1 .forpoly(ECH-b-S),Q~0.07 Å - 1 forpoly(PO-stat-PS),andQ~0.033 Å - 1 .for poly(PO-b-PS)
Figure 3-17 ¹ H NMR and ¹³ C NMR spectra of BnOPPS. a) ¹ H NMR (500 MHz, CDCl ₃) δ 2.91- 2.80 (m, -S-CH ₂ -CH(CH ₃)-S-), 2.65-2.58 (m, -S-CH ₂ -CH(CH ₃)-S-), 1.39 (m, -S-CH ₂ -CH(CH ₃)-S-). b) ¹³ C NMR (126 MHz, CDCl ₃) δ 41.14 (-S-CH ₂ -CH(CH ₃)-S), 38.18 (-S-CH ₂ -CH(CH ₃)-S), 20.63 (-S-CH ₂ -CH(CH ₃)-S-)
Figure 3-18 SEC trace of targeted 30k BnOPPS. the M _n is determined to be 31.6 kg/mol with Đ of 1.32
Figure 3-19 DSC trace of BnOPPS. The data from the second heating curve were collected which reveals one Tg at -42 °C
Figure 3-20 ¹ H NMR and ¹³ C NMR spectra of d-H initiator. (a) ¹ H NMR (500 MHz, CDCl ₃) δ 1.7-3.41 (b, ₂ (CH ₃)Al-CH ₂ CH ₂ CH ₂ S-Al(CH ₃) ₂ , 6H), -0.92-0.24 (b, ₂ (CH ₃)Al- CH ₂ CH ₂ CH ₂ S-Al(CH ₃) ₂ , 6H). Peaks at 0.88 and 1.26 in ¹ H NMR spectrum, are corresponded to hexane. (b) ¹³ C NMR (126 MHz, CDCl ₃) δ 29.65 ₂ (CH ₃)Al-CH ₂ CH ₂ CH ₂ S- Al(CH ₃) ₂ , 27.73 ₂ (CH ₃)Al-CH ₂ CH ₂ CH ₂ S-Al(CH ₃) ₂ , 11.31 ₂ (CH ₃)Al-CH ₂ CH ₂ CH ₂ S-

- Figure 3-23 SEC traces of (a) d-h PPS and (b) t-H PPS. For d-h PPS), the M_n is determined to be 34.5 kg/mol with Đ of 1.37. And for d-h PPS, the M_n is determined to be 88.7 kg/mol with Đ of 1.51.
- Figure 3-24 ¹H NMR and ¹³C NMR spectrum of d-H poly(PS-*b*-PO). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.72–3.2 (bm, –O–CH₂–CH(CH₃)–O–), 2.91-2.54 (bm, –S–CH₂–CH(CH₃)–S–), 1.31 (m, –S–CH₂–CH(CH₃)–S–), 1.11 (m, –O–CH₂–CH(CH₃)–O–). (b) ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (–O–CH₂–CH(CH₃)–O–), 73.35 (–O–CH₂–CH(CH₃)–O–), 40.6 (–S–CH₂–CH(CH₃)–S–), 37.9 (–S–CH₂–CH(CH₃)–S–), 20.98 (–S–CH₂–CH(CH₃)–S–), 16.83 (–O–CH₂–CH(CH₃)–O–). (124

- Figure 3-27 DSC analysis of (a) d-H poly(PS-*b*-PO) and (b) t-H poly(PS-*b*-PO). The data from the second heating curve were collected which reveals two T_gs at -66 °C and -45 for d-H poly(PS-*b*-PO) corresponded to PECH and PPS blocks. For t-H poly(PS-*b*-PO), DSC reveals two T_gs at -65 °C and -47 for d-H poly(PS-*b*-PO) corresponded to PECH and PPS blocks. 125

Figure 3-28 SAXS data for the synthesized copolymers. The phase behavior of the d-H poly(PS- $h = PO$) and t H poly(PS $h = PO$) are more obvious at $O_{2}(0.018 \text{ Å}) = 1$ and $O_{2}(0.022 \text{ Å}) = 1$
1
Figure 3-29 ¹ H NMR and ¹³ C NMR spectrum of PEG- <i>b</i> -PPS a) ¹ H NMR (500 MHz, CDCl ₃) δ 3.65-3.48 (b, -O-CH ₂ -CH ₂ -O-), 2.92-2.78 80 (m, -S-CH ₂ -CH(CH ₃)-S-), 2.66-2.59 (m, -S-CH ₂ -CH(CH ₃)-S-), 1.38 (m, -S-CH ₂ -CH(CH ₃)-S-). b) ¹³ C NMR (126 MHz, cdcl ₃) δ 70.55 (-O-CH ₂ -CH ₂ -O-), 41.26 (-S-CH ₂ -CH(CH ₃)-S-), 38.38 (-S-CH ₂ -CH(CH ₃)-S-), 20.79 (-S-CH ₂ -CH(CH ₃)-S-)126
Figure 3-30 DSC analysis of PEG- <i>b</i> -PPS. The data from the second heating curve were collected which reveals one T _g at -41 °C for PPS block and another T _m at 58 °C127
Figure 3-31 ¹ H NMR and ¹³ C NMR spectrum of BnSAlMe ₂ . a) ¹ H NMR (500 MHz, CDCl ₃) δ 7.38 – 7.21 (m, 5H, PhCH ₂ S-Al(CH ₃) ₂), 3.91 (s, 2H, PhCH ₂ S-Al(CH ₃) ₂), -0.43 (s, 6H, PhCH ₂ SAl(CH ₃) ₂). b) ¹³ C NMR (126 MHz, CDCl ₃) δ 141.46, 128.56, 127.97, 126.89 (PhCH ₂ S-Al(CH ₃) ₂ , 32.00 (PhCH ₂ S-Al(CH ₃) ₂), 28.78 (PhCH ₂ S-Al(CH ₃) ₂)
Figure 3-32 ¹ H NMR and ¹³ C NMR spectrum of PrSAlMe ₂ . a) ¹ H NMR (500 MHz, CDCl ₃) δ 2.62 (m, 2H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 1.65 (dq, 2H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 1.04-0.95 (m, 3H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), -0.49 (S, 6H, CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂). b) ¹³ C NMR (126 MHz, CDCl ₃) δ 30.33 (CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 25.97 (CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), 13.15 (CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂), -9.21 (CH ₃ CH ₂ CH ₂ S-Al(CH ₃) ₂)
Figure 3-33 1H NMR and 13C NMR spectra of poly(ECH-stat-PS). a) 1H NMR (500 MHz, CDC13) δ 3.80-3.29 (bm, -O-CH2-CH(CH2Cl)-O-), 3.16-2.51 (bm, -S-CH2-CH(CH3)-S-), 1.63-1.54 (m, -O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-), 1.37-1.17 O-CH2-CH(CH3)-S-), 1.40-1.33 (m, -S-CH2-CH(CH3)-S-), 1.37-1.17 O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-). b) 13C NMR (126 MHz, CDC13) 79.37(-O-CH2-CH(CH2Cl)-O-), 75.58 (-O-CH2-CH(CH2Cl)-O-), 44.72 (-O-CH2-CH(CH2Cl)-O-), 41.16 (-S-CH2-CH(CH3)-S-), 38.39 (-O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-), 20.63 (-S-CH2-CH(CH3)-S-), 20.85 (-O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-)
Figure 3-34 ¹ H NMR and ¹³ C NMR spectrum of poly(PO- <i>stat</i> -PS). (a) ¹ H NMR (500 MHz, $CDC1$) 5 2 82 2 24 (hm $\sim O$ CH $\sim CH(CH)$ O) 2 10 2 41 (hm $\sim S$ CH $\sim CH(CH)$ S

Figure 3-35 ¹H NMR and ¹³C NMR spectrum of poly(ECH-*b*-PS). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.77-3.55 (bm, -O-CH₂-CH(CH₂Cl)-O-), 2.91-2.80 (m,

$\begin{array}{l} -S-CH_2-CH(CH_3)-S-), 2.65-2.58 \ (m, -S-CH_2-CH(CH_3)-S-), 1.35 \ (m, -S-CH_2-CH(CH_3)-S-). \ (b) \ ^{13}C \ NMR \ (126 \ MHz, \ CDCl_3) \ \delta \ 78.97 \ (-O-CH_2-CH(CH_2Cl)-O-), \ 69.51 \ (-O-CH_2-CH(CH_2Cl)-O), \ 43.47 \ (-O-CH_2-CH(CH_2Cl)-O-), \ 41.17 \ (-S-CH_2-CH(CH_3)-S-), \ 38.24 \ (-S-CH_2-CH(CH_3)-S-), \ 20.86 \ (-S-CH_2-CH(CH_3)-S-). \ (129) \end{array}$
Figure 3-36 ¹ H NMR and ¹³ C NMR spectrum of poly(PO- <i>b</i> -PS). (a) ¹ H NMR (500 MHz, CDCl ₃) δ 3.72–3.2 (bm, –O–CH ₂ –CH(CH ₃)–O–), 2.91-2.54 (bm, –S–CH ₂ –CH(CH ₃)–S–), 1.31 (m, –S–CH ₂ –CH(CH ₃)–S–), 1.11 (m, –O–CH ₂ –CH(CH ₃)–O–). (b) ¹³ C NMR (126 MHz, CDCl ₃) δ 75.26 (–O–CH ₂ –CH(CH ₃)–O–), 73.35 (–O–CH ₂ –CH(CH ₃)–O–), 40.6 (–S–CH ₂ –CH(CH ₃)–S–), 37.9 (–S–CH ₂ –CH(CH ₃)–S–), 20.98 (–S–CH ₂ –CH(CH ₃)–S–), 16.83 (–O–CH ₂ –CH(CH ₃)–O–)
Figure 3-37 ¹ H NMR and ¹³ C NMR spectrum of d-H PPS. (a) ¹ H NMR (500 MHz, CDCl ₃) δ 2.91-2.80 (m, -S-CH ₂ -CH(CH ₃)-S-), 2.65-2.58 (m, -S-CH ₂ -CH(CH ₃)-S-), 1.39 (m, -S-CH ₂ -CH(CH ₃)-S-). (b) ¹³ C NMR (126 MHz, CDCl ₃) δ ¹³ C NMR (126 MHz, CDCl ₃) δ 41.14 (-S-CH ₂ -CH(CH ₃)-S), 38.18 (-S-CH ₂ -CH(CH ₃)-S), 20.63 (-S-CH ₂ -CH(CH ₃)-S-). (130
Figure 3-38 ¹ H NMR and ¹³ C NMR spectrum of t-H PPS. (a) ¹ H NMR (500 MHz, CDCl ₃) δ 2.91-2.80 (m, -S-CH ₂ -CH(CH ₃)-S-), 2.65-2.58 (m, -S-CH ₂ -CH(CH ₃)-S-), 1.39 (m, -S-CH ₂ -CH(CH ₃)-S-). (b) ¹³ C NMR (126 MHz, CDCl ₃) δ ¹³ C NMR (126 MHz, CDCl ₃) δ 41.14 (-S-CH ₂ -CH(CH ₃)-S), 38.18 (-S-CH ₂ -CH(CH ₃)-S), 20.63 (-S-CH ₂ -CH(CH ₃)-S-). (131
Figure 3-39 DSC analysis of (a) d-H PPS and (b) t-H PPS. The data from the second heating curve were collected which reveals one T _g at -41 °C for both these
Figure 3-40 ¹ H NMR and ¹³ C NMR spectrum of BnOAlMe ₂ . a) ¹ H NMR (500 MHz, CDCl ₃) δ 7.47 – 7.38 (m, 5H, PhCH ₂ O-Al(CH ₃) ₂), 3.33 (s, 2H, PhCH ₂ O-Al(CH ₃) ₂), 0.15 - 0.6 (s, 6H, PhCH ₂ OAl(CH ₃) ₂). b) ¹³ C NMR (126 MHz, CDCl ₃) δ138.64, 137.57, 130.04, 126.69 (PhCH ₂ O-Al(CH ₃) ₂ , 50.76 (PhCH ₂ O-Al(CH ₃) ₂), -7.71 (PhCH ₂ O-Al(CH ₃) ₂)132
Figure 4-1 FTIR spectrum of PPO-PECH (yellow color), PPO-PECH-TEA (green color), PPO- PECH-DEA (red color), PPO-PECH-TMA (blue color), and PPO-PECH-DMA (purple color). The C-N characteristic starching frequency of amin modified membranes are represented by a vertical line that is not presented in the pristine membrane
Figure 4-2 DSC measurements (a) and TGA characterization of (b) PPO-PECH (yellow color), and amine modified membranes PPO-PECH-TEA (green color), PPO-PECH-DEA (red color), PPO-PECH-TMA (blue color), and PPO-PECH-DMA (purple color)150
Figure 4-3 conductivity measurement of PPO-PECH and amine modified membranes PPO- PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA
Figure 4-4 rheology measurements of PPO-PECH and amine tethered membranes PPO-PECH- TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA152

Figure 4-5 ¹ H NMR and ¹³ C NMR spectra of t-H initiator. a) ¹ H NMR (500 MHz, CDCl ₃) δ 4.21-1.42 (24 H, -[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), -0.36 to -1.09 (24 H, -[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), b) ¹³ C NMR (126 MHz, CDCl ₃) 198.53 -[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), 42.42-[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), 31.61-[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), 29.61, -[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), 25.10 -[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -), 9.81-[C-CH ₂ COOCH ₂ CH ₂ S-Al(CH ₃) ₂] ₄ -). Peaks at 14.14, 22.35, and 31.87 in ¹³ C NMR spectra are corresponded to hexane. Broadening effects of the peaks are observed due to oligomerization in ¹ H NMR spectrum153
Figure 4-6 DSC measurement of star shape membrane with different ratios of PO:ECH ranging from 50:50 to 90:10
Figure 4-7 ¹ H NMR spectroscopy of the polymeric solution with the ratio of PPO-PECH with ratio of PO:ECH (90:10). All the corresponding peaks are assigned
Figure 4-8 water uptake and the swelling ratio of PPO-PECH and amine modified membranes PPO-PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA. Red circle is corresponded to water uptake (WU) and blue dimond is corresponded to welling ratio (SR)
Figure 5-1 FT-IR spectra of the copolymer membranes: pristine membrane PPO-PECH (red color) and amine modified membranes PPO-PECH-MeA (green color), PPO-PECH-nBuA (purple color), PPO-PECH-isoBuA (yellow line), and PPO-PECH-tBuA(wine color). Amine modified membranes are showing the characteristic peak of C-N at 1640 cm ⁻¹ (dashed line)
Figure 5-2 DSC measurements (a) and TGA characterization of (b) PPO-PECH (red color), and amine modified membranes PPO-PECH-MeA (green color), PPO-PECH-nBuA (purple color), PPO-PECH-isoBuA (yellow color), and PPO-PECH-tBuA(wine color)
Figure 5-3 the plateau modulus (G') of the cross-linked membranes (PPO-PECH) and amine modified membranes PPO-PECH-MeA, PPO-PECH-nBuA, PPO-PECH-isoBuA, and PPO-PECH-tBuA
Figure 5-4 ¹ H NMR and ¹³ C NMR spectroscopy of MOB. ¹ H NMR (CDCl ₃ , 500 MHz) δ: -0.95 ([(CH ₃) ₂ NCH ₂ CH ₂ (μ ₂ - O)Al(CH ₃) ₂ ·Al(CH ₃) ₂ ·Al(CH ₃) ₃], -0.74 3.46 ([(CH ₃) ₂ NCH ₂ CH ₂ (μ ₂ - O)Al(CH ₃) ₂ ·Al(CH ₃) ₃], 2.58 (s, CH ₃ -N-), 2.92 (t, -N-CH ₂ -CH ₂ -O-), 3.98 (t, -N-CH ₂ -CH ₂ -O-). ¹³ C NMR (CDCl ₃ , 100 MHz) δ: 45.2 ([(CH ₃) ₂ NCH ₂ CH ₂ (μ ₂ - O)Al(CH ₃) ₂ ·Al(CH ₃) ₃], 55.11 (CH ₃ -N-), 58.84 (-N-CH ₂ -CH ₂ -O-), 67.30 (-N-CH ₂ -CH ₂ -O-). ¹⁷ C
Figure 5-5 ¹ H NMR spectroscopy of the polymeric solution with the ratio of PPO-PECH with ratio of PO:ECH (80:20)

LIST OF SCHEMES

Scheme 1-2 a) Using SAl for episulfide polymerization and copolymerization. b) general scheme for synthesis of ABA terblcok and star shape copolymer
Scheme 1-3 chemical structure of star shape membrane7
Scheme 1-4 general of scheme of amine modified membranes
Scheme 2-1 SAl-initiated polymerization of ECH
Scheme 3-1 Data exclusion criteria with number of included and excluded subjects and measurement sets
Scheme 3-2 Statistical (a) and block (b) copolymerization of PS and epoxides
Scheme 3-3 BnOAlMe2 initiated PS polymerization110
Scheme 4-1 Synthesis of cross-linked polyether membrane using the star shape initiator (PPO- PECH)
Scheme 4-2 Synthesis of amine modified cross-linked PPO-PECH Membranes Using the t-H Initiator. Image of the representative cross-linked polyether membrane demonstrating optical transparency and flexibility is presented
Scheme 5-1 a) Synthesis of Amine Modified Cross-linked Polyether Membranes Using the MOE Initiator. b) Images of the representative cross-linked polyether membrane demonstrating optical transparency and flexibility

Chapter 1. Introduction

1.1 Background

Aluminum-containing polymerization platforms have been around for decades. Common industrial examples abound; For instance, the Vandenberg catalyst, produced in the 1960's, allowed for the industrial synthesis of high molecular weight polyether copolymers.¹⁻²¹ This catalyst was the result of a reaction of trialkylaluminum, water, and acetyl acetone. Prior to that, in the 1950's, the Ziegler-Natta catalyst, which revolutionized industrial polymer production from olefins, utilized a co-catalyst containing a trialkylaluminum component.^{22, 23} Both of these polymerization schemes are still in use today. Aluminum-based polymerization platforms have also been used to create polymers from other monomers (*e.g.*, anhydride,²⁴ lactone,^{25, 26} CO₂^{27, 28}). However, despite aluminum being a component in all of these polymerization schemes, there is no uniting chemistry or mechanism that forms a coherent polymerization platform to polymerize all of these monomers.

Lewis's acid-base pairs (LPs) have been increasingly utilized as catalysts for the polymerization of a diverse array of monomers. LPs consist of both a Lewis acid and base component that can be bound together as an adduct or exist separately as a frustrated LP.^{29, 30} There are a variety of Lewis acids and bases, but aluminum containing acids, such as methyl aluminum di(2,6-di-tert-butyl-4-methylphenoxy) (MAD), and nitrogen-containing bases, such as N-heterocyclic carbenes / olefins, are common.²⁹⁻³¹ LPs are attractive as catalysts for polymerizations because they are easy to synthesize, highly tunable, and can polymerize a wide variety of monomers controllably and to high molecular weight.^{29, 30, 32, 33} There are some restrictions however. LPs are most compatible with polar monomers,³⁰ although polymerization of nonpolar monomers has also been demonstrated.³⁴ LP copolymerizations of homologous sets

of monomers are common,^{11, 35} as well as alternating polymerizations of disparate monomers,^{36, 37} but few demonstrations of statistical copolymerizations of disparate monomers have been demonstrated. This is most likely due to the efficiency of LP polymerizations being strongly tied to the chemistry of the LP and the monomer.²⁹ Because of the strong catalyst chemistry-polymerization kinetics relationship, no single LP can polymerize all monomers efficiently or several disparate monomers simultaneously.

Both the polymer backbone and polymer pendant are important in controlling polymer properties. The polymer backbone is borne from the chemical "handle" that is used to polymerize the chosen monomer (*i.e.*, the vinyl group on styrene), while the polymer pendant comes from the monomer chemical substituents that persist after polymerization. However, most polymerization methods polymerize only a homologous set of monomers, that is monomers with different chemical substituents, but the same chemical "handle." The incorporation of different monomer types into a polymer is important both from a property standpoint³⁸ and from a sustainability standpoint.³⁹ For instance, copolymerizations of disparate monomers have led to degradable polymers,⁴⁰ sustainable polymers made from renewable feedstocks,⁴¹ and polymers with unique properties.⁴² Unfortunately, incorporation of disparate monomers into a growing polymer chain is non-trivial, but some recent examples highlight potential strategies. Work from Coates' group utilized two catalysts, each active for a different monomer, and a chain shuttling agent to incorporate epoxides and lactones into a growing polymer chain.⁴³ Rieger's group created terpolymers of an epoxide, CO₂, and butyrolactone, by using a single Zn catalyst that catalyzed each of the separate polymerization reactions, allowing them to control monomer sequence through CO₂ concentration.⁴² Lynd's group employed the aluminum-based Vandenberg catalyst to copolymerize epoxides and lactones.⁴⁰ While these works represent interesting steps

forward for disparate monomer copolymerization, they are still restricted by monomer choice and, in some cases, complex polymerization procedures.

A polymerization platform that can adroitly incorporate several disparate monomers in a facile way is necessary to realize the future of polymer science. This year is the 100th anniversary of Staudinger's landmark work describing the macromolecular theory of polymers. To mark this occasion, several recent editorials have outlined the future of polymer science for the next 100 years.^{2, 44} In these articles, the authors have invariably described the future of polymer science as being defined by *new, non-precious metal containing polymerization methods* that create *sustainable polymers* with *unique properties*. We would also argue that *ease of use* of these methods is vitally important. The broad uptake of an easy-to-use method like reversible addition fragmentation with chain transfer (RAFT) polymerization underscores this point.³ Therefore, the future of polymer science lies in a universal polymerization platform borne of abundant precursor materials that anyone can use. We believe that our recently described, aluminum-based polymerization platform achieves all of these goals.

A polymerization strategy that combines the versatility of LP catalysts and aluminumbased initiators can usher in the future of polymer science. Recently, Lynd and co-workers described a general polymerization platform for epoxides.^{44, 45} The platform utilized a simple LP catalyst consisting of an organoaluminum and organoamine adduct along with an aluminum alkoxide initiator. The initiator and the catalyst were simple to synthesize, and polymerizations were simple to execute, requiring mild temperatures and no solvent. The initiator behaved like a traditional anionic initiator while the catalyst activated the monomers to add them more easily to the growing chain end. Both the catalyst and initiator were necessary for the polymerization to proceed. The result of the marriage of the LP catalyst and anionic initiator was a facile polymerization platform that allowed for the controlled polymerization of practically any

epoxide. Building on this, we found that by replacing the aluminum alkoxide initiator in Lynd's work with a thio-aluminum initiator (SAI) results in not only the same ability to polymerize epoxides, but also allows for the polymerization of other monomer types, including vinyls and thiiranes. Furthermore, we found that we could use this strategy to copolymerize epoxides and vinyls, which we do not believe has been demonstrated before. Our goal is that we can utilize our SAI initiators and LP catalysts, both based on abundant aluminum pre-cursors, as a facile universal polymerization platform. In this way, we can continue the storied legacy of aluminum-based polymerization platforms, dating from the time of Staudinger, through to the next century of polymer science.

As mentioned earlier, synthesis of polyethers using a previously reported anionic polymerization is facile and controlled, however, there is only few methods published in literature that targeting high molecular weight polyether to 100 kg/mol with end group control, especially for epoxides carrying a pendant group. Moreover, there is no methodology reported for copolymerization of epoxides and episulfides since the importance of this copolymer for drug delivery and biomedical application is well-known. As a result, introducing a new methodology for copolymerization is still essential. Furthermore, we investigated the application prospective of the introduced method to design a new strategy for synthesis of cross-linked membranes for CO₂ separation.

In the first study, we presented a new method for epoxide polymerizations utilizing, aluminum-based initiators, which leverage the chemical versatility of thiol compounds to control polymer end group. The homo- and co-polymerization of various epoxides, such as epichlorohydrin and propylene oxide, demonstrate the flexibility of the initiators. Polymer molecular weight was controlled up to 100 kg/mol for the epoxides studied while maintaining

relatively narrow dispersity ($\oplus < 1.4$). We further characterized the kinetics of epoxide polymerizations through ¹H NMR spectroscopy and studied how the initiator structure impacted the kinetics. Finally, we employed our initiators to polymerize from thiol-end functionalized poly(methyl methacrylate) (PMMA) synthesized through RAFT polymerization, which allows us to easily create block copolymers made from vinyl and epoxide monomers. Therefore, this new synthetic tool allows for the facile polymerization of epoxides into well-defined, functional, polyether materials.



Scheme 1-1 general method for (co)polymerization for different range of epoxides.

In the second experimental study, we examined the versatility of the mentioned method to produce propylene sulfide (PS) homopolymers up to 100 kg/mol and PS – epoxide statistical, block, ABA, and star copolymers using inexpensive and versatile thio-aluminum (SAI) based initiators. Homopolymerizations of PS with SAI initiators are living and controlled, with number averaged molecular weights (M_n) up to 100 kg/mol while maintaining narrow polydispersity (D < 1.4). Statistical and block-copolymers of PS and epichlorohydrin (ECH) or propylene oxide (PO) are synthesized and characterized by size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), ¹H and ¹³C NMR spectroscopy, diffusion ordered spectroscopy (DOSY), and small angle X-ray scattering (SAXS). This work represents the first statistical copolymerization of PS and epoxides with similar reactivity ratios, allowing fine control over composition. Block-copolymers of PS and epoxides are synthesized by simple sequential addition, without intermediate preparative steps. Polymer architecture is controlled through modification of the initiator; we synthesized di-functional (d-H) and tetra-functional (t-H) SAI initiators to produce ABA tri-block and star-(co)polymers, respectively. Finally, polyethylene glycol (PEG) was used as a macroinitiator to create PEG-*b*-PPS block copolymers and characterized by ¹H, ¹³C NMR spectroscopy, DOSY, DSC, and SEC.



Scheme 1-2 a) Using SAl for episulfide polymerization and copolymerization. b) general scheme for synthesis of ABA terblcok and star shape copolymer

Third, we further expanded upon application of the introduced method to target synthesis of ion exchange membranes. We used the star shape composition of initiator to present a one-pot and solvent free platform for synthesis of architecturally controlled star shape polyether-based membrane. Tuning the monomer feed ratio of propylene oxide (PO) and epichlorohydrin (ECH) for synthesis of poly(propylene oxide-stat-epichlorohydrin (PPO-PECH) in the presence of poly(ethylene oxide)-diglycidyl ether as a cross linker evolute a 3-D structure of membrane. The copolymerizations produced optically clear, flexible films in all cases with different PO:ECH ratios. To provide compositional control of the chemical properties of the prepared films we explored their structure-property relationships within the context of monomer ratio. The optimized PPO-PECH with ratio of 90:10 further modified with a range of amines like trimethylamine (TEA), dimethylamine (DMA), triethylamine (TEA), and diethylamine (DEA) by membrane dipping method. The chemical, physical and mechanical properties of resultant secondary amine grafted and gaurtenized membranes were characterized. PPO-PECH-TMA shows higher conductivity, higher water uptake, swelling ratio, and alkaline stability in compare with pristine and the other modified membranes due to higher basicity of TMA in the structure of the membrane. This membrane will be characterized for CO_2/CH_4 selectivity and permeability to compare the effect of different amines in the membrane structure.



Scheme 1-3 chemical structure of star shape membrane.

Finally, we used previously reported Bis(µ-oxo)alkylaluminum (BOD) to synthesis crosslinked poly (propylene oxide-*stat*-epichlorohydrin) (PPO-PECH) membranes utilizing bifunctional, poly(ethylene glycol) diglycidyl ether as a cross linking agent. This enables us to

compare the efficiency different membrane structure, including star shape and linear membranes for CO₂ transport. In this study, was post modified with the range of unhindered to hindered primary amine *via* dipping method. In this study, we also can compare the effect of amine groups with the previous membrane having quartenized and tertiary amines. The chemical structure and physical properties of the membranes were characterized by FT-IR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheometer. Theses membranes are candidates for CO₂ separation and capture due to favorable interaction of C-O bond in the backbone with CO₂ and presence of grafted amine for facilitation of CO₂ transport.



Scheme 1-4 general of scheme of amine modified membranes.

In the following chapters we are describing a novel, aluminum-based polymerization platform for epoxide monomers as well as episulfide to synthesis homo and copolymers of these monomers. The polymerization platform consists of a thio-aluminum (SAI) initiatior and organoamine-organoaluminum adduct (NAI) catalyst platform which allows for the controlled, living polymerization of epoxide monomers. We further expanded the architecture of SAI to synthesize star shape initiator which utilized further to prepare crosslinked amine grafted polyether-based membrane for CO_2 transport. And finally, we designed robust, flexible, and optically transparent facilitated transport membranes that are tethered with hindered and unhindered primary amines for CO_2 capture and separation. BIBLIOGRAPHY

BIBLIOGRAPHY

(1) Staudinger, H. Über Polymerisation. *Berichte der deutschen chemischen Gesellschaft (A and B Series)* **1920,** 53 (6), 1073-1085.

(2) Hartmann, L.; Staffilani, M.; Unterlass, M. M. Polymers for the Future. *Macromol. Chem. Phys.* **2020**, 221 (7), 2000077.

(3) Perrier, S. 50th Anniversary Perspective: RAFT Polymerization—A User Guide. *Macromolecules* **2017**, 50 (19), 7433-7447.

(4) Imbrogno, J.; Ferrier, R. C.; Wheatle, B. K.; Rose, M. J.; Lynd, N. A. Decoupling Catalysis and Chain-Growth Functions of Mono(μ-alkoxo)bis(alkylaluminums) in Epoxide Polymerization: Emergence of the N–Al Adduct Catalyst. *ACS Catalysis* **2018**, 8 (9), 8796-8803.

(5) Parkatzidis, K.; Wang, H. S.; Truong, N. P.; Anastasaki, A. Recent Developments and Future Challenges in Controlled Radical Polymerization: A 2020 Update. *Chem* **2020**, 6 (7), 1575-1588.

(6) Jung, P.; Ziegler, A. D.; Blankenburg, J.; Frey, H. Glycidyl Tosylate: Polymerization of a "Non-Polymerizable" Monomer permits Universal Post-Functionalization of Polyethers. *Angew. Chem. Int. Ed.* **2019**, 58 (37), 12883-12886.

(7) Vandenberg, E. J. Organometallic catalysts for polymerizing monosubstituted epoxides. *Journal of Polymer Science* **1960**, 47 (149), 486-489.

(8) Carlotti, S.; Labbé, A.; Rejsek, V.; Doutaz, S.; Gervais, M.; Deffieux, A.
 Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin with
 Tetraoctylammonium Bromide–Triisobutylaluminum Initiating Systems. *Macromolecules* 2008, 41 (19), 7058-7062.

(9) Labbé, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum. *Macromolecules* **2007**, 40 (22), 7842-7847.

(10) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. Immortal polymerization: polymerization of epoxide and .beta.-lactone with aluminum porphyrin in the presence of protic compound. *Macromolecules* **1988**, 21 (5), 1195-1202.

(11) Wang, Q.; Zhao, W.; He, J.; Zhang, Y.; Chen, E. Y. X. Living Ring-Opening Polymerization of Lactones by N-Heterocyclic Olefin/Al(C6F5)3 Lewis Pairs: Structures of Intermediates, Kinetics, and Mechanism. *Macromolecules* **2017**, 50 (1), 123-136.
(12) Aida, T.; Ishikawa, M.; Inoue, S. Alternating copolymerization of carbon dioxide and epoxide catalyzed by the aluminum porphyrin-quaternary organic salt or -triphenylphosphine system. Synthesis of polycarbonate with well-controlled molecular weight. *Macromolecules* **1986**, 19 (1), 8-13.

(13) Whiteoak, C. J.; Kielland, N.; Laserna, V.; Escudero-Adán, E. C.; Martin, E.; Kleij, A. W. A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates. *JACS* **2013**, 135 (4), 1228-1231.

(14) Carlotti, S.; Ménoret, S.; Barabanova, A.; Desbois, P.; Deffieux, A. Effect of aluminum derivatives in the retarded styrene anionic polymerization. *Polymer* **2005**, 46 (18), 6836-6843.

(15) Jutemar, E. P.; Jannasch, P. Influence of the Polymer Backbone Structure on the Properties of Aromatic Ionomers with Pendant Sulfobenzoyl Side Chains for Use As Proton-Exchange Membranes. *ACS Applied Materials & Interfaces* **2010**, 2 (12), 3718-3725.

(16) Chochos, C. L.; Choulis, S. A. How the structural deviations on the backbone of conjugated polymers influence their optoelectronic properties and photovoltaic performance. *Prog. Polym. Sci.* **2011**, 36 (10), 1326-1414.

(17) Jiang, T.; Hall, A.; Eres, M.; Hemmatian, Z.; Qiao, B.; Zhou, Y.; Ruan, Z.; Couse, A. D.; Heller, W. T.; Huang, H.; de la Cruz, M. O.; Rolandi, M.; Xu, T. Single-chain heteropolymers transport protons selectively and rapidly. *Nature* **2020**, 577 (7789), 216-220.

(18) Vandenberg, E. J. High polymers from symmetrical disubstituted epoxides. *Journal of Polymer Science* **1960**, 47 (149), 489-491.

(19) Vandenberg, E. J. Epoxide polymers: Synthesis, stereochemistry, structure, and mechanism. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1969**, 7 (2), 525-567.

(20) Vandenberg, E. J. Some aspects of the bimetallic μ-oxo-alkoxides for polymerizing epoxides to polyether elastomers. *Journal of Polymer Science Part A: Polymer Chemistry* **1986**, 24 (7), 1423-1431.

(21) Ferrier, R. C.; Pakhira, S.; Palmon, S. E.; Rodriguez, C. G.; Goldfeld, D. J.; Iyiola, O. O.; Chwatko, M.; Mendoza-Cortes, J. L.; Lynd, N. A. Demystifying the Mechanism of Regio- and Isoselective Epoxide Polymerization Using the Vandenberg Catalyst. *Macromolecules* **2018**, 51 (5), 1777-1786.

(22) Natta, G. Une nouvelle classe de polymeres d'α-olefines ayant une régularité de structure exceptionnelle. *Journal of Polymer Science* **1955**, 16 (82), 143-154.

(23) Berger, M. N.; Grieveson, B. M. Kinetics of the polymerization of ethylene with a ziegler-natta catalyst. I. Principal kinetic features. *Die Makromolekulare Chemie* **1965**, 83 (1), 80-99.

(24) AIDA, T.; SANUKI, K.; INOUE, S. Well-controlled polymerization by metalloporphyrin. Synthesis of copolymer with alternating sequence and regulated molecular weight from cyclic acid anhydride and epoxide catalyzed by the system of aluminum porphyrin coupled with quaternary organic salt. *Macromolecules* **1985**, 18 (6), 1049-1055.

(25) Yasuda, T.; Aida, T.; Inoue, S. Synthesis of polyester-polyether block copolymer with controlled chain length from β -lactone and epoxide by aluminum porphyrin catalyst. *Macromolecules* **1984**, 17 (11), 2217-2222.

(26) Endo, M.; Aida, T.; Inoue, S. Immortal polymerization of .epsilon.-caprolactone initiated by aluminum porphyrin in the presence of alcohol. *Macromolecules* **1987**, 20 (12), 2982-2988.

(27) Wang, Y.; Zhao, Y.; Ye, Y.; Peng, H.; Zhou, X.; Xie, X.; Wang, X.; Wang, F. A One-Step Route to CO2-Based Block Copolymers by Simultaneous ROCOP of CO2/Epoxides and RAFT Polymerization of Vinyl Monomers. *Angewandte Chemie International Edition* **2018**, 57 (14), 3593-3597.

(28) Cao, H.; Qin, Y.; Zhuo, C.; Wang, X.; Wang, F. Homogeneous Metallic Oligomer Catalyst with Multisite Intramolecular Cooperativity for the Synthesis of CO2-Based Polymers. *ACS Catalysis* **2019**, 9 (9), 8669-8676.

(29) McGraw, M. L.; Chen, E. Y. X. Lewis Pair Polymerization: Perspective on a Ten-Year Journey. *Macromolecules* **2020**, 8 (9) 3321-3325.

(30) Hong, M.; Chen, J.; Chen, E. Y. X. Polymerization of Polar Monomers Mediated by Main-Group Lewis Acid–Base Pairs. *Chemical Reviews* **2018**, 118 (20), 10551-10616.

(31) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. Synthetic Routes to N-Heterocyclic Carbene Precursors. *Chem. Rev.* **2011**, 111 (4), 2705-2733.

(32) Walther, P.; Krauß, A.; Naumann, S. Lewis Pair Polymerization of Epoxides via
Zwitterionic Species as a Route to High-Molar-Mass Polyethers. *Angew. Chem. Int. Ed.* 2019, 58
(31), 10737-10741.

(33) McGraw, M.; Chen, E. Y. X. Catalytic Lewis Pair Polymerization of Renewable Methyl Crotonate to High-Molecular-Weight Polymers. *ACS Catalysis* **2018**, 8 (10), 9877-9887.

(34) Sajid, M.; Stute, A.; Cardenas, A. J. P.; Culotta, B. J.; Hepperle, J. A. M.; Warren, T. H.; Schirmer, B.; Grimme, S.; Studer, A.; Daniliuc, C. G.; Fröhlich, R.; Petersen, J. L.; Kehr, G.; Erker, G. N,N-Addition of Frustrated Lewis Pairs to Nitric Oxide: An Easy Entry to a Unique Family of Aminoxyl Radicals. *JACS* **2012**, 134 (24), 10156-10168.

(35) Chen, Y.; Shen, J.; Liu, S.; Zhao, J.; Wang, Y.; Zhang, G. High Efficiency Organic Lewis Pair Catalyst for Ring-Opening Polymerization of Epoxides with Chemoselectivity. *Macromolecules* **2018**, 51 (20), 8286-8297.

(36) Ji, H.-Y.; Wang, B.; Pan, L.; Li, Y.-S. Lewis pairs for ring-opening alternating copolymerization of cyclic anhydrides and epoxides. *Green Chemistry* **2018**, 20 (3), 641-648.

(37) Yang, J.-L.; Wu, H.-L.; Li, Y.; Zhang, X.-H.; Darensbourg, D. J. Perfectly Alternating and Regioselective Copolymerization of Carbonyl Sulfide and Epoxides by Metal-Free Lewis Pairs. *Angew. Chem. Int. Ed.* **2017**, 56 (21), 5774-5779.

(38) Wang, H.; Wu, X.; Yang, Y.; Nishiura, M.; Hou, Z. Co-syndiospecific Alternating Copolymerization of Functionalized Propylenes and Styrene by Rare-Earth Catalysts. *Angew. Chem. Int. Ed.* **2020**, 59 (18), 7173-7177.

(39) Poland, S. J.; Darensbourg, D. J. A quest for polycarbonates provided via sustainable epoxide/CO2 copolymerization processes. *Green Chemistry* **2017**, 19 (21), 4990-5011.

(40) Chwatko, M.; Lynd, N. A. Statistical Copolymerization of Epoxides and Lactones to High Molecular Weight. *Macromolecules* **2017**, 50 (7), 2714-2723.

(41) Wang, Y.; Li, A.-L.; Liang, H.; Lu, J. Reversible addition–fragmentation chain transfer radical copolymerization of β -pinene and methyl acrylate. *Eur. Polym. J.* **2006**, 42 (10), 2695-2702.

(42) Kernbichl, S.; Reiter, M.; Mock, J.; Rieger, B. Terpolymerization of β -Butyrolactone, Epoxides, and CO2: Chemoselective CO2-Switch and Its Impact on Kinetics and Material Properties. *Macromolecules* **2019**, 52 (21), 8476-8483.

(43) Clayman, N. E.; Morris, L. S.; LaPointe, A. M.; Keresztes, I.; Waymouth, R. M.; Coates, G. W. Dual catalysis for the copolymerisation of epoxides and lactones. *Chem. Commun.* **2019**, 55 (48), 6914-6917.

(44) Abd-El-Aziz, A. S.; Antonietti, M.; Barner-Kowollik, C.; Binder, W. H.; Böker, A.;
Boyer, C.; Buchmeiser, M. R.; Cheng, S. Z. D.; D'Agosto, F.; Floudas, G.; Frey, H.; Galli, G.;
Genzer, J.; Hartmann, L.; Hoogenboom, R.; Ishizone, T.; Kaplan, D. L.; Leclerc, M.; Lendlein,
A.; Liu, B.; Long, T. E.; Ludwigs, S.; Lutz, J.-F.; Matyjaszewski, K.; Meier, M. A. R.; Müllen,
K.; Müllner, M.; Rieger, B.; Russell, T. P.; Savin, D. A.; Schlüter, A. D.; Schubert, U. S.;
Seiffert, S.; Severing, K.; Soares, J. B. P.; Staffilani, M.; Sumerlin, B. S.; Sun, Y.; Tang, B. Z.;
Tang, C.; Théato, P.; Tirelli, N.; Tsui, O. K. C.; Unterlass, M. M.; Vana, P.; Voit, B.; Vyazovkin,
S.; Weder, C.; Wiesner, U.; Wong, W.-Y.; Wu, C.; Yagci, Y.; Yuan, J.; Zhang, G. The Next 100
Years of Polymer Science. *Macromol. Chem. Phys.* 9 (6), 2000216-2000222.

(45) Rodriguez, C. G.; Ferrier, R. C.; Helenic, A.; Lynd, N. A. Ring-Opening Polymerization of Epoxides: Facile Pathway to Functional Polyethers via a Versatile Organoaluminum Initiator. *Macromolecules* **2017**, 50 (8), 3121-3130.

Chapter 2. Aluminum-based Initiators from Thiols for Epoxide Polymerization

2.1 Introduction

Polyethers are important industrial polymers where they are used in the production polyurethanes,^{1, 2} and are found in common consumer products such as laxatives, eye drops, medicines, and lubricants as well as in the technological applications such as lithium ion batteries,³ separation membranes,^{4, 5} anti-fouling coatings^{6, 7}, and biomedical applications.⁸ The ubiquity and utility of polyether materials are the results of their functional monomer precursors, epoxides. Epoxides hold great promise as a polymeric materials platform due to their tunable functional group(s) and indiscriminate ring strain driving force for polymerization.9-11 Furthermore, epoxides are widely available, relatively inexpensive, and easy to synthesize making them prime candidates as a feedstock for polymeric materials.¹² However, in traditional anionic ring opening polymerization (AROP) schemes, various epoxide substitutions such as alkyls and halides can cause side reactions during polymerization, such as chain transfer to monomer, resulting in a loss of control, limited molecular weight, and/or no conversion at all.¹³ To address these shortcomings, numerous catalytic strategies have been reported for epoxide polymerizations. Catalytic methods can result in polymers and also copolymers^{14, 15} with high molecular weight,¹⁶ narrow dispersity,¹⁷⁻¹⁹ and controlled stereochemistry.²⁰⁻²³ However, the catalyst synthesis in these methods can be complex and/or use expensive starting materials making them less suitable for non-experts that may want to utilize polyether materials.

Recently developed mono(µ-alkoxo)bis(alkylaluminum) (MOB) compounds are tolerant to monomer functional group while still providing molecular weight control for epoxide polymerizations without any chain transfer reactions present.^{24, 25} Additionally, the MOB compounds are trivial to synthesize and use for epoxide polymerizations and therefore provide

access for non-experts to polyethers with tunable molecular weight, composition, and architecture.^{4, 24, 25} The MOB compounds can be split into two separate components that facilitate epoxide polymerization; one consisting of a polymerization catalyst portion (*e.g.*, Et₃NAlMe₃) and one consisting of a bis((µ-alkoxo)-dialkylaluminum) (BOD) initiator portion (*e.g.*, [Et₂Al(µ-OCH₂CH₂OMe)]₂).²⁶ The result of this split was that the polymer end group could be controlled using different initiator chemistries with a limited effect on polymerization kinetics. Previously, all MOB / BOD initiators were based on alcohol-containing ligands, which limits the potential ligand moieties.

Expanding the ligand system for aluminum-based initiators to include functional groups beyond alcohols can enhance the functionality of polyethers. Thiols are particularly attractive due to the vast library of thiol compounds available, allowing us to precisely tune polyether end group. Additionally, thiol-end terminated polymers are commercially available and easily synthesizable via post-modification of polymers obtained from techniques like reversible addition-fragmentation chain transfer polymerization (RAFT).²⁷ Thus, block copolymers of vinyls and epoxides can be readily synthesized through a combination of simple-to-use techniques. While thiol-containing compounds have been utilized in polymerizations either through specific 'click' interactions²⁸ or for ring-opening polymerizations of lactones,²⁹ they have not been applied to epoxide polymerizations.

In this work, we explore thiols as the ligand for aluminum-based initiators for epoxide polymerizations. Thio-aluminum initiators (SAls) can be easily synthesized from the reaction of a thiol containing ligand and trimethylaluminum. The kinetic and molecular weight control of epoxide polymerizations initiated by SAls was investigated by tuning catalyst concentration and monomer to initiator ratio and characterized by ¹H NMR spectroscopy and size exclusion

chromatography (SEC). Initiator chemistry was varied to investigate polymer end-group control as well as the effect on polymerization kinetics. Finally, polymer compositional control was examined via the copolymerization of two different monomers. Polyethers with controlled end group were produced from a diverse set of thiol-containing small molecules and polymers. Macroinitiators derived from RAFT produced polymers allowed for the facile synthesis of vinyl*b*-epoxide polymers without the need for hazardous reagents or complex synthetic procedures, providing access to these materials for non-chemists.

2.2 Experimental section

Trimethylaluminum solution (AlMe₃, Sigma-Aldrich, 2.0 M in hexane), triethylamine (TEA, Sigma-Aldrich, ≥99.5%), benzyl mercaptan (Sigma-Aldrich, 99%), 1-propane thiol (Sigma-Aldrich, 99%), cyclopentyl thiol (Sigma-Aldrich, 97%), 4-chlorobenzenemethanethiol (Sigma-Aldrich, 98%), 2-cyano-2-propyl benzodithioate (Sigma-Aldrich, >HPLC 97%), hexylamine (Sigma-Aldrich, 99%), 2,2'-azobisisobutyronitrile (Sigma-Aldrich, 98%), and sodium hydrogen sulfate (NaHSO₄, Sigma-Aldrich, technical grade), CDCl₃ (Cambridge Analytica), D₂dichloromethane (Cambridge Analytica) were used without any further purification. Hexanes (Sigma-Aldrich, anhydrous, >99%), tetrahydrofuran (THF, Sigma-Aldrich, anhydrous, >99.5%, inhibitor free) were used for experiments in the glove box. Methanol (MeOH, Fisher, Certified ACS), hexane (Fisher, Certified ACS) and dichloromethane (DCM, Fisher, Certified ACS) were used for washing polymers. Epichlorohydrin (ECH, Sigma-Aldrich, ≥99%), propylene oxide (PO, Sigma-Aldrich, GC, ≥99.5%), butylene oxide (BO, Sigam-Aldrich, 99%), and allyl glycidyl ether (AGE, Sigma-Aldrich, \geq 99%) were all used as received. Methyl methacrylate (MMA, contains \leq 30 ppm MEHQ as inhibitor, 99%) and styrene (contains 4-tert-butylcatechol as stabilizer, ≥99%) were filtered over activated basic alumina column to remove inhibitors. All air

and moisture sensitive reactions were prepared under a dry nitrogen atmosphere inside a glovebox.

2.2.1 Characterization

¹H NMR spectroscopy was performed on a 500 MHz Varian NMR spectrometer at room temperature and chemical shifts are reported in parts per million (ppm) and are referenced using the residual ¹H peak from the deuterated solvent. The structure of the compounds was determined by ¹³C NMR spectroscopy on a 126 MHz Varian NMR spectrometer. All diffusion ordered spectroscopy (DOSY) measurements were performed at 25° C on a Varian Inova 600 spectrometer operating at 599.72 MHz and equipped with a 5mm Z-gradient HCN inverse probe capable of producing gradients in the Z direction with strength of 63 G/cm. All DOSY measurements were run using the dbppste pulse sequence with 128-160 scans and 20 increments with gradient strengths from 2.7 to 59.22 G/cm. The relaxation delay was set to 3s, the diffusion delay to 24ms, and the gradient length to 2.0ms. Size exclusion chromatography (SEC) was carried out on the Malvern OMNISEC system with an isocratic pump, degasser, and temperature-controlled column oven held at 35 °C containing 2 Viscotek 300×8.0 mm columns (T3000 and T4000) with an exclusion limit of 400 kDa. Triple detection with light scattering, viscometer, and refractive index has been used for absolute molecular weight determination of polymers. Calibration was carried out using polystyrene standards (from scientific polymer) in THF. Differential scanning calorimetric (DSC) tests were conducted on a TA250 instrument with a heating rate of 10 °C min⁻¹ under a N₂ atmosphere, and the data from the second heating curve were collected. Samples were analyzed by electrospray ionization with mass spectrometry in positive ion mode using a Waters Xevo G2XS Q-Tof mass spectrometer interfaced with a Waters Acquity UPLC. 5 ul of a sample (diluted in 90% methanol containing 1mM ammonium formate)

were flow-injected (no UPLC column) using a mobile phase of 80% methanol and 20% 10 mM ammonium formate in water pumped at 0.2 ml/min. Data were acquired over an m/z range of 200-6000 in continuum mode. Single crystal X-ray diffraction XRD data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 173.0 K. Data were measured using ω and φ of 1 ° per frame for 10 s using CuK α radiation (sealed tube, 40.0 kV, 30.0 mA). The total number of runs and images was based on the strategy calculation from the program COSMO (BRUKER, V1.61, 2009). MALDI-TOF spectra were acquired using a Shimadzu Axima cfr+ operating in linear mode with a laser power setting of 50. The matrix used was alpha-cyanohydroxycinnamic acid (CHCA, 10 mg/ml in acetonitrile/water (50:50 v/v) containing 0.1% TFA).

2.2.2 Synthesis of trimethylaluminum and triethylamine adduct (NAl).²⁶

A reaction vial was charged with a stir bar, 6.35 mL anhydrous hexanes, and 2.0 M AlMe₃ in hexane (6.35 mL, 12.7 mmol) in a dry nitrogen glove box and cooled to -78 °C. Then, TEA (1.5 ml, 10.7 mmol) was added dropwise to the vial. The solution was set to stir and warm to room temperature overnight. To crystallize the desired product, the solution was then directly cooled to -40 °C and the resultant crystals were washed three times with anhydrous hexanes (3×5 ml) and dried *in vacuo*. ¹H NMR (500 MHz, CDCl₃) δ 2.80 (q, 6H), 1.18 (t, 9H), -0.89 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 47.78, 9.20.

2.2.3 General procedure for synthesis of initiators

A vial of anhydrous hexane (6.35 ml) and 2.0 M AlMe₃ in hexanes (6.35 mL, 12.7 mmol) equipped with a stir bar, cooled down to -78 °C in a cold well. At a desired temperature, a thiol ligand (12.7 mmol) was added dropwise. Then, the solution was stirred at 900 rpm for 24 hours while warming to room temperature. To remove unreacted AlMe₃ and purify the initiator, the

synthesized compound was washed three times with anhydrous hexanes $(3 \times 5 \text{ ml})$ and dried *in vacuo*.

(Benzylthio)dimethylaluminum (BnSAlMe₂)

¹H NMR (500 MHz, CD₂Cl₂) δ 9.43 – 8.98 (m, 5H), 5.88 (s, 2H), 1.51 (s, 6H). ¹³C NMR (126

MHz, CD₂Cl₂) δ 141.46, 128.56, 127.97, 126.89, 32.00, 28.78.

((4-Chlorobenzyl)thio)dimethylaluminum (ClBnSAlMe₂)

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.22 (m, 4H), 3.89 (s, 2H), -0.45 (s, 6H). ¹³C NMR (126

MHz, CDCl₃) δ 127.50, 126.84, 51.18, 26.37.

Dimethyl(propylthio)aluminum (PrSAlMe₂)

¹H NMR (500 MHz, CDCl₃) δ 2.63 (t, J = 7.3 Hz, 2H), 1.64 (m, 2H), 0.98 (t, J = 7.3 Hz, 3H), -

0.51 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 30.33, 25.97, 13.15, -9.21.

(Cyclopentylthio)dimethylaluminum (cPenSAlMe₂)

¹H NMR (500 MHz, CDCl₃) δ 2.62 (m, 2H), 1.65 (dq, 2H), 1.04-0.95 95 (m, 3H), -0.49 (S, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 42.65, 37.24, 24.51, -7.83.

2.2.4 General procedure for synthesis and purification of polymers

All polymerizations were performed neat in 20 ml septum-capped reaction vials and charged with a stir bar in the inert atmosphere. Initiator, NAl, and monomer were added to the vial. The solution was heated up to 50°C until completion of the polymerization. Reactions were quenched with methanol and dissolved in dichloromethane. Then, the resulting solution was added dropwise into acidic MeOH (0.01 M HCl in MeOH) to precipitate the desired polymer product. Then, it was washed 3 times with water to remove residual aluminum. After precipitation out of MeOH, the polymer was dried *in vacuo* overnight at 70 °C. M_n was determined by ¹H NMR spectroscopy by taking the ratio of the backbone proton signals to the integral of the end group signal on the initiator. Average molecular weights and dispersity (Đ) were determined by SEC with triple detection (refractive index, light scattering, and viscometry) with respect to polystyrene standards. All other polymerizations were performed under identical experimental conditions and characterized by ¹H NMR, ¹³C NMR spectroscopy, and SEC.

Poly(epichlorohydrin) (PECH)

¹H NMR (500 MHz, CDCl₃) δ 3.70 (bm, –O–C<u>H</u>₂–C<u>H</u>(C<u>H</u>₂Cl)–O–). ¹³C NMR (126 MHz, CDCl₃) δ 79.18-79.09 (–O–CH₂–<u>C</u>H(CH₂Cl)–O–), 69.80 (–O–<u>C</u>H₂–CH(CH₂Cl)–O– m), 69.50 (–O–<u>C</u>H₂–CH(CH₂Cl)–O– rrm or mrr), 43.80 (–CH₂–Cl).

Poly(propylene oxide) (PPO)

¹H NMR (500 MHz, CDCl₃) δ 3.80 – 3.17 (bm, –O–C<u>H</u>₂–C<u>H</u>(CH₃)–O–), 1.12 (m, -CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 75.89 (–O–CH₂–<u>C</u>H(CH₃)–O–, mm), 75.68 (–O–CH₂–<u>C</u>H(CH₃)–O–, mr + rm), 75.48 (–O–CH₂–<u>C</u>H(CH₃)–O–, rr), 73.71 (–O–<u>C</u>H₂–CH(CH₃)–O–, m), 73.16 (–O– <u>C</u>H₂–CH(CH₃)–O–, rrm or mrr), 17.81 (–<u>C</u>H₃).

Poly(butylene oxide) (PBO)

¹H NMR (500 MHz, CDCl₃) δ 3.68 – 3.25 (bm, –O–C<u>H</u>₂–C<u>H</u>(CH₂–CH₃)–O–), 1.68 – 1.37 (m,

CH2-CH3), 0.91 (t, -CH2-CH3). ¹³C NMR (126 MHz, CDCl3) δ 80.84-80.42 (-O-CH2-

<u>C</u>H(CH₂–CH₃)–O–), 72.37 (–O–<u>C</u>H₂–CH(CH₂–CH₃)–O–, m), 71.53 (–O–<u>C</u>H₂–CH(CH₂–CH₃)–

O–, rrm or mrr)), 24.72 (–<u>C</u>H₂–CH₃), 9.76 (–CH₃).

Poly(allyl glycidyl ether) (PAGE)

¹H NMR (500 MHz, Chloroform-d) δ 5.88 (m, –O–CH₂–C<u>H</u>=CH₂), 5.27-5.14 (doublet of

doublets, $-O-CH_2-CH=CH_2$), 3.98 (d, $-O-CH_2-CH=CH_2$), 3.75-3.42 (bm, $-O-CH_2-CH(CH_2-CH_2)$), 3.98 (d, $-O-CH_2-CH=CH_2$), 3.98 (d, $-O-CH_2-CH=CH_2$), 3.75-3.42 (bm, $-O-CH_2-CH=CH_2$), 3.98 (d, $-O-CH_2-CH=CH_2$), 3.75-3.42 (bm, $-O-CH_2-CH=CH_2$), 3.98 (d, $-O-CH_2-C$

O-CH₂-CH=CH₂)-O-). ¹³C NMR (126 MHz, Chloroform-d) δ 134.93 (-O-CH₂-<u>C</u>H=CH₂), 116.74 (-O-CH₂-CH=<u>C</u>H₂), 78.89 (-O-CH₂-<u>C</u>H(CH₂-O-CH₂-CH=CH₂)-O-), 72.26 (-O-<u>C</u>H₂-CH=CH₂), 70.25-69.84 (-O-<u>C</u>H₂-CH(<u>C</u>H₂-O-CH₂-CH=CH₂)-O-, *m*), 69.74 (-O-<u>C</u>H₂-CH(CH₂-O-CH₂-CH=CH₂)-O-, *rrm* or *mrr*).

CH(CH₂-O-CH₂-CH=CH₂)-O-, *rrm* or *mrr*).
2.2.5 Procedure for synthesis and reactivity ratio measurement of P(PO-grad-ECH)

A vial with a stir bar was charged with PrSAlMe₂ (0.013 g, 0.1 mmol) and NAl (0.017 g, 0.1 mmol). A mixture of ECH (1.5 ml, 1.84 g, 0.019 mol) and PO (1.39 ml, 1.15g, 0.019 mol) was added to the vial slowly and then heated up to 50°C. To measure reactivity ratios of ECH and PO, small aliquots (ca. 30 µL) were taken out of reaction mixture and dissolved in CDCl₃. The conversion of each monomer was calculated based on the integration of backbone area to the unreacted corresponding monomer by ¹H NMR spectroscopy. After a given time, the mixture was diluted with DCM and precipitated in a threefold excess of acidic methanol (0.01 M). The polymer was dried under vacuum at room temperature. Dispersity and M_n were characterized by SEC and the structure of the copolymer was confirmed by ¹H NMR and ¹³C NMR spectroscopy. ¹H NMR (500 MHz, CDCl₃) δ 3.82 – 3.40 (bm, –O–CH₂–CH(CH₂Cl)–O– and –O–CH₂– CH(CH₃)–O–), 1.18 – 1.10 (bm, –O–CH₂–CH(CH₃)–O–). ¹³C NMR (126 MHz, CDCl₃) δ 79.67-78.65 (-O-CH2-CH(CH2CI)-O-), 75.85-75.17 (-O-CH2-CH(CH3)-O-), 74.44-74.04 (-O-CH₂-CH(CH₃)-O- and -O-CH₂-CH(CH₂Cl)-O-), 73.37-72.84 (-O-CH₂-CH(CH₂Cl)-O-), 69.72-69.24 (-O-CH2-CH(CH3)-O-), 68.68-68.13 (-O-CH2-CH(CH3)-O- and -O-CH2-CH(CH₂Cl)–O–), 44.05-43.23 (–CH₂–Cl), 17.10 (–CH₃).

2.2.6 General procedure for synthesis of P(PO-b-ECH)

PrSAlMe₂ (0.009 g, 0.068 mmol) and NAl (0.011 g, 0.063 mmol) were added into a vial with stir bar. After the addition of the ECH (0.84 ml,1g, 0.01 mol), the vial was placed in the hotplate at

50°C. Completion of polymerization was monitored by ¹H NMR spectroscopy and when the first monomer is consumed, the PO (0.7 ml, 0.58 g, 0.01 mol) was injected to the vial. Stirring was continued at 50 °C for enough time until the second monomer is fully converted. The product was then dissolved in DCM and the resulting solution was precipitated out of MeOH to yield the desired polymer product. The supernatant was removed, and the polymer was dried *in vacuo*. Structure of the block copolymer characterized by ¹H NMR and ¹³C NMR spectroscopy. Dispersity and M_n were characterized by SEC and glass transition temperature confirmed by DSC.

¹H NMR (500 MHz, CDCl₃ δ 3.70 (bm, (–O–C<u>H</u>₂–C<u>H</u> (C<u>H</u>₂–Cl)–O– and –O–C<u>H</u>₂ (CH₃)-O-), 1.13 (m, -CH₃). ¹³C NMR (126 MHz, CDCl₃) δ 79.07-78.99 (–O–CH₂–<u>C</u>H(CH₂Cl)–O–), 75.52-75.11 (–O–CH₂–<u>C</u>H(CH₃)–O–), 73.35-72.79 (–O–<u>C</u>H₂–CH(CH₂Cl)–O–), 69.67- 69.35 (–O–<u>C</u>H₂–CH(CH₃)–O–), 43.65 (–<u>C</u>H₂–Cl), (17.45-17.32) (–<u>C</u>H₃).

2.2.7 Polymerization procedure for synthesis of P(MMA-b-ECH)

Polymerization was performed in a round-bottom flask capped with a septum. The reaction vessel with a stir bar was loaded with THF (5 mL), MMA (1.87 ml, 2.0×10^{-2} mol), 2-cyano-2-propyl benzodithioate (0.022 g, 9.9×10^{-5} mol), and AIBN (0.005 g, 3.1×10^{-5} mol). The mixture was deoxygenated by sparging a reaction mixture with N₂. The temperature was then raised to 90 °C using an oil bath and polymerization was carried out under N₂ atmosphere. Monomer consumption was followed by ¹H NMR spectroscopy and after 72 h, 70% of monomer was converted. Poly(methyl methacrylate) (PMMA) was precipitated out of MeOH and the excess monomer and solvent removed by evaporation at ambient temperature was confirmed by ¹H and ¹³C NMR spectroscopy. In the next step, the aminolysis of PMMA with hexylamine was performed for conversion of dithioester into a thiol end-group. The procedure was as follows. PMMA (0.5 g) was

dissolved in THF and 0.5 ml of NaHSO₄ (5% aqueous solution) was added into a 50 ml 3-necks flask with a stir bar. The flask was sparged with N_2 for 15 mins. Hexylamine (3.7 mmol, 0.38 g, 0.5 ml) was added dropwise, and the reaction was stirred for 10 h under N₂. Solution color changed from pink to light yellow while adding the hexylamine and after aminolysis was done, the reaction mixture was light yellow (an indication of the conversion). Next, the reaction vessel was taken into the glove box and the solution was added dropwise into 5-fold excess of MeOH. The PMMA functionalized with thiol (PMMA-SH) was collected by precipitation and then drying *in vacuo*. In order to synthesis a macroinitiator, in one 20 ml vial, 0.14 g of PMMA-SH was dissolved on 1 ml of benzene and AlMe₃ (0.3 ml of 2 M in hexane) added dropwise to the solution and stirred overnight at RT. To synthesize poly(methyl methacrylate)-block-(epichlorohydrin), NAI (0.003 g, $1.7\times10^{\text{-5}}$ mol) and 0.2 ml of ECH (0.23 g, 2.4 mmol) were added into the same vial and heated up to 50 °C. Conversion of ECH was monitored by ¹H NMR spectroscopy and the reaction terminated by MeOH after 3 days (full conversion). The block copolymer was purified by redissolving in DCM, precipitating out of MeOH, and drying in vacuo. The resulted poly(MMA)b-(ECH) characterized by SEC, DSC, ¹H NMR, and ¹³C NMR spectroscopy. ¹H NMR spectroscopy of P(MMA-*b*-ECH). ¹H NMR (500 MHz, Methylene Chloride-d₂) δ 3.99–3.62 (bm, -OCH₂CH(CH₂Cl)O-), 3.63-3.56 $(bm, -CH_2C(CH_3)(COOCH_3)-),$ 2.19-1.66 (bm, $CH_2C(CH_3)(COOCH_3)$ -), 1.67 – 0.58 (bm, - $CH_2C(CH_3)(COOCH_3)$ -). ¹³C NMR spectroscopy of P(MMA-b-ECH). ¹³C NMR (126 MHz, cdcl₃) δ 178.12- 177.00 (-CH₂-C(CH₃)(<u>C</u>OOCH₃)-), 81.58-67.83 (-O-CH₂-<u>C</u>H(CH₂-Cl)-O-), 51.84 (-CH₂-<u>C</u>(CH₃)(COOCH₃)-), 44.89 (-CH₂-C(CH₃)(COO<u>C</u>H₃)-), 45.93-45.32 (H-T diads, -O-<u>C</u>H₂-CH(CH₂-Cl)-O-), 44.89-44.54 (-<u>C</u>H₂-C(CH₃)(COOCH₃)-), 43.87-42.63 (H-H and T-T diads, -O-<u>C</u>H₂-CH(CH₂-Cl)-O-), 25.07 (-O-CH₂-CH(<u>C</u>H₂-Cl)-O-), 18.70-16.41(-CH₂-C(CH₃)(COO<u>C</u>H₃)-).

2.2.8 Detailed purification procedure for synthesized polymers

After completion of the polymerization monitored by ¹H NMR spectroscopy, the reaction was quenched by exposing to the air and adding 0.1 ml of MeOH. Then, the polymer was dissolved in 3 ml of DCM by stirring and heating to 50 °C. The dissolved polymer was added dropwise to 6 ml of 0.01 M HCl in MeOH (acidic MeOH) to be precipitated. After sufficient time, the supernatant was removed. The polymer was re-dissolved in DCM, washed three times with DI water, and precipitated by adding to the 3 ml of MeOH. Finally, the polymer was dried in *vacuo* overnight at 70 °C. It should be noted that PPO did not precipitate out of a number of different solvents and so the above steps were followed without precipitation for PPO.

2.2.9 Kinetic study for different concentrations of NA1 by ¹H NMR spectroscopy at specified time points

In a glove box, a reaction vial was charged with a stir bar, BnSAlMe (0.018 g, 0.099 mmol), NA1 (0.25 eq. (0.004 g, 2.3×10^{-2} mmol), 0.5 eq. (0.008 g, 4.6×10^{-2} mmol), 1 eq. (0.0175 g, 0.1 mmol), 2 eq (0.035 g, 0.2 mmol), and epichlorohydrin (3 g, 2.5 ml). the reaction vessel then placed on a stir plate at 50 °C. Small aliquots (*ca.* 30 µL) were taken at sp,ecified time points. These samples were dissolved in d-chloroform and conversion was determined using ¹H NMR spectroscopy. The conversion of each monomer was calculated based on the integration of the backbone area to the unreacted corresponding monomer by ¹H NMR spectroscopy. The samples were quenched by exposing them to the air which deactivates the catalyst.

2.2.10 Kinetic study for different initiators by ¹H NMR spectroscopy specified time

A reaction vial was charged with a stir bar, NAI (0.035 g, 0.2 mmol), epichlorohydrin (3 g, 2.5 ml), and initiator (0.099 mmol) and then it heated up to 50 °C in a glove box. Small aliquots (*ca*. $30 \,\mu$ L) were taken at specified time points. These samples were dissolved in d-chloroform and the

conversion was determined using ¹H NMR spectroscopy. The conversion of each monomer was calculated based on the integration of backbone area to the unreacted corresponding monomer by ¹H NMR spectroscopy. The samples were quenched by exposing to the air which deactivates the catalyst.

2.2.11 Polymerization procedure for synthesis of poly(styrene-block-epichlorohydrin) (P(styerne-b-ECH))

Polymerization was performed in a round-bottom flask capped with a septum. The reaction vessel with a stir bar was loaded with tetrahydrofuran (5 mL), styrene (2.3 ml, 2×10^{-2} mol), 2-cyano-2propyl benzodithioate (0.022 g, 9.9×10^{-5} mol), and AIBN (0.005 g, 3.1×10^{-5} mol). The mixture was deoxygenated by sparging a reaction mixture with N₂. The temperature was then raised to 90°C using an oil bath and polymerizations were carried out under N₂ atmosphere. Monomer consumption was followed by ¹H NMR analysis and after 72 h, 68% of monomer was converted. Poly(styrene) (PS) was precipitated out of MeOH, and the excess monomer and solvent removed by evaporation at ambient temperature under vacuum. In the next step, the aminolysis of PS with hexylamine was performed for conversion of dithioester into a thiol end-group. The procedure was as follows. Functionalized PS (0.1 g) was dissolved in THF and 0.1 ml of NaHSO₄ (5% aqueous solution) were added to a 50 ml 3-necks flask with a stir bar. The flask was sparged with N₂ for 15 mins. Hexylamine (0.69 mmol, 0.07 g, 0.1 ml) was added dropwise, and the reaction was stirred for 10 h under N₂. Solution color changed from pink to light yellow while adding the hexylamine and after aminolysis was done, the reaction mixture was light yellow (an indication of conversion). Next, the reaction vessel was taken into the glove box and the solution was added dropwise into 5-fold excess of MeOH. The PS functionalized thiol (PS-SH) was collected by precipitation and then drying in vacuo. In order to synthesis a macroinitiator, 0.18 g of PS-SH was dissolved in 1

ml of benzene and added into a reaction vial with a septum. AlMe₃ (0.3 ml of 2 M in hexane) added dropwise into the solution and stirred overnight at RT. To synthesis poly(styrene-*block*-epichlorohydrin), NAl (0.005 g, 2.8×10^{-3} mol), and 0.2 ml of ECH (0.4 ml, 0.472 g, 5.1mmol) were added into the same vial and heated up to 50 °C. Conversion of ECH was monitored by ¹H NMR spectroscopy and the reaction terminated by MeOH after 6 days. The block copolymer was purified by redissolving in DCM, precipitating out of MeOH, and drying *in vacuo*.

2.3 Results and discussion

A potential initiator for epoxide polymerizations, a thio-aluminum (SAI) compound, was synthesized from the reaction of benzyl mercaptan and trimethyl aluminum at -78 °C. The resulting SAI (BnSAIMe₂) was crystallized from the reaction medium and characterized via X-Ray crystallography as seen in **Figure 2-1** as well as ¹H NMR and ¹³C NMR spectroscopy (SI, **Figure 2-11 to 2-14**). X-Ray crystallography revealed a unit structure of dimethyl aluminum bound to benzyl thiolate, consistent with trimethyl aluminum reacting with the benzyl mercaptan. This unit, we propose, defines our initiator for epoxide polymerizations. The entire crystal structure reveals these individual units to be datively bound to adjacent units in a linear chain (*c.f.*, **Figure 2-13, 2-14**), which is consistent with other SAI structures in literature.³⁰ Details of the crystallography can be found in the SI.



Figure 2-1 (top) Chemical reaction scheme for the synthesis of BnSAlMe₂. (bottom) Resultant chemical structure of the asymmetric structure determined by X-Ray crystallography. Thermal ellipsoids are shown at 50% probability level.

BnSAlMe₂ was utilized as an initiator to polymerize the epoxide epichlorohydrin (ECH). Here, we targeted 30 kg/mol polyepichlorohydrin (PECH) using BnSAlMe₂ in an equimolar ratio with NAl catalyst²⁶ in the absence of a solvent, as shown in **Scheme 2-1**. The polymerization was monitored with ¹H NMR spectroscopy until completion at 12 hours with >99% conversion of ECH. The observed rate constant (k_{obs}) was determined from a fit to the kinetic data as seen in **Figure 2-2** (a log-linear plot can be seen in SI **Figure 2-15**) and was calculated to be $k_{obs} = 7.38 \times 10^{-5} \pm 5.41 \times 10^{-6} \, \text{s}^{-1}$. The first order in monomer kinetics suggests polymerizations initiated by BnSAlMe₂, just NAl catalyst, and benzyl mercaptan (ligand) and catalyst (*i.e.*, no initiator). Using exclusively the initiator, slow conversion was observed (*ca.* 10% after 7 days), while just catalyst and catalyst and ligand resulted in no conversion, which is consistent with previous work with BOD-initiated polymerizations.²⁶ ¹H NMR spectra for ECH polymerizations with just NAl catalyst, just BnSAlMe₂, and benzyl mercaptan with NAl can be found in the supplemental

information (SI, Figures 2-16, 2-17). Based on these results, we suggest that the polymerization follows an anionic coordination-insertion of activated monomer mechanism assisted by a Lewis pair (i.e., NAl), where the NAl adduct acts as a strong activator of the monomer via oxygenaluminum coordination as proposed by Carlotti³¹ and the covalent nature of the Al-S bond suggests polymerization via a coordination mechanism.^{32, 33} The resulting PECH was characterized via size-exclusion chromatography (SEC). The M_n was found to be 30.7 kg/mol with D = 1.17, consistent with the targeted molecular weight, and compared favorably to the molecular weight calculated through ¹H NMR spectroscopy via end group analysis of 31.6 kg/mol (SI, Figure 2-19). The results for this polymerization can be found in Table 2-1, sample 2. Differential scanning caolorimetry (DSC) was also performed on this polymer and showed a single glass transition temperature (T_g) at -26 °C (SI, Figure 2-20). We also have observed the hydrogenation reaction of the end group for BnSPECH in a higher concentration of acidic MeOH (1 M HCl in MeOH) confirmed by ¹ H NMR spectroscopy (SI, Figure 2-21), which suggests we can achieve hetero-bifunctional polymers with two addressable end groups (i.e., alcohol and thiol).

Sample	Monomer	Initiator	Time (hr.) ^a	$M_n^{(theo)}$ (kg/mol)	M _n ^{(calc) b} (kg/mol)	M _n ^c (kg/mol)	Ðď
1	ECH	BnSAlMe ₂	6	15	17.5	17.7	1.37
2	ECH	BnSAlMe ₂	10	30	31.6	30.7	1.17
3	ECH	BnSAlMe ₂	48	50	46.8	49.4	1.28
4	ECH	BnSAlMe ₂	70	70	75.0	75.7	1.25
5	ECH	BnSAlMe ₂	102	100	97.1 ^f	94.6	1.28
6	BO	BnSAlMe ₂	48	30	22.7	23.6 ^e	1.16 ^e
7	BO	BnSAlMe ₂	97	100	81.2^{f}	80.2 ^e	1.02 °
8	РО	BnSAlMe ₂	40	30	38.1	38.9 ^e	1.04 °
9	РО	BnSAlMe ₂	97	100	78.4^{f}	80.1 ^e	1.02 °
10	AGE	BnSAlMe ₂	22	30	28.3	29.6	1.45
11	ECH	cPenSAlMe ₂	12	30	33.9	29.3	1.25
12	ECH	ClBnSAlMe ₂	12	30	27.3	30.9	1.28
13	ECH	PrSAlMe ₂	4	30	30.2	28.6	1.24
14	РО	PrSAlMe ₂	22	30	19.9	19.8 ^e	1.07 ^e
15	BO	PrSAlMe ₂	48	30	27.4	23.5 °	1.17°

Table 2-1 Control experiment.



Scheme 2-1 SAl-initiated polymerization of ECH.



Figure 2-2 Plot of normalized ECH concentration over time with BnSAlMe₂ initiator and NAl catalyst. Monomer concentration was monitored via ¹H NMR spectroscopy. The full conversion was achieved in *ca.* 10 hours with the combined catalyst and initiator system, with $k_{obs} = 7.38 \times 10^{-5} \pm 5.41 \times 10^{-6} \text{ s}^{-1}$, whereas no conversion is present with just catalyst and slow conversion is present with just BnSAlMe₂ as initiator. The inset is a plot of the k_{obs} as a function of equivalents of NAl catalyst to BnSAlMe₂ initiator, where a linear relationship was observed.

The effect of catalyst concentration on the polymerization rate was investigated with ¹H NMR spectroscopy. We monitored the conversion of ECH with a targeted molecular weight of 30 kg/mol with varying ratio of catalyst to initiator concentration $([C_0]/[I_0]) = 0.25, 0.50, 1.00,$ and 2.00. The resulting kinetic data of normalized monomer concentration as a function of time can be seen in **SI** (supplemental information, **Figure 2-22 to 2-25**) and the k_{obs} as a function of $[C_0]/[I_0]$ can be seen in **Figure 2-2** inset. A linear increase in k_{obs} as a function of $[C_0]/[I_0]$ was observed, which differs from Lynd's work on the BOD system,²⁶ but is consistent with other polymerization catalysts behavior in the literature.^{34, 35} It should also be noted that there is an apparent induction period,³⁶ denoted by the characteristic sigmoidal shape of the conversion

curve for samples with $[C_0]/[I_0] = 0.25$ and 0.50 and the reported k_{obs} was determined from a fit to the conversion *after* the induction period, where conversion is first order in monomer. The induction period can be observed in the full kinetic data plots found in the supplementary information (SI, **Figures 2-22, 2-23**). No induction period was observed for samples with $[C_0]/[I_0] = 1.00$ or 2.00. In work by Huang et al.³⁷ for polymerization of PO using a double metal catalyst (DMC), they observed that when the ratio of [C]/[I] decreases, the induction period increases, which is the same observation for our catalyst and initiator system. The addition of more initiators can inhibit the addition of the monomer to the activated chain end, which may be due to the higher donor ability of sulfur anion to oxy anion which can deactivate the catalyst (NAI). Moreover, the ring opening reaction of epoxides and consequently activation of the monomer is directly dependent on the amount of NAI. This justifies the lower rate of this reaction at the first stage of polymerization, which refers to the induction period. The induction period of the NAI catalyst will be further addressed by a future paper from the Lynd laboratory at UT Austin.

Molecular weight control was investigated for SAl-initiated polymerizations of ECH. Control over PECH molecular weight was achieved by varying the monomer to initiator ratio $([M_0]/[I_0])$ with targeted molecular weights of 15, 30, 50 75, and 100 kg/mol. For these polymerizations, the NAl catalyst was pinned at 63.5 µmol, or equimolar with the BnSAlMe₂ BnSAlMe₂ initiator for a 30 kg/mol polymer. All polymerizations were carried out to full conversion prior to termination. The final M_n of the polymers was consistent with the targeted molecular weights as determined by both SEC and end group analysis via ¹H NMR spectroscopy. The details of the polymers can be found in **Table 2-1**, samples 1–5. **Figure 2-3** is a plot of M_n (blue left axis) and Đ (red right axis) as a function of [ECH]/[BnSAlMe₂]

determined by SEC. A linear trend in the M_n as a function of [ECH]/[BnSAlMe₂] can be seen in the plot, implying good control over M_n up to 100 kg/mol. Furthermore, D < 1.4 for all polymers produced suggests no side reactions are occurring. The corresponding SEC traces for each of these polymerizations can be found in the SI (supplemental information, **Figure 2-26 to 2-29**).



Figure 2-3 Plot of M_n (left axis, blue circles) and D (right axis, red triangles) as a function of ECH to initiator BnSAlMe₂ ratio ([ECH]/[BnSAlMe₂]). M_n increased linearly at increasing ratio of epichlorohydrin, while D remained consistently low (D < 1.4) suggesting a controlled chain growth polymerization of ECH.

Similar molecular weight control was demonstrated for polymerizations of propylene oxide (PO) and butylene oxide (BO). PO and BO are difficult to polymerize via traditional methods (*i.e.*, AROP) to even moderate molecular weights (*i.e.*, $M_n > 10$ kg/mol) due to their propensity to chain transfer,³⁸ but work by several different researchers like Carlotti,³⁹ Deffieux,⁴⁰ Naumann,⁴¹ and Coates⁴² over the past two decades have demonstrated the high molecular weight synthesis of PPO by other means. However, high molecular PBO still remains a challenge. We targeted polymer molecular weights of 30 and 100 kg/mol for each monomer using BnSAlMe₂ as the initiator and using 63.5 µmol of NAl catalyst. The results can be found in **Table 2-1** and were generally consistent with the targeted molecular weights. Specifically, the M_n determined from SEC for the polymers were: 38.1 kg/mol (PPO, 30 kg/mol), 80.1 kg/mol (PPO, 100 kg/mol), 23.1 kg/mol (PBO, 30 kg/mol), and 80.1 kg/mol (PBO, 100 kg/mol) all with narrow D < 1.1. Molecular weights determined by end group analysis from ¹H NMR spectra of polymers were consistent with the M_n determined by SEC (SI, **Figures 2-30 to 2-34**) and no peaks suggesting any chain transfer occurred. DSC was also performed on the 30 kg/mol samples of PPO and PBO and showed single T_g consistent with the synthesized polymers The DSC data can be found in SI (**Figures 2-36, 2-37**). Therefore, the SA1 initiator allows for facile and controlled synthesis of mid-range molecular weight (*i.e.*, 100 kg/mol > M_n >10 kg/mol) PPO and PBO.

As a further demonstration of functional monomer polymerization, allyl glycidyl ether (AGE) was polymerized. We targeted PAGE molecular weight of 30 kg/mol using BnSAlMe₂ as the initiator and using 63.5 μ mol of NAl catalyst. The results can be found in **Table 2-1**. Specifically, the M_n determined from SEC was 29.6 kg/mol with D = 1.45, which is consistent with the targeted molecular weight. The resulting PAGE was also characterized by ¹H NMR spectroscopy with calculated molecular weight based on end group analysis to 31.2 kg/mol, consistent with the SEC results. NMR spectra and SEC trace for PAGE can be found in the supporting information (**Figures 2-37 to 2-40**).

Three additional SAI initiators were synthesized from different thiol-containing ligands to tune polymer end-group. SAI initiators were synthesized in a similar way to the BnSAlMe₂ initiator above but utilizing ligands of propyl thiol (PrSAlMe₂), cyclopentylthiol (cPenSAlMe₂), and chloro-benzyl thiol (ClBnSAlMe₂) in a reaction with trimethylaluminum. These ligands were chosen due to their unique chemical signature in ¹H NMR spectra compared with the polymer, allowing for a facile determination of the end group. All SAI initiators were characterized via ¹H and ¹³C NMR spectroscopy (supplemental information, **Figures 2-41** to **2-46**) and cPenSAlMe₂

and ClBnSAlMe₂ were characterized by X-Ray crystallography (full XRD data are available in the SI). Characterization of PrSAlMe₂ by X-Ray crystallography was unsuccessful due to the instability of the resulting crystals. The structure of cPenSAlMe₂ and ClBnSAlMe₂ determined by X-Ray crystallography can be seen in **Figure 2-4**. cPenSAlMe₂ (**Figure 2-4 a**) consists of a dimer of dimethyl aluminum cyclopentyl sulfur forming a four-membered thio-aluminum ring. This structure is reminiscent of BODs from literature^{26, 43} as well as similar thio-aluminum compounds in the literature,^{29, 44, 45} but it is distinct from the crystal structure of BnSAlMe₂. Meanwhile, ClBnSAlMe₂ (**Figure 2-4 b**) is similar in structure to BnSAlMe₂ and exists as a linear chain of adjacent initiator units connected through dative bonds of aluminum and sulfur.



cPenSAIMe₂

CIBnSAIMe₂

Figure 2-4 Resultant structure of cPenSAlMe₂ (a) and ClBnSAlMe₂ (b) formed from the reaction of cyclopentyl thiol and 4-chlorobenzenemethanethiol, respectively, with trimethyl aluminum determined by X-Ray crystallography. cPenSAlMe2 forms a dimer (shown) consisting of a four membered thio-aluminum ring while the ClBnSAlMe₂ forms a chain of initiator units connected via dative bonds to aluminum and sulfur atoms of adjacent initiators, like BnSAlMe₂ (*cf.*, **Figure 1**). Thermal ellipsoids are shown at 50% probability level.

Polymerizations of ECH with all SAl initiators were performed to demonstrate polymer end group control. The polymerizations of ECH were carried out in the bulk with a 2:1 ratio of NAl catalyst to SAl initiator with a targeted molecular weight of 30 kg/mol. A summary of the polymerizations initiated with all SAl initiators can be found in **Table 2-1** and SEC traces can be found in SI (**Figures 2-47 to 2-49**). The resultant PECH were characterized by ¹H NMR spectroscopy and SEC. The molecular weights for all polymers were consistent with the targeted molecular weight of 30 kg/mol. The ¹H NMR spectra for polymers synthesized from SA1 initiators can be seen in **Figure 2-5**. All spectra are consistent with the anticipated ones. The molecular weight calculation via end group analysis (*c.f.*, **Table 2-1**) is consistent with the SEC results. To further confirm the polymer end group, a 5 kg/mol molecular weight PPO was synthesized with all SA1 initiators and the resultant polymers were characterized via electrospray ionization with mass spectroscopy (ESI-MS) and matrix assisted laser desorption/ionization time of flight (MALDI-TOF). The results from this analysis can be found in the **SI** (supplemental information, **Figures 2-50 to 2-54**).



Figure 2-5 ¹H NMR Spectra of PECH initiated by PrSAlMe₂ (a), cPenSAlMe₂ (b), BnSAlMe₂ (c), and ClBnSAlMe₂ (d) in CD₂Cl₂ (c, d) or CDCl₃ (a, b). The peaks corresponding to the various end groups are clearly visible in each of the spectra and are marked with letters '**a**' through '**c**' and their chemical shift and multiplicity is consistent with expectations. Peaks marked with '**x**' correspond to CD₂Cl₂ and peaks marked with '**y**' correspond to water impurity in CDCl₃. Intensity increased to accentuate peaks corresponding to end groups.

Kinetic studies of ECH polymerization with all SAI initiators were performed to determine whether the initiator structure influenced polymerization kinetics. Based on our assumption of a coordination-insertion polymerization mechanism with ionic character, the initiator end group should play a little role in the reaction kinetics as the end group moves away from the site of insertion as the monomer is consumed. Polymerizations of ECH were carried out with each SAl initiator and two equivalents to initiator of NAl catalyst and monitored with ¹H NMR spectroscopy over 2.5 hours. A plot of the resulting kinetic data can be seen in Figure 2-6. The k_{obs} was determined from the slope of the fit to the $-\ln([ECH]/[ECH]_0)$ and was k_{obs} = (3.83) ± 0.15) × 10⁻⁴ s⁻¹ (PrSAlMe₂), (1.86 ± 0.08) × 10⁻⁴ s⁻¹ (BnSAlMe₂), (1.34 ± 0.05) × 10⁻⁴ s⁻¹ ¹(ClBnSAlMe₂), and $(0.21 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$ (cPenSAlMe₂). The results of the initiator kinetic study were unexpected, as they suggest initiator structure affects polymerization kinetics. The PrSAlMe₂ initiator was approximately two times faster than either benzyl containing initiator (*i.e.*, BnSAlMe₂ and ClBnSAlMe₂) and more than 10 times faster than cPenSAlMe₂. The results of both end group analyses via ¹H NMR spectroscopy and ESI-MS suggest that the polymer is growing linearly (*i.e.*, the end group moves further away from the site of enchainment as polymerization progresses), so the exact role of the end group on kinetics remains unclear. However, the benzyl containing initiators have similar kobs to each other along with similar crystal structures, while the crystal structure, and resulting kobs, for cPenSAIMe2 differs significantly from them. Therefore, the more open structure of the benzyl containing initiators may facilitate monomer enchainment and enhance kinetics compared with cPenSAlMe₂. Moreover, the electron density of the initiator may affect the rate of polymerization as an electron rich ligand like PrSAlMe₂ is the fastest one, while ClBnSAlMe₂, the most electron deficient, is the slowest between all initiators. This effect has been seen before for cationic

polymerizations.⁴⁶ The crystallographic structure of PrSAlMe₂ or an intermediate after enchainment would elucidate the genesis of these kinetic differences and this will be followed up further in future work.



Figure 2-6 Plot of the $-\ln([ECH]/[ECH]_0)$ as a function of time for the polymerization of ECH with SAl initiators PrSAlMe₂ (red squares), BnSAlMe₂ (blue circles), ClBnSAlMe₂ (purple triangles), and cPenSAlMe₂ (green diamonds). Monomer conversion was monitored via ¹H NMR spectroscopy for 2.5 hours by taking aliquots from the reaction vessel and an observed rate constant (k_{obs}) was determined to be k_{obs} = $(3.83 \pm 0.15) \times 10^{-4} \text{ s}^{-1}$ (PrSAlMe₂), $(1.86 \pm 0.08) \times 10^{-4} \text{ s}^{-1}$ (BnSAlMe₂), $(1.34 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$ (ClBnSAlMe₂), and $(0.21 \pm 0.03) \times 10^{-4} \text{ s}^{-1}$ (cPenSAlMe₂).

To investigate the generality of our method to target specific polymer architecture, we synthesized copolymers of ECH and PO. The copolymerization of ECH and PO in a 1:1 ratio was performed using PrSAlMe₂, which was chosen due to the enhanced celerity over the other initiators. The polymerization was monitored by ¹H NMR spectroscopy and the total conversion of monomers was determined. The reactivity ratios were fit to the non-terminal copolymerization model reported by Beckingham–Sanoja–Lynd (BSL)^{47, 48} and **Figure 2-55** shows the fit of BSL to the conversion as a function of the normalized molar concentration of each monomer ([M]/[M]₀). From BSL, the reactivity ratios for ECH (r_{ECH}) and PO (r_{PO}) were determined to be

 $r_{ECH} = 2.56 \pm 0.29$ and $r_{PO} = 0.44 \pm 0.03$, which suggests a gradient copolymer with ECH preferentially adding over PO. The resulting polymer was also characterized by SEC with a M_n of 29.0 kg/mol and Đ of 1.28, consistent with the targeted molecular weight of 30 kg/mol. We further synthesized a block copolymer of ECH and PO by sequential addition of monomers initiated with PrSAlMe₂. The resulting copolymer was characterized by SEC with M_n of 33.4 kg/mol and Đ of 1.27, consistent with the targeted molecular weight of 30 kg/mol (15 kg/mol for each block). The ¹H and ¹³C NMR spectra for the block and gradient copolymers with labeled chemical structures can be seen in **Figure 2-7**. The ¹H NMR spectra for the gradient and block copolymers, Figure 2-7a and 7c, respectively, are similar to each other and consistent with the anticipated spectra. The ¹³C NMR spectra for the gradient and block copolymers, Figure 2-7b and 2-7d, respectively, differ in that the gradient copolymer has additional carbon peaks compared with the block copolymer due to adjacency of the different monomers.²⁴ Furthermore, the PECH-b-PPO sample was characterized by diffusion ordered spectroscopy (DOSY). The DOSY spectrum can be seen in supporting information (Figure 2-56) and is consistent with block copolymer formation. Copolymerization demonstrates the ability of our method to synthesize multifunctional polymeric materials with controlled compositions.



Figure 2-7 ¹H and ¹³C NMR spectra and labeled chemical structures for PECH-*grad*-PPO (a and b, respectively) and PECH-*b*-PPO (c and d, respectively) in CDCl₃. The ¹³C NMR spectrum of the PECH-*grad*-PPO (b) reveals additional cross-peaks compared with PECH-*b*-PPO (d).

We synthesized a block copolymer consisting of vinyl and epoxide units through a combination of reversible addition-fragmentation with chain transfer (RAFT) polymerization and AROP to demonstrate the utility of our method as a materials platform. Specifically, a block copolymer of poly(methyl methacrylate) (PMMA) and PECH was synthesized as outlined in **Figure 2-8**. Utilizing this method to synthesize vinyl-*block*-epoxide polymers has advantage over traditional anionic polymerization as the synthesis can be performed without the need for specialized glassware or the use of dangerous reagents (*e.g.*, ethylene oxide). In the RAFT polymerization of MMA, 2-cyano-2-propyl benzodithioate was used as a chain transfer agent along with AIBN as a radical initiator to produce PMMA. The resultant PMMA was characterized via SEC (**Figure 2-9**, right trace, red) with $M_n = 6.3$ kg/mol and D = 1.13 and ¹H NMR spectroscopy (**Figure 2-10 c**). The dithioester, which remained as an end group from the

RAFT polymerization, was cleaved down to a terminal thiol via aminolysis and the thiol terminated PMMA was characterized via ¹H NMR spectroscopy, which revealed the loss of protons associated with the benzyl group (Figure 2-10 b). The thiol end terminated PMMA was transformed into a macro-initiator for epoxide polymerization through the reaction of the thiol group with trimethyl aluminum in benzene at room temperature overnight. A polymerization of ECH, initiated from the end of the thio-aluminum end-terminated PMMA, was carried out (for 3 days) at 50 °C in the presence of NAI catalyst. The resulting P(MMA-b-ECH) was characterized via SEC, ¹H and ¹³C NMR spectroscopy, and DSC. The SEC trace (RI) of P(MMA-*b*-ECH) can be seen in Figure 2-9 (left trace, blue) and the M_n was determined to be 18.4 kg/mol with D =1.05. A clear shift to smaller retention volume can be seen in SEC of the block-co-polymer compared with the homopolymer, consistent with the ECH block growing from the PMMA chain end. The ¹H (Figure 2-10 a) and ¹³C (SI, Figure 2-57) NMR spectra are consistent with the expected polymer structure. DOSY was also performed on this sample and the resulting spectrum is consistent with block co polymer formation (supporting information, Figure 2-58). Moreover, in a control experiment, after working up the thiol end-terminated PMMA, we added epichlorohydrin into the reaction vial (without the addition of AlMe₃) and monitored the conversion of ECH. No conversion for ECH was observed after 7 days (SI, Figure 2-59) by ¹H NMR spectroscopy. This observation suggests that PECH is not forming separately and must be polymerized off of the macro-initiator. DSC (SI, Figure 60) reveals a single broad T_g which is to be expected as PMMA and PECH are miscible polymers.^{49, 50} The broadening behavior for glass transition has been observed due to miscibility of PMMA and PECH.^{51, 52} The ¹³C NMR spectrum shows additional peaks, which we think corresponds to different regiostructures of PECH. These peaks are consistent with head-to-head, tail-to-tail and head-to-tail addition of

ECH to the growing chain end.⁵³ The regio-*ir* regularity of the PECH block is inconsistent with polymerizations carried out above using SAl initiators and previous work with MOB²⁴⁻²⁶ and BOD^{26, 43} initiators. We suspect it has to do with the favorable interaction between MMA and ECH. To test this, we polymerized ECH from the end of RAFT synthesized polystyrene (PS) in a similar manner to the PMMA. The resulting ¹³C NMR spectrum (SI, **Figure 2-61**) for PS-*b*-PECH polymer is consistent with a regioregular PECH block. DSC (supplemental information, **Figure 2-62**) reveals two T_g, one at –27 °C corresponding to the PECH block and one at 74 °C corresponding to the PS block. DOSY was also performed on this sample and the resulting spectrum is consistent with block co polymer formation (SI, **Figure 2-63**). Therefore, vinyl-block-epoxide polymers can be synthesized through relatively simple means that are accessible to non-experts at polymer synthesis.



Figure 2-8 PMMA-block-PECH synthetic route.



Figure 2-9 SEC traces (RI) of RAFT synthesized PMMA (right, red curve) and P(MMA-*b*-ECH) (left, blue curve). The M_n and D was determined to be 6.3 kg/mol and 1.13 (PMMA) and 18.4 kg/mol and 1.05 (P(MMA-*b*-ECH)).



Figure 2-10. ¹H NMR spectra in CDCl₃ of RAFT synthesized PMMA (c), thiol-end terminated PMMA (b), and P(MMA-*b*-ECH) (a). The peak associated with the benzyl end group from the RAFT agent (*cf.*, c) disappears after the aminolysis step (*cf.*, b), which reveals a free thiol.

In conclusion, four different thio-aluminum compounds (SAls) were synthesized and their efficacy as initiators for epoxide polymerizations was investigated. SAl initiators performed similarly to other recently reported Al-based initiators for epoxide polymerizations. SAl initiators resulted in the living polymerizations with controlled molecular weight, low dispersity, and were tolerant to the epoxide functional group. Polymer end group was tuned through the thiol ligand used in the SAl synthesis and was confirmed through both ¹H NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). Polymerization kinetics were investigated and found to depend on catalyst concentration and SAl end group. Finally, we synthesized poly(methyl methacrylate-*b*-epichlorohydrin) (P(MMA-*b*-ECH)) by combining the traditional RAFT polymerization technique with our SAl initiators, allowing for facile synthesis of vinyl-*b*-epoxide copolymers. This technique allows us to further tune polyether chemistry by giving us access to the vast array of thiol compounds that can act as end groups as well as facilitates the synthesis of block copolymers from disparate monomer classes.

2.4 Supporting information



Figure 2-11 ¹H NMR spectroscopy of BnSAlMe₂. ¹H NMR (500 MHz, Chloroform-d) δ 7.38 – 7.21 (m, 5H, <u>Ph</u>CH₂S-Al(CH₃)₂), 3.91 (s, 2H, PhC<u>H₂S-Al(CH₃)₂), -0.43 (s, 6H, PhCH₂S-Al(C<u>H₃)₂)</u>.</u>



ppm Figure 2-12 ¹³C NMR spectrum of BnSAlMe₂. ¹³C NMR(126 MHz, CD₂Cl₂) δ 141.46, 128.56, 127.97, 126.89 <u>Ph</u>CH₂S-Al(CH₃)₂, 32.00 Ph<u>C</u>H₂S-Al(CH₃)₂, 28.78 PhCH₂S-Al(<u>C</u>H₃)₂.



Figure 2-13 Carbon labeling scheme for BnSAlMe₂. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1 for BnSAlMe₂.



Figure 2-14 The Unit structure of dimethyl aluminum bound to benzyl thiolate, consistent with trimethyl aluminum reacting with the benzyl mercaptan. This unit, we propose, defines our initiator for epoxide polymerizations. The entire crystal structure reveals these individual units to be datively bound to adjacent units in a linear chain.



Figure 2-15 Plot of the $-\ln([ECH]/[ECH]0)$ over time for the polymerization of ECH with BnSAl and 1 eq of NAl showing a linear slope consistent with a living polymerization. $r^2 = 0.96$.



Figure 2-16 ¹H NMR spectroscopy for ECH polymerizations with just NAl after 7 days which shows no conversion to PECH. ¹H NMR (500 MHz, Chloroform-d) δ 3.62 – 3.50 (m, 2H, ECH OCH₂CH(CH₂Cl)), 3.22 (dddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.88 (ddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.67 (dd, 1H, ECH OCH₂CH(CH₂Cl)).



Figure 2-17 ¹H NMR spectroscopy for ECH polymerizations with just BnSAlMe₂ after 7 days which shows slow conversion (ca. 10% after 7 day). ¹H NMR (500 MHz, Chloroform-d) δ 3.77-3.49 (bm, PECH, -OCH₂CH(CH₂Cl)O-), 3.62 – 3.49 (m, 2H, ECH OCH₂CH(CH₂Cl)), 3.22 (dddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.88 (ddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.67 (dd, 1H, ECH OCH₂CH(CH₂Cl)).


Figure 2-18 ¹H NMR spectroscopy for ECH polymerizations with benzyl mercaptan (ligand) and NAl after 7 days which shows no conversion to PECH. ¹H NMR (500 MHz, Chloroform-d3.62 – 3.50 (m, 2H, ECH OCH₂CH(CH₂Cl)), 3.22 (dddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.88 (ddd, 1H, ECH OCH₂CH(CH₂Cl)), 2.67 (dd, 1H, ECH OCH₂CH(CH₂Cl)).



Figure 2-19 RI trace of targeted 30k PECH synthesized by BnSAlMe₂ initiator. The M_n is determined to be 30.7 with D = 1.17.



Figure 2-20 DSC analysis of targeted 30k PECH with BnSAlMe₂. The data from the second heating curve were collected which reveals one Tg at -26 °C.



Figure 2-21 ¹H NMR spectroscopy of 30K PECH treated with 1 M HCl in MeOH. This is magnified ¹H NMR to verify benzyl signal loss. ¹H NMR (500 MHz, Chloroform-d) δ 3.83-3.39 (bm, -OCH₂CH(CH₂Cl)O-).



Figure 2-22 Plot of normalized ECH concentration over time with BnSAlMe₂ initiator and 0.25 eq. of NAl catalyst. Monomer concentration was monitored via ¹H NMR spectroscopy and the rate of reaction calculated based on it ($k_{obs} = 5.06 \times 10^{-6} \pm 5.54 \times 10^{-7} \text{ s}^{-1}$). Sigmoidal shape of conversion curve for 0.25 eq. of NAl can be seen in this figure which is related to induction period. The k_{obs} is calculated using the data collected after the induction period, where conversion is first order in monomer.



Figure 2-23 Plot of normalized ECH concentration over time with BnSAlMe₂ initiator and 0.5 eq. of NAL catalyst. Monomer concentration was monitored via ¹H NMR spectroscopy, and the rate of reaction calculated based on it ($k_{obs} = 2.34 \times 10^{-5} \pm 2.21 \times 10^{-6} \text{ s}^{-1}$). Sigmoidal shape of conversion curve for 0.5 eq. of NAl can be seen in this figure which is related to induction period. The k_{obs} is calculated using the data collected after the induction period, where conversion is first order in monomer.



Figure 2-24 Plot of normalized ECH concentration over time with BnSAlMe₂ initiator and 2 eq. of NA1. Monomer concentration was monitored via ¹H NMR spectroscopy. Full conversion was achieved in *ca*. 10 hours with the combined catalyst and initiator system, with $k_{obs} = 1.91 \times 10^{-4} \pm 5.79 \times 10^{-6} \text{ s}^{-1}$.



Figure 2-25 Plot of the $-\ln([ECH]/[ECH]_0)$ over time for the polymerization of ECH with BnSAl and 2 equivalents of catalyst showing a linear slope consistent with a living polymerization. $r^2 = 0.96$.



Figure 2-26 RI trace of targeted 15k PECH synthesized by BnSAlMe₂ initiator. The M_n is determined to be 17.7 with D = 1.37.



Figure 2-27 RI trace of targeted 50k PECH synthesized by BnSAlMe₂ initiator. The M_n is determined to be 49.4 with D = 1.28.



Figure 2-28 RI trace of targeted 70k PECH synthesized by BnSAlMe₂ initiator. The M_n is determined to be 75.7 with D = 1.25.



Figure 2-29 RI trace of targeted 100k PECH synthesized by BnSAlMe₂ initiator. The M_n is determined to be 94.6 with D = 1.28.



Figure 2-30 RI trace of targeted 30k PBO synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 23.6 with D = 1.16.



Figure 2-31 RI trace of targeted 100k PBO synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 80.2 with D = 1.02.



Figure 2-32 RI trace of targeted 30k PPO synthesized by $PrSAlMe_2$ initiator. The M_n is determined to be 23.5 with D = 1.17.



Figure 2-33 RI trace of targeted 30k PPO synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 38.9 with D = 1.04.



Figure 2-34 RI trace of targeted 100k PPO synthesized by $BnSAlMe_2$ initiator. The M_n is determined to be 80.1 with D = 1.02.



Figure 2-35 DSC analysis of targeted 30k PPO with BnSAlMe₂. The data from the second heating curve were collected which reveals one T_g at -70 °C.



Figure 2-36 DSC analysis of targeted 30k PBO with BnSAlMe₂. The data from the second heating curve were collected which reveals one T_g at -73 °C.



Figure 2-37 ¹H NMR spectroscopy of targeted 30K poly(allyl glycidyl ether) (PAGE) with BnSAlMe₂. ¹H NMR (500 MHz, Chloroform-d) δ 5.88 (m, –O–CH₂–C<u>H</u>=CH₂), 5.27-5.14 (doublet of doublets, –O–CH₂–CH=CH₂), 3.98 (d, –O–C<u>H</u>₂–CH=CH₂), 3.75-3.42 (bm, –O–C<u>H</u>₂–C<u>H</u>(C<u>H</u>₂–O–CH₂–CH=CH₂)–O–).



Figure 2-38 ¹³C NMR spectroscopy of targeted 30K poly(allyl glycidyl ether) (PAGE) with BnSAlMe₂. ¹³C NMR (126 MHz, Chloroform-d) δ 134.93 (-O-CH₂-<u>C</u>H=CH₂), 116.74 (-O-CH₂-CH=<u>C</u>H₂), 78.89 (-O-CH₂-<u>C</u>H(CH₂-O-CH₂-CH=CH₂)-O-), 72.26 (-O-<u>C</u>H₂-CH=CH₂), 70.25-69.84 (-O-<u>C</u>H₂-CH(<u>C</u>H₂-O-CH₂-CH=CH₂)-O-, m), 69.74 (-O-<u>C</u>H₂-CH(CH₂-O-CH₂-CH=CH₂)-O-, rrm or mrr).



Figure 2-39 DSC analysis of Targeted 30k PAGE with compound BnSAlMe₂. The data from the second heating curve were collected which reveals one T_g at -76 °C.



Figure 2-40 RI trace of targeted 30k PAGE synthesized with BnSAlMe₂. The M_n is determined to be 29.6 Kg/mol with D = 1.45. The first modal peak is due to aggregation of polymer in presence of Al trace.



Figure 2-41 ¹H NMR spectrum of PrSAlMe₂.¹H NMR (500 MHz, Chloroform-d) δ 2.62 (m, 2H, CH₃CH₂CH₂S-Al(CH₃)₂), 1.65 (dq, 2H, CH₃CH₂CH₂S-Al(CH₃)₂), 1.04-0.95 (m, 3H, CH₃CH₂CH₂S-Al(CH₃)₂), -0.49 (S, 6H, CH₃CH₂CH₂S-Al(CH₃)₂).



Figure 2-42 ¹³C NMR spectrum of PrSAlMe₂ ¹³C NMR (126 MHz, Chloroform-d) δ 30.33 CH₃CH₂CH₂S-Al(CH₃)₂, 25.97 CH₃CH₂CH₂S-Al(CH₃)₂, 13.15 CH₃CH₂CH₂S-Al(CH₃)₂, -9.21 CH₃CH₂CH₂S-Al(CH₃)₂.



Figure 2-43 ¹H NMR spectrum of cPenSAlMe₂. ¹H NMR (500 MHz, Chloroform-d) δ 3.39 – 3.33 (m, 1H, cyclopentane -C<u>H</u>-), 2.10 – 1.99 (m, 2H, cyclopentane -C<u>H</u>₂-C<u>H</u>₂-), 1.83 – 1.73 (m, 2H, cyclopentane -C<u>H</u>₂-C<u>H</u>₂-), 1.62–1.53 (m, 4H, cyclopentane -C<u>H</u>₂-C<u>H</u>₂-), -0.49 (s, 6H, cyclopentane-S-Al(C<u>H</u>₃)₂).



Figure 2-44 ¹H ¹³C NMR spectrum of cPenSAlMe₂ ¹³C NMR (126 MHz, Chloroform-d) δ 30.33 (cyclopentane -<u>C</u>H-), 25.97 (cyclopentane -<u>C</u>H₂-<u>C</u>H₂-), 13.15 (cyclopentane -<u>C</u>H₂-<u>C</u>H₂-), -9.21 (cyclopentane-S-Al(<u>C</u>H₃)₂).



Figure 2-45 ¹H NMR spectrum of ClBnSAlMe₂. ¹H NMR (500 MHz, Chloroform-d) δ 7.34 – 7.22 (m, 4H, (Cl)<u>Ph</u>CH₂S-Al(CH₃)₂), 3.89 (s, 2H, (Cl)PhC<u>H₂S-Al(CH₃)₂), -0.45 (s, 6H, (Cl)PhCH₂S-Al(C<u>H₃)₂)</u>.</u>



Figure 2-46 ¹³C NMR spectrum of ClBnSAlMe₂. ¹³C NMR (126 MHz, Chloroform-d) δ 127.50, 126.84 (Cl)<u>Ph</u>CH₂S-Al(CH₃)₂, 51.18 (Cl)Ph<u>C</u>H₂S-Al(CH₃)₂, 26.37 (Cl)PhCH₂S-Al(<u>C</u>H₃)₂.



Figure 2-47 RI trace of targeted 30k PECH synthesized by PrSAlMe₂ initiator. The M_n is determined to be 30.2 with D = 1.24.



Figure 2-48 RI trace of targeted 30k PECH synthesized by cPenSAlMe₂ initiator. The M_n is determined to be 29.3 with D = 1.25.



Figure 2-49 RI trace of targeted 30k PECH synthesized by ClBnSAlMe₂ initiator. The M_n is determined to be 30.9 with D = 1.28.



Figure 2-50 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The triply charged ion with m/z 1610.5194 [M+(NH₄)₃]³⁺ corresponds to a neutral mass of 4777.4568 (1610.5194 * 3 – 3 * 18.0338) which is consistent with a molecule containing 81 total propylene oxide units and a propylthiol end group (expected mass = 4777.426, 6.4 ppm mass error). The next abundant signal at m/z 1629.8662 corresponds to a neutral mass of 4835.4972, which is 58 Da heavier and represents one additional propylene oxide repeating unit.



Figure 2-51 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The doubly charged ion with m/z 1386.0093 $[M+(NH_4)_2]^{2+}$ corresponds to a neutral mass of 2735.951 (1386.0093 * 2 – 2 * 18.0338) which is consistent with a molecule containing 45 total propylene oxide units and a BnS end group (expected mass = 2735.919, 11.7 ppm mass error). The next abundant signal at m/z 1415.0305 corresponds to a neutral mass of 2793.9934, which is 58 Da heavier and represents one additional propylene oxide repeating unit.



Figure 2-52 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The doubly charged ion with m/z 1896.2792 $[M+(NH_4)_2]^{2+}$ corresponds to a neutral mass of 3756.5252 (1896.2964 * 2 – 2 * 18.0338) which is consistent with a molecule containing 62 total propylene oxide units and a CIBnS end group (expected mass = 3756.591, -17.5 ppm mass error). The next abundant signal at m/z 1925.3075 corresponds to a neutral mass of 3814.5474, which is 58 Da heavier and represents one additional propylene oxide repeating unit.



Figure 2-53 Samples were analyzed by electrospray ionization in a solvent containing ammonium formate to facilitate ionization as ammonium adducts. Panel A shows the positive ion mode ESI spectrum with the inset showing the results of a deconvolution of charge states to show the neutral mass distribution of the polymer sample. Focusing on the higher m/z range where the charge states are lowest (panel B), the neutral mass can easily be calculated. The doubly charged ion with m/z 1897.3320 [M+(NH4)2]2+ corresponds to a neutral mass of 3758.5964 (1897.3320 * 2 - 2 * 18.0338) which is consistent with a molecule containing 63 total propylene oxide units and a cyPenS end group (expected mass = 3758.688, 24.4 ppm mass error). The next abundant signal at m/z 1926.3486 corresponds to a neutral mass of 3816.6296, which is 58 Da heavier and represents one additional propylene oxide repeating unit.



Figure 2-54 MALDI-TOF analysis of 5kg/mol PPO with 4 different initiators (A). The X-axis is the same for all four plots and is the mass range (in m/z). The mass distribution with MALDI-TOF matches with ESI-MS data. (B) Expanded prospective of MALDI-TOF. The difference between each subsequent peak is equal to mass of one propylene oxide. The order of polymers are the same for A and B.



Figure 2-55 Fit of BSL to the conversion as a function of the normalized molar concentration of each monomer ([M]/[M]₀). From BSL, the reactivity ratios for ECH (r_{ECH}) and PO (r_{PO}) were determined to be $r_{ECH} = 2.56 \pm 0.29$ and $r_{PO} = 0.44 \pm 0.03$, which suggests a gradient copolymer with ECH preferentially adding over PO.



Figure 2-56 600 MHz 2D Figure 2-57 DOSY NMR spectra obtained at 298 K in Chloroform-d solution of the PECH-b-PPO. ¹H NMR (600 MHz, Chloroform-d) δ 3.70 (bm, (–O–C<u>H</u>₂–C<u>H</u> (C<u>H</u>₂–Cl)–O– and –O–C<u>H</u>₂ (CH₃)-O-), 1.13 (m, -CH₃).



Figure 2-58 ¹³C NMR spectroscopy of P(MMA-*b*-ECH). ¹³C NMR (126 MHz, cdcl₃) δ 178.12-177.00 (-CH₂-C(CH₃)(<u>C</u>OOCH₃)-), 81.58-67.83 (-O-CH₂-<u>C</u>H(CH₂-Cl)-O-), 51.84 (-CH₂-<u>C</u>(CH₃)(COOCH₃)-), 44.89 (-CH₂-C(CH₃)(COO<u>C</u>H₃)-), 45.93-45.32 (H-T diads, -O-<u>C</u>H₂-CH(CH₂-Cl)-O-), 44.89-44.54 (-<u>C</u>H₂-C(CH₃)(COOCH₃)-), 43.87-42.63 (H-H and T-T diads, -O-<u>C</u>H₂-CH(CH₂-Cl)-O-), 25.07 (-O-CH₂-CH(<u>C</u>H₂-Cl)-O-), 18.70-16.41(-CH₂-C(CH₃)(COO<u>C</u>H₃)-). Different regiostructures of ECH monomer in the PECH block can be seen in this spectrum due to head-to-tail, head-to-head, and tail-to-tail diads. In H-T diads, γ gauche effect on the carbon of CH₂ (-O-<u>C</u>H₂-CH(CH₂-Cl)-O-), cause related signals to be shifted and this is why two sets of peaks are observed in the ¹³C NMR spectrum. Peaks at 29.77, 19.78, and 9.42 are corresponded to hexanes.



Figure 2-59 600 MHz 2D DOSY NMR spectra obtained at 298 K in Chloroform-d solution of the PMMA-b-PECH. ¹H NMR (600 MHz, Chloroform-d) δ 3.99–3.62 (bm, -OC<u>H₂CH(CH₂Cl)O-</u>), 3.63-3.56 (bm,-CH₂C(CH₃)(COOC<u>H₃</u>)-), 2.19-1.66 (bm, -C<u>H₂C(CH₃)(COOCH₃)-).</u>



Figure 2-60 ¹H NMR spectroscopy of thiol end-terminated PMMA without AlMe₃, in the presence of ECH and NAl, at 50°C after 7 days. 1H NMR (500 MHz, Chloroform-d) δ 3.52-3.48 (bm-CH₂-C(CH₃)(COOCH₃)-), 3.47–3.42 (d, J = 5.4 Hz, 2H, ECH, OCH₂CH(CH₂Cl)), 3.22 (tdd, J = 5.4, 3.9, 2.5 Hz, 1H, ECH, OCH₂CH(CH₂Cl)), 2.88 (dd, J = 4.8, 3.9 Hz, 1H, ECH, OCH₂CH(CH₂Cl)), 2.67 (dd, J = 4.8, 2.5 Hz, 1H, ECH OCH₂CH(CH₂Cl)), 2.03-1.59 (bm,-CH₂-C(CH₃)(COOCH₃)-), 1.31-0.72 (bm -CH₂- C(CH₃)(COOCH₃)-). The only NAl peaks correspond to Me groups on Al below zero but Et groups are overlapping with other peaks and cannot be specified.



Figure 2-61 DSC analysis of P(MMA-b-ECH). The data from the second heating curve were collected which reveals a broad T_g centered at 0 °C.



Figure 2-62 ¹³C NMR spectroscopy of P(styrene-*b*-ECH) which is consistent with a regioregular PECH block. ¹³C NMR (126 MHz, cdcl₃) δ 145.21(-CH₂-CH(Ph,<u>C</u>)-) 128.00-127.11 (-CH₂-CH(Ph,<u>C</u>H)-), 125.68-125.25 (-CH₂-CH(Ph,<u>C</u>H)-), 78.97 (-O-CH₂-<u>C</u>H(CH₂Cl)-O-), 69.33(-O-<u>C</u>H₂-CH(CH₂Cl)-O-), 43.57 (-O-CH₂-CH(<u>C</u>H₂Cl)-O-), 44.46(-CH₂-<u>C</u>H(Ph)-), 40.21(-<u>C</u>H₂-CH(Ph)-) 29.59(-<u>C</u>H₂-Cl).



Figure 2-63 DSC analysis of P(styrene-b-ECH). The data from the second heating curve were collected which reveals two T_g , one at -27 °C corresponding to the PECH block and one at 74 °C corresponding to the PS block.



Figure 2-64 600 MHz 2D DOSY NMR spectra obtained at 298 K in Chloroform-d solution of the PS-b-PECH. ¹H NMR (600 MHz, Chloroform-d) δ 7.25- 6.30 (bm, -CH₂-CH(<u>Ph</u>)-), 3.77- 3.49 (broad m, -OCH₂CH(CH₂Cl)O-), 2.07-1.10 (bm, -CH₂-CH(Ph)-).



Figure 2-65 ¹H NMR spectroscopy of (P(styrene-*b*-ECH). ¹H NMR (500 MHz, cdcl₃) δ 7.25-6.30 (bm, -CH₂-CH(<u>Ph</u>)-), 3.77- 3.49 (bm, -OC<u>H₂CH(CH₂Cl)</u>O-), 2.07-1.10 (bm, -C<u>H₂-CH(Ph)-)</u>.



Figure 2-66 ¹H NMR spectroscopy of targeted 30K PECH with BnSAlMe₂ initiator. ¹H NMR (500 MHz, Chloroform-d) δ 3.83-3.39 (bm, -OC<u>H₂CH(CH₂Cl)O-)</u>.



Figure 2-67 ¹³C NMR spectroscopy of targeted 30K PECH with BnSAlMe₂. ¹³C NMR (126 MHz, cdcl3) δ 79.18-79.09 (-O-CH₂-<u>C</u>H(CH₂-Cl)-O-), 69.80 (-O-<u>C</u>H₂-CH(CH₂-Cl)-O-m), 69.50 (-O-<u>C</u>H₂-CH(CH₂-Cl)-O-rrm or mrr)), 43.80 (-CH₂-Cl).



Figure 2-68 ¹H NMR spectroscopy of targeted 30K PPO with BnSAlMe₂ initiator. ¹H NMR (500 MHz, Chloroform-d) δ 3.80 – 3.17 (bm, –O–C<u>H</u>₂–C<u>H</u>(CH₃)–O–), 1.12 (m, -CH₃).



Figure 2-69 ¹³C NMR spectroscopy of targeted 30K PPO with BnSAlMe₂ initiator. ¹³C NMR (126 MHz, cdcl₃) δ 75.89 (-O-CH₂-<u>C</u>H(CH₃)-O-, mm), 75.68 (-O-CH₂-<u>C</u>H(CH₃)-O-, mr + rm), 75.48 (-O-CH₂-<u>C</u>H(CH₃)-O-, rr), 73.71 (-O-<u>C</u>H₂-CH(CH₃)-O-, m), 73.16 (-O-<u>C</u>H₂-CH(CH₃)-O-, rrm or mrr), 17.81 (-<u>C</u>H₃).



Figure 2-70 ¹H NMR spectroscopy of targeted 30K PBO with BnSAlMe₂ initiator. ¹H NMR (500 MHz, Chloroform-d) δ 3.68 – 3.25 (bm, –O–C<u>H₂</u>–C<u>H</u>(CH₂–CH₃)–O–), 1.68 – 1.37 (m, C<u>H₂</u>–CH₃), 0.91 (t, –CH₂–C<u>H₃</u>).



Figure 2-71 ¹³C NMR spectroscopy of targeted 30K PBO with BnSAlMe₂ initiator. ¹³C NMR (126 MHz, cdcl3) δ 80.84-80.42 (-O-CH₂-<u>C</u>H(CH₂-CH₃)-O-), 72.37 (-O-<u>C</u>H₂-CH(CH₂-CH₃)-O-, m), 71.53 (-O-<u>C</u>H₂-CH(CH₂-CH₃)-O-, rrm or mrr)), 24.72 (-<u>C</u>H₂-CH₃), 9.76 (-CH₃).



Figure 2-72 ¹H NMR spectroscopy of targeted 30K PECH with PrSAlMe₂ initiator. ¹H NMR (500 MHz, Methylene Chloride-d₂) δ 3.80 – 3.51 (bm, -OC<u>H₂CH(CH₂Cl)O-)</u>.



Figure 2-73 ¹H NMR spectroscopy of targeted 30K PECH with ClBnSAlMe₂ initiator. ¹H NMR (500 MHz, Methylene Chloride-d₂) δ 3.80 – 3.51 (bm, -OC<u>H₂CH(CH₂Cl)O-)</u>.



Figure 2-74 ¹H NMR spectroscopy of targeted 30K PECH with cPenSAlMe₂ initiator. ¹H NMR (500 MHz, Methylene Chloride-d₂) δ 3.80 – 3.51 (bm, -OC<u>H₂CH(CH₂Cl)O-)</u>.



Figure 2-75 ¹H NMR spectroscopy of P(MMA-*b*-ECH). ¹H NMR (500 MHz, Methylene Chloride-d₂) δ 3.99–3.62 (bm, -OC<u>H₂CH(CH₂Cl)O-</u>), 3.63-3.56 (bm, -CH₂C(CH₃)(COOC<u>H₃</u>)-), 2.19-1.66 (bm, -C<u>H₂C</u>(CH₃)(COOCH₃)-), 1.67 – 0.58 (bm, -CH₂C(CH₃)(COOC<u>H₃</u>)-).



Figure 2-76 DSC analysis of P(PO-grad-ECH). The data from the second heating curve were collected which reveals one T_g , one at -41 °C.



Figure 2-77 DSC analysis of P(ECH-b-PO). The data from the second heating curve were collected which reveals two T_g , one at -30 °C corresponding to the PECH block and one at -67 °C corresponding to the PO block.



Figure 2-78 RI trace of targeted P(ECH-grad-PO). The M_n is determined to be 29.0 kg/mol with D = 1.28.



Figure 2-79 RI trace of targeted P(ECH-b-PO). The M_n is determined to be 33.4 kg/mol with D = 1.27.

BIBLIOGRAPHY

BIBLIOGRAPHY

- Scharfenberg, M.; Hofmann, S.; Preis, J.; Hilf, J.; Frey, H. Rigid Hyperbranched Polycarbonate Polyols from CO₂ and Cyclohexene Based Epoxides. *Macromolecules* 2017, 50 (21), 6088–6097.
- (2) Hilf, J.; Schulze, P.; Seiwert, J.; Frey, H. Controlled Synthesis of Multi-Arm Star Polyether–Polycarbonate Polyols Based on Propylene Oxide and CO2. *Macromol. Rapid Commun.* 2014, 35 (18), 198–203.
- (3) Xue, Z.; He, D.; Xie, X. Poly(ethylene oxide)-based electrolytes for lithium-ion batteries. J. Mater. Chem. A 2015, 3 (7), 19218–19253.
- (4) Rodriguez, C. G.; Chwatko, M.; Park, J.; Bentley, C. L.; Freeman, B. D.; Lynd, N. A. Compositionally Controlled Polyether Membranes via Mono(μalkoxo)bis(alkylaluminum)-Initiated ChainGrowth Network Epoxide Polymerization: Synthesis and Transport Properties. *Macromolecules* 2020, 53 (7), 1191-1198.
- (5) Luo, S.; Stevens, K. A.; Park, J. S.; Moon, J. D.; Liu, Q.; Freeman, B. D.; Guo, R. Highly CO2-Selective Gas Separation Membranes Based on Segmented Copolymers of Poly(Ethylene oxide) Reinforced with Pentiptycene-Containing Polyimide Hard Segments. ACS Appl. Mater. Interfaces 2016, 8 (26), 2306–2317.
- (6) Patterson, A. L.; Wenning, B.; Rizis, G.; Calabrese, D. R.; Finlay, J. A.; Franco, S. C.; Zuckermann, R. N.; Clare, A. S.; Kramer, E. J.; Ober, C. K.; Segalman, R. A. Role of Backbone Chemistry and Monomer Sequence in Amphiphilic Oligopeptide- and OligopeptoidFunctionalized PDMS- and PEO-Based Block Copolymers for Marine Antifouling and Fouling Release Coatings. *Macromolecules* 2017, 50 (6), 2656–2667.
- (7) Kang, T.; Banquy, X.; Heo, J.; Lim, C.; Lynd, N. A.; Lundberg, P.; Oh, D. X.; Lee, H.-K.; Hong, Y.-K.; Hwang, D. S.; Waite, J. H.; Israelachvili, J. N.; Hawker, C. J. Mussel-Inspired Anchoring of Polymer Loops That Provide Superior Surface Lubrication and Antifouling Properties. ACS Nano 2016, 10 (21), 930–937.
- (8) Thomas, A.; Müller, S. S.; Frey, H. Beyond Poly(ethylene glycol): Linear Polyglycerol as a Multifunctional Polyether for Biomedical and Pharmaceutical Applications. *Biomacromolecules* 2014, 15 (7), 1935–1954.
- (9) Obermeier, B.; Frey, H. Poly(ethylene glycol-co-allyl glycidyl ether)s: A PEG-Based Modular Synthetic Platform for Multiple Bioconjugation. *Bioconjugate Chem.* 2011, 22 (8), 436–444.
- (10) Obermeier, B.; Wurm, F.; Mangold, C.; Frey, H. Multifunctional Poly(ethylene glycol)s. *Angew. Chem., Int. Ed.* **2011**, 50 (14), 7988–7997.

- (11) Brocas, A.-L.; Mantzaridis, C.; Tunc, D.; Carlotti, S. Polyether synthesis: From activated or metal-free anionic ring-opening polymerization of epoxides to functionalization. Prog. *Polym. Sci.* 2013, 38 (2), 845–873.
- (12) Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F. R.; Frey, H. Polymerization of Ethylene Oxide, Propylene Oxide, and Other Alkylene Oxides: Synthesis, Novel Polymer Architectures, and Bioconjugation. *Chem. Rev.* 2016, 116 (17), 2170–2243.
- (13) Lee, B. F.; Wolffs, M.; Delaney, K. T.; Sprafke, J. K.; Leibfarth, F. A.; Hawker, C. J.; Lynd, N. A. Reactivity Ratios and Mechanistic Insight for Anionic Ring-Opening Copolymerization of Epoxides. *Macromolecules* **2012**, 45 (7), 3722–3731.
- (14) Danner, A.-K.; Leibig, D.; Vogt, L.-M.; Frey, H. Monomeractivated Copolymerization of Ethylene Oxide and Epichlorohydrin: In Situ Kinetics Evidences Tapered Block Copolymer Formation. Chin. J. *Polym. Sci.* 2019, 37 (11), 912–918.
- (15) Wurm, F.; Nieberle, J.; Frey, H. Double-Hydrophilic LinearHyperbranched Block Copolymers Based on Poly(ethylene oxide) and Poly(glycerol). *Macromolecules* 2008, 41 (9), 1184–1188.
- (16) Vandenberg, E. J. Organometallic catalysts for polymerizing monosubstituted epoxides. J. *Polym. Sci.* **1960** (24), 47, 486–489.
- (17) Morris, L. S.; Childers, M. I.; Coates, G. W. Bimetallic Chromium Catalysts with Chain Transfer Agents: A Route to Isotactic Poly(propylene oxide)s with Narrow Dispersities. *Angew. Chem., Int. Ed.* 2018, 57 (7), 5731–5734.
- (18) Asano, S.; Aida, T.; Inoue, S. 'Immortal' polymerization. Polymerization of epoxide catalysed by an aluminium porphyrinalcohol system. J. Chem. Soc., Chem. Commun. 1985 (8), 17, 1148–1149.
- (19) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. Lewis Acid-Assisted Anionic Ring-Opening Polymerization of Epoxide by the Aluminum Complexes of Porphyrin, Phthalocyanine, Tetraazaannulene, and Schiff Base as Initiators. *Macromolecules* 1994, 27 (4), 2013–2018.
- (20) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. Stereoselective Epoxide Polymerization and Copolymerization. *Chem. Rev.* 2014, 114 (19), 8129–8152.
- (21) Widger, P. C. B.; Ahmed, S. M.; Hirahata, W.; Thomas, R. M.; Lobkovsky, E. B.; Coates, G. W. Isospecific polymerization of racemic epoxides: a catalyst system for the synthesis of highly isotactic polyethers. *Chem. Commun.* 2010, 46 (27), 2935–2937.
- (22) Childers, M. I.; Vitek, A. K.; Morris, L. S.; Widger, P. C. B.; Ahmed, S. M.; Zimmerman, P. M.; Coates, G. W. Isospecific, Chain Shuttling Polymerization of Propylene Oxide Using a Bimetallic Chromium Catalyst: A New Route to Semicrystalline Polyols. *J. Am. Chem. Soc.* 2017, 139 (6), 11048–11054.
- (23) Ghosh, S.; Lund, H.; Jiao, H.; Mejía, E. Rediscovering the Isospecific Ring-Opening Polymerization of Racemic Propylene Oxide with Dibutylmagnesium. *Macromolecules* 2017, 50, 1245–1250.
- (24) Rodriguez, C. G.; Ferrier, R. C.; Helenic, A.; Lynd, N. A. RingOpening Polymerization of Epoxides: Facile Pathway to Functional Polyethers via a Versatile Organoaluminum Initiator. *Macromolecules* 2017, 50 (18), 3121-3127.
- (25) Ferrier, R. C.; Imbrogno, J.; Rodriguez, C. G.; Chwatko, M.; Meyer, P. W.; Lynd, N. A. Four-fold increase in epoxide polymerization rate with change of alkyl-substitution on mono-[small mu]- oxo-dialuminum initiators. *Polym. Chem.* 2017, 8 (3), 4503–4511.
- (26) Imbrogno, J.; Ferrier, R. C.; Wheatle, B. K.; Rose, M. J.; Lynd, N. A. Decoupling Catalysis and Chain-Growth Functions of Mono(μalkoxo)bis(alkylaluminums) in Epoxide Polymerization: Emergence of the N–Al Adduct Catalyst. ACS Catal. 2018, 8 (2), 8796–8803.
- (27) You, Y.-Z.; Manickam, D. S.; Zhou, Q.-H.; Oupicky, D. A Versatile Approach to Reducible Vinyl Polymers via Oxidation of Telechelic Polymers Prepared by Reversible Addition Fragmentation Chain Transfer Polymerization. *Biomacromolecules* 2007, 8 (12), 2038–2044.
- (28) Brandle, A.; Khan, A. Thiol⁻⁻epoxy 'click' polymerization: efficient construction of reactive and functional polymers. *Polym. Chem.* **2012**, 3 (12), 3224–3227.
- (29) Huang, C.-H.; Wang, F.-C.; Ko, B.-T.; Yu, T.-L.; Lin, C.-C. Ring-Opening Polymerization of ε-Caprolactone and l-Lactide Using Aluminum Thiolates as Initiator. *Macromolecules* 2001, 34 (14), 356–361.
- (30) Brauer, D. J.; Stucky, G. D. Stereochemistry of polynuclear compounds of the main group elements. XI. Dimethyl(methylthiol)- aluminum, [(CH₃)₂AlSCH₃]_n, a new type of stereochemistry for an organoaluminum compound. *J. Am. Chem. Soc.* **1969**, 91 (7), 5462–5466.
- (31) Carlotti, S.; Labbe, A.; Rejsek, V.; Doutaz, S.; Gervais, M.; Deffieux, A. Living/Controlled Anionic Polymerization and Copolymerization of Epichlorohydrin with Tetraoctylammonium Bromide– Triisobutylaluminum Initiating Systems. *Macromolecules* 2008, 41 (13), 7058–7062.
- (32) Aida, T.; Mizuta, R.; Yoshida, Y.; Inoue, S. Polymerization of epoxides catalysed by metalloporphine. Die *Makromol. Chem.* **1981**, 182 (4), 1073–1079.

- (33) Ni, Q.; Yu, L. Synthesis of Novel Poly(ε-caprolactone)s Functionalized with a Thioester End-Group via a Living Ring Opening Polymerization and Their Application in Chemoselective Ligation with Compounds Containing a Cysteine Terminal. J. Am. Chem. Soc. 1998, 120 (2), 1645–1646.
- (34) Berger, M. N.; Grieveson, B. M. Kinetics of the polymerization of ethylene with a zieglernatta catalyst. I. Principal kinetic features. *Die Makromol. Chem.* **1965**, 83 (13), 80–99.
- (35) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. Well-Defined Ruthenium Olefin Metathesis Catalysts: Mechanism and Activity. J. Am. Chem. Soc. 1997, 119 (5), 3887–3897.
- (36) Wu, L.-C.; Yu, A.-F.; Zhang, M.; Liu, B.-H.; Chen, L.-B. DMC catalyzed epoxide polymerization: Induction period, kinetics, and mechanism. J. *Appl. Polym. Sci.* 2004, 92 (14), 1302–1309.
- (37) Huang, Y.-J.; Zhang, X.-H.; Hua, Z.-J.; Chen, S.-L.; Qi, G.-R. Ring-Opening Polymerization of Propylene Oxide Catalyzed by a Calcium-Chloride-Modified Zinc-Cobalt Double Metal-Cyanide Complex. *Macromol. Chem. Phys.* 2010, 211 (24), 1229–1237.
- (38) Walther, P.; Vogler, C.; Naumann, S. Ultrahigh-MolecularWeight Poly(propylene oxide): Preparation and Perspectives. *Synlett*, **2020**, 31(6), 641-647.
- (39) Billouard, C.; Carlotti, S.; Desbois, P.; Deffieux, A. "Controlled" High-Speed Anionic Polymerization of Propylene Oxide Initiated by Alkali Metal Alkoxide/Trialkylaluminum Systems. *Macromolecules*, **2004**, 37 (5), 4038–4043.
- (40) Labbe, A.; Carlotti, S.; Billouard, C.; Desbois, P.; Deffieux, A. Controlled High-Speed Anionic Polymerization of Propylene Oxide Initiated by Onium Salts in the Presence of Triisobutylaluminum. *Macromolecules* **2007**, 40 (9), 7842–7847.
- (41) Walther, P.; Krauß, A.; Naumann, S. Lewis Pair Polymerization of Epoxides via Zwitterionic Species as a Route to High-Molar-Mass Polyethers. *Angew. Chem., Int. Ed.* 2019, 58 (16), 10737–10741.
- (42) Thomas, R. M.; Widger, P. C. B.; Ahmed, S. M.; Jeske, R. C.; Hirahata, W.; Lobkovsky, E. B.; Coates, G. W. Enantioselective Epoxide Polymerization Using a Bimetallic Cobalt Catalyst. J. Am. Chem. Soc. 2010, 132 (29), 16520–16525.
- (43) Ferrier, R. C.; Pakhira, S.; Palmon, S. E.; Rodriguez, C. G.; Goldfeld, D. J.; Iyiola, O. O.; Chwatko, M.; Mendoza-Cortes, J. L.; Lynd, N. A. Demystifying the Mechanism of Regio- and Isoselective Epoxide Polymerization Using the Vandenberg Catalyst. *Macromolecules* 2018, 51 (19), 1777-1782.

- (44) Haaland, A.; Stokkeland, O.; Weidlein, J. The molecular structure of dimethylaluminium thiomethoxide dimer, [(CH₃)- ₂AlSCH₃]₂, as determined by gas phase electron diffraction. *J. Organomet. Chem.* **1975**, 94 (19), 353–360.
- (45) Szumacher, S.; Madura, I.; Zachara, J.; Kunicki, A. R. Cyclopentadienylaluminum thiolates synthesis and structure. *J. Organomet. Chem.* **2005**, 690 (27), 1125–1132.
- (46) Ortiz, R. A.; Lopez, D. P.; Cisneros, M. d. L. G.; Valverde, J. C. R.; Crivello, J. V. A kinetic study of the acceleration effect of substituted benzyl alcohols on the cationic photopolymerization rate of epoxidized natural oils. *Polymer* **2005**, 46 (18), 1535–1541.
- (47) Beckingham, B. S.; Sanoja, G. E.; Lynd, N. A. Simple and Accurate Determination of Reactivity Ratios Using a Nonterminal Model of Chain Copolymerization. *Macromolecules* 2015, 48 (7), 6922–6930.

Chapter 3. Investigation of Aluminum-based initiators for Propylene Sulfide (Co)Polymerization with Compositional and Architectural Control

3.1 Introduction

Poly(propylene sulfide) (PPS) is a versatile, non-toxic, sulfur-containing polymer that has widespread use in biomedical¹⁻³ and patterning^{4, 5} contexts. The sulfur in the polymer backbone can readily be converted to hydrophilic sulfone groups in the presence of oxidative species, making PPS ideal for targeted drug delivery.⁶ Additionally, PPS consisting of pure converted sulfone groups undergoes interesting solvent-mediated self-assembly.⁷ Sigwalt and co-workers demonstrated classical anionic polymerization of PS in the 1960's using sodium naphthalene as an initiator.⁸ Modern anionic synthesis of PPS utilizes thiolate anions as an initiator either produced directly from deprotonation of a thiol or via protected thiol ala acyl group transfer.⁶ While these methods are effective, they typically produce polymers with molecular weight *ca*. 10 kg/mol. Very recent work by Rumyantsev demonstrated PPS at molecular weights above 100 kg/mol at D < 1.4 using xanthates, but molecular weight control was not straightforward.⁹ Initiation from thiolates is robust, and several thiols with a variety of chemistries and structures are available for end group and / or architecture control. For instance, dithiols can be employed to create ABA co-polymers¹⁰ and multi-armed thiols^{11, 12} can be used to create star polymers. This architectural and chemical control over PPS, along with the ability of PPS to switch from a hydrophobic to hydrophilic character as well as PPS inherent biocompatibility has made it practically ubiquitous as a component in drug delivery schemes.

PPS is frequently paired with other biologically relevant polymers. PPS acts as the hydrophobic block in a block copolymer paired with a hydrophilic polymer, like poly(ethylene glycol) (PEG). Amphiphilic block copolymers consisting of PPS and another hydrophilic block have been used

87

to create vesicular^{13, 14} and micellar structures¹¹ through self-assembly that hold medicinal cargo, which can be released in the presence of oxidative species that causes the PPS block to become hydrophilic. Hubbell and Tirelli have develop synthetic methods for block-co-polymers containing PPS. Typically, either a macroinitiator^{6, 15, 16} or a coupling strategy¹⁶ is employed for block copolymer synthesis; in the former case the second polymer is polymerized from the first polymer and in the latter case two pre-formed polymers are coupled end to end (e.g., through a 'click' reaction). Both methods require multiple steps. Recently, Frey and co-workers¹⁷ demonstrated the use of a multifunctional initiator, cysteine, to synthesize copolymers of PPS and sarcosine of varying ratio by a protection / deprotection strategy for the cysteine. Wang and co-workers employed a combined RAFT and AROP polymerization strategy to copolymerize PPS with N-isopropylmethacrylamide (NIPMAM).¹⁸ However, this resulted in some incorporation of the NIPMAM into the PS block. Developing facile synthetic techniques that allow for synthesizing PS containing block copolymers, especially those with epoxides, through sequential addition of monomer would allow for finer control over copolymer physical properties and increase access to these materials.

Aside from block copolymers, copolymers containing both ethers and sulfur in the backbone have found use in optical and electronic applications.^{19, 20} Frequently, these polymers are produced through the alternating copolymerization of epoxides and sulfur containing species like carbonyl sulfide²¹ and carbon disulfide.²² Aside from alternating copolymers, limited compositional control over copolymers from epoxides and thiol containing monomers has been demonstrated. Episulfides in particular are difficult to copolymerize with epoxides due to the propensity of the episulfide to homopolymerize^{20, 23} resulting in block- instead of statistical-copolymers. While some patents exist involving statistical-copolymers of epoxides and

88

episulfides, they only achieve a small percentage (<10%) of epoxide incorporation.^{24, 25} Diversifying the epoxide monomers compatible with PS in copolymerization schemes will allow for new PPS materials with tunable or unique property sets.

In this work, we investigate our previously report SAl initiators²⁶ with NAl catalyst for PS and PS-co-epoxide polymerizations. We explore molecular weight control of PPS by tuning PS to initiator ratio and quantify this by size exclusion chromatography (SEC) and NMR spectroscopy. The influence of catalyst and initiator interaction on polymerization control and kinetics is characterized through ¹H NMR spectroscopy and SEC. Copolymerization of PS and epoxides are performed to determine polymer compositional control. Finally, we demonstrate both block and statistical copolymers and characterize these polymers through ¹H, ¹³C, and diffusion ordered NMR spectroscopy as well as SEC, differential scanning calorimetry (DSC), and small angle X-ray scattering (SAXS). Initiator chemistry was varied to control polymer architecture, and we synthesized both ABA copolymers and star (co)polymers. Synthesis of biomedically applicable poly(EG-*b*-PS) was achieved by the addition of PS to macroinitiator PEG. This work demonstrates methods that allow for the direct synthesis of PS-block-epoxide polymers as well as the statistical copolymerization of PS and epoxide, which has been difficult to achieve in the past.

3.2 Experimental section

3.2.1 Materials

Trimethylaluminum solution (AlMe₃, 2.0 M in hexane), triethylamine (TEA, ≥99.5%), benzyl mercaptan (99%), benzyl alcohol, 1-propane thiol (99%), 1,3-Propanedithiol (Sigma-Aldrich, 99%), pentaerythritol tetrakis(3-mercaptopropionate) (99%), and polyethylene glycol (5500 g/mol) were purchased from Sigma-Aldrich. CDCl₃ (Cambridge Analytica) was used without

any further purification. Hexanes (Sigma Aldrich, anhydrous, >99%) was used for initiator / catalyst purification in the glovebox. Methanol (MeOH, Fisher, Certified ACS), hexane (Fisher, Certified ACS), and dichloromethane (DCM, Fisher, Certified ACS) were used for washing the polymers. Propylene sulfide (PS, 96%, ACROS Organics), propylene oxide (PO, Sigma-Aldrich, GC, \geq 99.5%), and epichlorohydrin (ECH, Sigma-Aldrich, \geq 99%), were all used as received. All air and moisture-sensitive reactions were prepared under a dry nitrogen atmosphere inside a glovebox.

3.2.2 Characterization

¹H NMR spectroscopy was performed on a 500 MHz Varian NMR spectrometer at room temperature, and chemical shifts are reported in parts per million (ppm), referenced using the residual ¹H peak from the deuterated solvent. The structure of the compounds was determined by ¹³C NMR spectroscopy on a 126 MHz Varian NMR spectrometer. All diffusion ordered spectroscopy (DOSY) measurements were performed at 25 °C on a Varian Inova 600 spectrometer operating at 599.72 MHz and equipped with a 5 mm Z-gradient HCN inverse probe capable of producing gradients in the Z direction with a strength of 63 G/cm. All DOSY measurements were run using the dbppste pulse sequence with 128–160 scans and 20 increments with gradient strengths from 2.7 to 59.22 G/cm. The relaxation delay was set to 3 s, the diffusion delay to 24 ms, and the gradient length to 2.0 ms. Size-exclusion chromatography (SEC) was carried out on the Malvern OMNISEC system with an isocratic pump, degasser, and temperature-controlled column oven held at 35 °C containing 2 Viscotek 300 × 8.0 mm² columns (T3000 and T4000) with an exclusion limit of 400 kDa. Triple detection with light scattering, viscometer, and the refractive index has been used for the absolute molecular weight determination of the polymers. The reported M_n are all absolute molecular weights. Differential

scanning calorimetric (DSC) tests were conducted on a TA250 instrument with a heating rate of 10 °C/min under a N2 atmosphere, and the data from the second heating curve were collected. PPS homopolymer was analyzed by electrospray ionization with mass spectrometry (ESI-MS) in positive ion mode using a Waters Xevo G2XS Q-Tof mass spectrometer interfaced with a Waters Acquity UPLC. Five microlitres of a sample (diluted in 90% methanol containing 1 mM ammonium formate) was flow-injected (no UPLC column) using a mobile phase of 80% methanol and 20% 10 mM ammonium formate in water pumped at 0.2 mL/min. SAXS measurements were performed at the beamline 12-ID-B at Advanced Photon Source of Argonne National Laboratory with the x-ray energy of 13.3 keV with a two-dimensional (2-D) Pilatus 2M detector. The sample to detector distance was set to 2.0 m. In all measurements, the sample thickness was kept around 0.1 mm and the exposure time of 0.5 s. The scattering of the air has been measured as the background noise.

3.2.3 Synthesis of trimethylaluminum and triethylamine Adduct (NAI) In a reaction vial with a stir bar, 6.35 mL of anhydrous hexanes and 2.0 M AlMe₃ in hexane (6.35 mL, 12.7 mmol) were added and cooled to -78 °C. Then, triethylamine (1.5 mL, 10.7 mmol) was added dropwise into the vial. The solution was set to stir and warm to room temperature overnight. To crystallize the desired product, the solution was then directly cooled to -40 °C and the resultant crystals were washed three times with anhydrous hexanes (3 × 5 mL) and dried in vacuo. ¹H NMR (500 MHz, CDCl₃) δ 2.80 (q, 6H, 3(CH₃CH₂)N:Al(CH₃)₃), 1.18 (t, 9H, 3(CH₃CH₂)N:Al(CH₃)₃), -0.89 (s, 9H, 3(CH₃CH₂)N:Al(CH₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ 64.54 3(CH₃CH₂)N:Al(CH₃)₃), 47.78 3(CH₃CH₂)N:Al(CH₃)₃, 9.20 3(CH₃CH₂)N:Al(CH₃)₃).

91

3.2.4 Synthesis of (Benzylthio)dimethylaluminum (BnSAlMe₂),
(benzyloxy)dimethylaluminum (BnOAlMe₂) and dimethyl(propylthio)aluminum (PrSAlMe₂)

In a 20 mL vial, anhydrous hexane (6.35 mL) and 2.0 M AlMe₃ in hexanes (6.35 mL, 12.7 mmol) were added and cooled down to -78 °C. Then, benzyl mercaptan/benzyl alcohol/propyl thiol (12.7 mmol) was added dropwise, and the solution was stirred for 24 h while warming to room temperature. To remove unreacted AlMe₃ and purify the initiator, the synthesized compound was washed three times with anhydrous hexanes (3 × 5 mL) and dried *in vacuo*. **BnSAIMe₂:** ¹H NMR and ¹³C NMR spectrum of BnSAIMe₂. ¹H NMR (500 MHz, CDCl₃) δ 7.38 to 7.21 (m, 5H, <u>Ph</u>CH₂S-Al(CH₃)₂), 3.91 (s, 2H, PhC<u>H</u>₂S-Al(CH₃)₂), -0.43 (s, 6H, PhCH₂SAl(C<u>H₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 141.46, 128.56, 127.97, 126.89 (<u>Ph</u>CH₂S-Al(CH₃)₂), 28.78 (PhCH₂S-Al(CH₃)₂).</u>

BnOAlMe₂: ¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.38 (m, 5H, <u>Ph</u>CH₂O-Al(CH₃)₂), 3.33 (s, 2H, PhC<u>H₂</u>O-Al(CH₃)₂), 0.15 - -0.6 (s, 6H, PhCH₂OAl(C<u>H₃</u>)₂). b) ¹³C NMR (126 MHz, CDCl₃) δ138.64, 137.57, 130.04, 126.69 (<u>Ph</u>CH₂O-Al(CH₃)₂, 50.76 (Ph<u>C</u>H₂O-Al(CH₃)₂), -7.71 (PhCH₂O-Al(<u>C</u>H₃)₂).

PrSAIMe₂: ¹H NMR (500 MHz, CDCl₃) δ 2.62 (m, 2H, CH₃CH₂C<u>H</u>₂S-Al(CH₃)₂), 1.65 (dq, 2H, CH₃C<u>H</u>₂CH₂S-Al(CH₃)₂), 1.04-0.95 (m, 3H, C<u>H</u>₃CH₂CH₂S-Al(CH₃)₂), -0.49 (S, 6H, CH₃CH₂CH₂S-Al(C<u>H</u>₃)₂). ¹³C NMR (126 MHz, CDCl₃) δ 30.33 (CH₃CH₂CH₂S-Al(CH₃)₂), 25.97 (CH₃CH₂CH₂S-Al(CH₃)₂), 13.15 (CH₃CH₂CH₂S-Al(CH₃)₂), -9.21 (CH₃CH₂CH₂S-Al(CH₃)₂).

3.2.5 Synthesis of di-functional initiator (d-H)

A reaction vial was charged with a stir bar and AlMe₃ (12.7 mmol, 6.35 mL) and anhydrous hexane (6.35 mL), cooled to -78 °C. 1,3-propanedithiol (12.7 mmol, 1.37 g, 1.27 ml) was added

3.2.6 Synthesis of tetra-functional initiator (t-H)

To a solution of AlMe₃ (12.7 mmol, 6.35 mL) and anhydrous hexane (6.35 mL) at -78 °C, pentaerythritol tetrakis(3-mercaptopropionate) (12.7 mmol, 6.20 g, 4.85 ml) was added dropwise. The reaction mixture was stirred and warmed up to room temperature overnight. The resultant yellow powders were washed three times with anhydrous hexanes and dried *in vacuo*. ¹H NMR (500 MHz, CDCl₃) δ 4.21-1.42 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), -0.36 to -1.09 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 42.42-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 31.61-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 29.61, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 25.10 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 9.81-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-).

3.2.7 Procedure for synthesis of poly(propylene sulfide) and its purification using BnsAlMe₂ or BnOAlMe₂

In a 20 mL septum-capped scintillation vial with a stir bar and under nitrogen

atmosphere, BnSAlMe₂ (0.018 g, 0.01 mmol) or BnOAlMe₂ (0.016

g, 0.01 mmol), NAI (0.0175 g, 0.01 mmol), and propylene sulfide (3.19 mL, 3g, 0.040 mol) were added. The solution was heated to 50 °C until the completion of the polymerization. The

reaction was quenched with methanol and dissolved in dichloromethane. The resulting solution was added dropwise into acidic MeOH (0.01 M HCl in MeOH) to precipitate and washed three times with water to remove residual aluminum. After precipitation out of MeOH, the polymer was dried *in vacuo* overnight at 70 °C. SEC with refractive index, light scattering, and viscosity detectors determined absolute molecular weights and polydispersities. Also, M_n was determined by ¹H NMR spectroscopy by taking the ratio of the backbone proton signals to the integral of the end group signal on the initiator. Resultant PPS is also characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, and DSC. ¹H NMR (500 MHz, CDCl₃) δ 2.91-2.80 (m, -S-CH₂-CH₂(CH₃)-S-), 2.65-2.58 (m, -S-CH₂-CH₂(CH₃)-S-), 1.39 (m, -S-CH₂-CH₂(CH₃)-S-). ¹³C NMR (126 MHz, CDCl₃) δ 41.14 (-S-CH₂-<u>C</u>H₂(CH₃)-S), 38.18 (-S-<u>CH₂-CH₂(CH₃)-S), 20.63 (-S-CH₂-CH(<u>CH₃)-S-</u>).</u>

3.2.8 Procedure for one-pot synthesis of poly(ECH-stat-PS) using BnSAlMe₂ as an initiator Polymerization was performed in a septum-capped reaction vial. The vial was charged with BnSAlMe₂ (0.022 g, 0.12 mmol), NAl (0.020 g, 0.12 mmol), 1.6 g of PS (0.021 mol, 1.69 ml), ECH (1.69 mL, 2 g, 0.021 mol), and a stir bar at 50 °C. After the full conversion of monomers, the mixture was diluted with DCM and precipitated in a 3-fold excess of acidic methanol (0.01 M). The copolymer was dried under a vacuum at room temperature. Polydispersity and M_n were characterized by SEC, and the structure of the copolymer was investigated by ¹H NMR, ¹³C NMR, and DOSY NMR spectroscopy. The thermal properties of the copolymer were studied using DSC. Poly(ECH-*stat*-PS): ¹H NMR (500 MHz, CDCl₃) δ 3.80-3.29 (bm, $-O-CH_2-CH(CH_2Cl)-O-$), 3.16-2.51 (bm, $-S-CH_2-CH(CH_3)-S-$), 1.63-1.54 (m, $-O-CH_2-CH(CH_2Cl)-O-$ and $-S-CH_2-CH(CH_3)-S-$), 1.40-1.33 (m, $-S-CH_2-CH(CH_3)-S-$), 1.37-1.17 $O-CH_2-CH(CH_2Cl)-O-$ and $-S-CH_2-CH(CH_3)-S-$). ¹³C NMR (126 MHz, CDCl₃)

$$79.37(-O-CH_2-\underline{C}H(CH_2Cl)-O-), 75.58(-O-\underline{C}H_2-CH(CH_2Cl)-O-), 44.72(-O-CH_2-CH(\underline{C}H_2Cl)-O-), 41.16(-S-CH_2-\underline{C}H(CH_3)-S-), 38.39(-O-CH_2-\underline{C}H(CH_2Cl)-O- and -S-CH_2-\underline{C}H(CH_3)-S-), 20.63(-S-\underline{C}H_2-CH(CH_3)-S-), 20.85(-O-\underline{C}H_2-CH(CH_2Cl)-O- and -S-\underline{C}H_2-CH(CH_3)-S-), 18.59(-S-CH_2-CH(\underline{C}H_3)-S-).$$

3.2.9 Procedure for one-pot synthesis of poly(PO-stat-PS) using BnSAlMe₂ as an initiator Polymerization was performed in a septum-capped reaction vial. The vial was charged with BnSAlMe₂ (0.027 g, 0.15 mmol), NAl (0.026 g, 0.15), PS (2.69 mL, 0.034 mol), PO (2.4 mL, 2 g, 0.034 mol) and a stir bar at 50 °C. After the full conversion of monomers, the mixture was diluted with DCM and precipitated in a 3-fold excess of acidic methanol (0.01 M). The copolymer was dried under a vacuum at room temperature. Polydispersity and M_n were characterized by SEC, and the structure of the copolymer was investigated by ¹H NMR, ¹³C NMR, and DOSY NMR spectroscopy. The thermal properties of the copolymer were studied using DSC. Poly(PO-stat-PS): ¹H NMR (500 MHz, CDCl₃) & 3.83-3.24 (bm, -O-CH2-CH(CH3)-O-), 3.10-2.41 (bm, -S-CH2-CH(CH3)-S-, -O-CH2-CH(CH3)-O- and -S-CH₂-CH_{(CH₃)-S-), 1.32-1.42 (m, -S-CH₂-CH_{(CH₃)-S-), 1.30-1.19 (bm,}} -O-CH₂-CH(CH₃)-O- and -S-CH₂-CH(CH₃)-S-), 1.17-1.04 (m, -O-CH₂-CH(CH₃)-O-).¹³C NMR (126 MHz, CDCl₃) δ75.85 (-O-CH₂-CH(CH₃)-O-), 73.34 (-O-CH₂-CH(CH₃)-O-), 72.90 (-O-CH₂-CH(CH₃)-O- and -S-CH₂-CH(CH₃)-S), 41.23 (-S-CH₂-<u>C</u>H(CH₃)-S-), 38.10 (-S-<u>C</u>H₂-CH(CH₃)-S-), 20.8 (-O-<u>C</u>H₂-CH(CH₃)-O- and -S-<u>C</u>H₂-CH(CH₃)-S), 19.3 (-S-CH₂-CH(<u>C</u>H₃)-S-), 17.4 (-O-CH₂-CH(<u>C</u>H₃)-O-).

3.2.10 Procedure for synthesis of poly(ECH-b-PS) using BnSAlMe₂ as an initiator BnSAlMe₂ (0.024 g, 0.13 mmol) and NAl (0.023 g, 0.13 mmol) were added into a vial with a stir bar. After adding ECH (1.69 mL, 2 g, 0.0216 mol), the vial was placed on the hotplate at 50 °C. When the first monomer was fully converted (determined by ¹H NMR

spectroscopy), PS (1.69 mL, 1.6 g, 0.0216 mol) was injected into the vial. The stirring was continued at 50 °C for enough time until the second monomer is fully converted. The product was then dissolved in DCM, and the resulting solution was precipitated out of MeOH to yield the desired polymer product. The supernatant was removed, and the copolymer was dried in vacuo at 70 °C. The block copolymer was characterized by ¹ H NMR, ¹³C NMR, and DOSY NMR spectroscopy. SEC analysis was performed to determine M_n and polydispersity. The glass transition corresponding to each block confirmed by DSC. Poly(ECH-*b*-PS): ¹H NMR (500 MHz, CDCl₃) δ 3.72–3.2 (bm, –O–CH₂–CH(CH₃)–O–), 2.91-2.54 (bm, –S–CH₂–CH(CH₃)–S–), 1.31 (m, –S–CH₂–CH(CH₂Cl)–O–), 69.51 (–O–CH₂–CH(CH₂Cl)–O), 43.47 (–O–CH₂–CH(CH₂Cl)–O–), 41.17 (–S–CH₂–CH(CH₃)–S–), 38.24 (–S–<u>CH₂–CH(CH₃)–S–), 20.86 (–S–CH₂–CH(CH₃)–S–).</u>

3.2.11 Procedure for synthesis of poly(PO-b-PS) using BnSAlMe₂ as an initiator BnSAlMe₂ (0.024 g, 0.13 mmol) and NAl (0.023 g, 0.13 mmol) were added into a vial with a stir bar. Adding of the PO (2.4 mL, 2 g, 0.034 mol), the vial was placed on the hotplate at 50 °C. When the first monomer was fully converted (determined by ¹H NMR spectroscopy), PS (2.69 mL, 2.5 g, 0.034 mol) was injected into the vial. Stirring was continued at 50 °C for enough time until the second monomer is fully converted. The product was then dissolved in DCM, and the resulting solution was precipitated out of MeOH to yield the desired polymer product. The supernatant was removed, and the polymer was dried in vacuo at 70 °C. The block copolymer was characterized by ¹H NMR, ¹³C NMR, and DOSY NMR spectroscopy. SEC analysis was performed to determine M_n and polydispersity and the glass

transition corresponded to each block confirmed by DSC. Poly(PO-*b*-PS): ¹H NMR (500 MHz, CDCl₃)
$$\delta$$
 3.77-3.55 (bm, $-O-CH_2-CH(CH_2Cl)-O-$), 2.91-2.80 (m, $-S-CH_2-CH(CH_3)-S-$), 2.65-2.58 (m, $-S-CH_2-CH_2(CH_3)-S-$), 1.35 (m, $-S-CH_2-CH(CH_3)-S-$). ¹³C NMR (126 MHz, CDCl₃) δ 75.26 ($-O-CH_2-CH(CH_3)-O-$), 73.35 ($-O-CH_2-CH(CH_3)-O-$), 40.6 ($-S-CH_2-CH(CH_3)-S-$), 37.9 ($-S-CH_2-CH(CH_3)-S-$), 20.98 ($-S-CH_2-CH(CH_3)-S-$), 16.83 ($-O-CH_2-CH(CH_3)-O-$).

3.2.12 Procedure for synthesis of poly(PS-b-PO) by d-H initiator

To a mixture of NAI (0.0175 g, 0.1 mmol) and di-functional initiator (0.0220 g, 0.1 mmol) in a septum-capped vial, 3 g of PS (3.17 mL, 0.04 mol) was added. The reaction mixture was placed at 50 °C bath. Conversion of PS was followed by ¹H NMR spectroscopy, and after full conversion of monomer, 2.32 g of PO (2.8 mL, 0.04 mol) was added to the vessel. The polymerization was quenched by MeOH after completion of the polymerization. The product was then dissolved in DCM, and the resulting solution was precipitated out of MeOH to yield the desired copolymer product. The supernatant was removed, and the polymer was dried in vacuo at 70 °C. Block copolymers were characterized by ¹H NMR, ¹³C NMR, and DOSY NMR spectroscopy. SEC analysis was performed to determine M_n and D. Glass transition corresponded to each block confirmed by DSC. d-H poly(PO-b-PS): ¹H NMR (500 MHz, CDCl₃) § 3.72–3.2 (bm, –O–CH₂–CH(CH₃)–O–), 2.91-2.54 (bm, –S–CH₂–CH(CH₃)–S–), 1.31 (m, -S-CH₂-CH(CH₃)-S-), 1.11 (m, -O-CH₂-CH(CH₃)-O-). ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (-O-CH₂-<u>C</u>H(CH₃)-O-), 73.35 (-O-<u>C</u>H₂-CH(CH₃)-O-), 40.6 (-S-CH₂-<u>C</u>H(CH₃)-S-), 37.9 (-S-<u>C</u>H₂-CH(CH₃)-S-), 20.98 (-S-CH₂-CH(<u>C</u>H₃)-S-), 16.83 (-O-CH₂-CH(CH₃)-O-).

3.2.13 Procedure for synthesis of poly(PS-b-PO) by t-H initiator

NAI (0.017 g, 0.1 mmol), tetra-functional initiator (0.022 g, 0.1 mmol), and PS (2 g, 0.033mmol, 2.11 mL) were heated in a vial until full conversion of PS (followed by ¹H NMR spectroscopy). Then, PO (1.93 g, 0.033 mmol, 2.3 mL) was added to the reaction vial. The polymerization was quenched by MeOH when all the PO was polymerized. The crude product was precipitated in acidic methanol, and the precipitate was dried in vacuo a 70 °C overnight to obtain pure copolymer product. The copolymer was fully characterized by SEC, DSC, ¹H NMR, ¹³C NMR, and DOSY NMR spectroscopy. t-H poly(PO-*b*-PS): ¹H NMR (500 MHz, CDCl₃) δ 3.72–3.2 (bm, –O–CH₂–CH(CH₃)–O–), 2.91-2.54 (bm, –S–CH₂–CH(CH₃)–S–), 1.31 (m, –S–CH₂–CH(CH₃)–S–), 1.11 (m, –O–CH₂–CH(CH₃)–O–). ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (–O–CH₂–CH(CH₃)–O–), 73.35 (–O–CH₂–CH(CH₃)–O–), 40.6 (–S–CH₂–CH(CH₃)–S–), 37.9 (–S–CH₂–CH(CH₃)–S–), 20.98 (–S–CH₂–CH(CH₃)–S–), 16.83 (–O–CH₂–CH(CH₃)–O–).

3.2.14 Procedure for control experiments by kinetics Studies using ¹H NMR spectroscopy of BnSAlMe₂ and NAl, only NAl, and only BnSAlMe₂ or PS polymerization: With only BnSAlMe₂

In a glove box, a reaction vial was charged with a stir bar, BnSAlMe₂ (0.063 g, 0.349 mmol), and PS (1 mL, 1 g, 0.013 mol). With only NAI: In a glove box, a reaction vial was charged with a stir bar, NAI (0.057 g, 0.332 mmol), and PS (1 mL, 1 g, 0.013 mol). With both NAI and BnSAlMe₂: In a glove box, a reaction vial was charged with a stir bar, NAI (0.057 g, 0.332 mmol), and PS (1 mL, 1 g, 0.013 mol). For all these experiments, the reaction vials heated up to 50 °C and small aliquots (ca. 30 μ L) every 15 minutes were taken. These samples were dissolved in d-chloroform and conversion was determined using ¹H NMR spectroscopy. The conversion of each monomer was calculated

98

based on the integration of the backbone area to the unreacted corresponding monomer by ¹H NMR spectroscopy. The samples were quenched by exposing them to the air, which deactivates the catalyst.

3.2.15 Procedure for Kinetics Studies by ¹H NMR spectroscopy of d-H initiator and PrSAlMe₂ for PS polymerization

In a glove box, a reaction vial was charged with a stir bar, d-H (0.0044, 0.1 mmol) or $PrSAlMe_2$ (0.0026 g, 0.1 mmol), and NAI (0.0034 g, 0.1 mmol for $PrSAlMe_2$ and 0.0068 g, 0.2 mmol for d-H initiator). Then, PS (2 g, 0.033 mol, 2.11 mL) was added. The reaction vial heated up to 50 °C and small aliquots (*ca.* 30 µL) every 15 minutes for 3 hours were taken. These samples were dissolved in d-chloroform, and conversion was determined using ¹H NMR spectroscopy. The conversion of each monomer was calculated based on the integration of the backbone area to the unreacted corresponding monomer by ¹H NMR spectroscopy. The samples were quenched by exposing them to the air, which deactivates the catalyst.

3.2.16 Procedure for synthesis of poly(EG-b-PS)

In a vial equipped with a stir bar, 1.5 g of PEG dissolved in 3 ml anhydrous benzene and purged with N₂. After dissolution, 0.1 ml of AlMe₃ solution was added dropwise to the dissolved PEG forming a macroinitiator. Further, PS (1 g, 0.013 mol, 0.092 ml) and NAI (0.03 g, 0.041 mmol) were added to the solution, and the reaction heated up to 50 °C overnight. After full consumption of PS, the solution was exposed to air and, the excess benzene was evaporated. The residue then dissolved in 2 ml DCM, precipitated out of MeOH, and dried on the vacuum at 70 °C. ¹H NMR (500 MHz, CDCl₃) δ 3.65-3.48 (b, $-O-\underline{CH_2}-\underline{CH_2}-O-$), 2.92-2.78 80 (m, $-S-\underline{CH_2}-\underline{CH}(\underline{CH_3})-\underline{S}-$), 2.66-2.59 (m, $-S-\underline{CH_2}-\underline{CH}(\underline{CH_3})-\underline{S}-$), 1.38 (m,

-S-CH₂-CH(C<u>H</u>₃)-S-). ¹³C NMR (126 MHz, CDCl₃) δ 70.55 (-O-<u>C</u>H₂-<u>C</u>H₂-O-), 41.26 (-S-CH₂-<u>C</u>H(CH₃)-S-), 38.38 (-S-<u>C</u>H₂-CH(CH₃)-S-), 20.79 (-S-CH₂-CH(<u>C</u>H₃)-S-).

3.3 Results and discussion

Previously, we developed a thio-aluminum based (SAI) initiator that quickly and controllably polymerized epoxides in the presence of a Lewis pair (LP) catalyst consisting of triethyl amine and trimethyl aluminum (NAI).²⁶ Since we suspect initiation occurs from a thiolate ion, we hypothesized that this would be amenable to episulfide polymerization. To test this idea, we investigated the homopolymerization of propylene sulfide (PS) with our SAl initiator (BnSAlMe₂) and NAl (Et₃NAlMe₃) catalyst. BnSAlMe₂ and NAl were synthesized by previously reported methods.^{26, 27} PS polymerization was performed neat at 50 °C in the presence of BnSAlMe₂ and NAl catalyst in an equimolar ratio, which resulted in PPS with a yield of 94.2% after purification procedure. A scheme of this reaction can be seen in Scheme 3-1. PPS was characterized via size-exclusion chromatography (SEC) with triple detection and the absolute M_n was found to be 33.7 kg/mol with polydispersity (D) = 1.21 (Figure 3-1b, purple line), consistent with the targeted molecular weight of 30 kg/mol. The M_n determined by SEC compared favorably to the molecular weight calculated through ¹H NMR spectroscopy via end group analysis of 36.2 kg/mol (SI, Figure 3-9 a). The ¹³C NMR revealed an atactic PPS, in line with polyethers synthesized previously.²⁶ The results for this polymerization can be found in Table 3-1, entry 2. It should be noted that the polymerization time in the table refers to the time at which the polymerization was terminated with conversion > 99%. This polymer was further characterized by differential scanning calorimetry (DSC) and showed one glass transition temperature (T_{o}) at -41 °C (SI, Figure 3-10), in accordance with the literature value.²⁸



Scheme 3-1 Data exclusion criteria with number of included and excluded subjects and measurement sets.

Control over PPS molecular weight was achieved by varying the monomer to initiator ratio ($[M_0]/[I_0]$) with constant catalyst concentration (63.5 µmol). Molecular weights of 15, 30, 50, 75, and 100 kg/mol were targeted. Here, we have direct control over M_n through $[M_0]/[I_0]$, which differs from a recent report that demonstrates high M_n PPS.⁹ The M_n determined by SEC and end group analysis via ¹H NMR spectroscopy was consistent with the targeted molecular weights. Bottom is a plot of the molecular weight (left) and Đ (right) as a function of the $[M_0]/[I_0]$. A linear fit (blue line) to the molecular weight data is provided to emphasize the controlled nature of the polymerization. The commensurate SEC traces for these polymers can be seen in the Figure. The molecular weight was narrow with Đ \approx 1.25 in most cases, further suggesting a controlled polymerization. We also synthesized 5 kg/mol PPS and characterized it with ESI-MS (**SI, Figure 3-11**) to confirm end group structure. The ESI-MS shows that a single end group from the initiator ligand remains on each polymer, suggesting linear chain growth proceeding from the BnSAlMe₂ initiator.

Entry	Polymer	Initiator	Time (hr.) ^a	Mn ^(theo) (kg/mol)	Mn ^b (kg/mol)	Mn ^c (kg/mol)	Đ¢
1	PPS	BnSAlMe ₂	6	15	14.8	14.3	1.20
2	PPS	BnSAlMe ₂	10	30	33.7	36.2	1.21
3	PPS	BnSAlMe ₂	48	50	47.1	46.7	1.32
4	PPS	BnSAlMe ₂	70	70	68.4	67.7	1.35
5	PPS	BnSAlMe ₂	102	100	98.2	97.1	1.24
6	P(ECH-stat-PS)	BnSAlMe ₂	168	30	29.2	27.3	1.56
7	P(PO-stat-PS)	BnSAlMe ₂	72	30	30.8	28.6	1.21
8	P(ECH- <i>b</i> -PS)	BnSAlMe ₂	168	30	29.9	30.3	1.74
9	P(PO-b-PS)	BnSAlMe ₂	72	30	29.6	27.8	1.32
10	PPS	d-H	5	30	34.5	-	1.37
11	P(PS-b-PO)	d-H	24	30	29.8	-	1.39
12	PPS ^d	t-H	10	80	88.7	-	1.51
13	$(PS-b-PO)^{d}$	t-H	24	80	84.3	-	1.09
14	PPS	PrSAlMe ₂	5	30	32.3	31.1	1.21
15	PPS	BnOAlMe ₂	48	30	31.7	32.4	1.24
16	P(EG-b-PS) ^e	mPEGAlMe ₂	18	20	22.2	23.8	1.18
^a Time terminated at > 99% conversion as determined by ¹ H NMR spectroscopy ^b Absolute							

Table 3-1 Polymerization and copolymerization characteristics.

^a Time terminated at > 99% conversion as determined by ¹H NMR spectroscopy. ^b Absolute molecular weight and Đ determined from SEC with LS, RI, and viscometry triple detection system. ^c Determined from end group analysis of the ¹H NMR spectra. ^d Polymerizations were conducted at room temperature. Reaction condition: NAI (1 mmol), initiator (1 mmol), PS (0.4 mol), and for synthesis of copolymers we used (1:1) ratio of monomers. ^e Initiated from macroinitiator.



Figure 3-1 a) Plot of M_n (left axis, blue circles) and \tilde{D} (right axis, red triangles) as a function of the PS to BnSAlMe₂ ratio ([PS]/[BnSAlMe₂]). M_n increased linearly at increasing ratio of propylene sulfide with $\tilde{D} < 1.4$. b) SEC traces for PPS with different targeted molecular weights. blue, for 15 kg/mol targeted PPS, the M_n is determined to be 14.8 kg/mol with \tilde{D} of 1.20. purple, for 30 kg/mol targeted PPS, the M_n is determined to be 33.7 kg/mol with \tilde{D} of 1.21. green, for 50 kg/mol targeted PPS, the M_n is determined to be 47.1 kg/mol with \tilde{D} of 1.32. pink, for 70 kg/mol targeted PPS, the M_n is determined to be 68.4 kg/mol with \tilde{D} of 1.35. red, for 100 kg/mol targeted PPS, the M_n is determined to be 98.2 kg/mol with \tilde{D} of 1.24.

We investigated the polymerization kinetics of PS in the presence of only initiator (BnSAlMe₂), only catalyst (NAl), and both catalyst and initiator. For each experiment, we targeted 20 kg/mol PPS. The polymerization kinetics were determined by monitoring the monomer conversion with ¹H NMR spectroscopy over time and a linear fit to $-ln([PS]/[PS]_0)$ vs. time was used to determine the observed rate constant (k_{obs}). For the case with catalyst and initiator, the polymerization proceeded swiftly, and the k_{obs} was found to be $1.67 \pm 0.19 \times 10^{-3} \text{ s}^{-1}$, which corresponds to conversion > 95% after time < 1 hour. Furthermore, characterization with SEC reveals a M_n = 21.2 kg/mol with a D = 1.23, in line with the targeted M_n. The first order in monomer nature of the kinetics and low D suggests the PS polymerization is living. The turnover frequency (TOF) was also calculated and found to be 40.4 hr⁻¹. Unexpectedly, the polymerization

rate of PS with only initiator $k_{obs} = 1.30 \pm 0.16 \times 10^{-3} \text{ s}^{-1}$ was comparable to PPS synthesized using NAI and BnSAlMe₂. However, the M_n obtained from SEC for the PPS is 45.3 kg/mol, with D = 1.30 more than double the targeted M_n. In the presence of only NAI, PS polymerizes markedly slower than using both catalyst and the initiator with a k_{obs} of $1.32 \pm 0.04 \times 10^{-5} \text{ s}^{-1}$ which has an M_n = 47.6 kg/mol and D = 1.31, determined by SEC, which also suggests a lack of control. The fact that the presence of only catalyst is sufficient to polymerize PS is in stark contrast to what is observed with epoxides, in which no polymerization occurs without presence of both catalyst and initiator.^{26, 27} PPS synthesized with only NAI is a classic Lewis pair polymerization; however, without the initiator the M_n cannot be controlled due to irreversible interaction of Lewis pairs (LP) which causes low initiator efficiency and it is the case for several reported LP systems.²⁹⁻³¹ Therefore, catalyst and initiator together are involved in a Lewis pair assisted coordination insertion mechanism with an anionic character for PS polymerization. The NAI only polymerization deserves further study and will be investigated as future work.



Figure 3-2 . a) Plot of normalized PS concentration over time with BnSAlMe₂ initiator and NAl catalyst (green line), plot of normalized PS concentration over time with only BnSAlMe₂ initiator (blue line), and plot of normalized PS concentration over time with only NAl catalyst (red line), for polymerization of targeted 20 Kg/mol PS. Monomer concentration was monitored via ¹H NMR spectroscopy, and the rate of reactions calculated based on it. The rates are as followings from the slope of each plot, $k_{obs} = (1.70 \pm 0.19) \times 10^{-3} \text{ s}^{-1}$ with both catalyst and initiator, $k_{obs} = 1.32 \pm 0.04 \times 10^{-5} \text{ s}^{-1}$ with only catalyst). b) SEC traces of (green) targeted 20 Kg/mol PPS with both the catalyst and the initiator, (red) 20 Kg/mol PPS with only the catalyst, and (blue) 20 Kg/mol PPS with only the initiator. With both the catalyst and the initiator the M_n is close to the targeted MW, $M_n = 21.2 \text{ Kg/mol}$ and PDI of 1.23. However, by using only the catalyst and only the initiator we lose the control over the MW. In a red SEC trace (only catalyst), the $M_n = 47.6 \text{ Kg/mol}$ and PDI of 1.31 and blue SEC trace (only initiator) has the $M_n = 45.3 \text{ Kg/mol}$ with PDI of 1.30.

We investigated the statistical copolymerization of PS with epoxides to tune polymer composition. Combining PS with functional epoxides could lead to new biologically relevant materials. Inoue noted the difficulty in typical epoxide-episulfide copolymerization due to the increased reactivity of the episulfide over the epoxide.³² We copolymerized epichlorohydrin (ECH) and propylene oxide (PO) with PS] in a 1:1 molar ratio with a targeted molecular weight of 30 kg/mol in the presence of BnSAlMe₂ and NAl at 50 °C to achieve statistical copolymers, poly(ECH-*stat*-PS) and poly(PO-*stat*-PS), respectively. The copolymerizations were monitored

by ¹H NMR spectroscopy, and the reactivity ratios fit to the nonterminal copolymerization model reported by Beckingham–Sanoja–Lynd (BSL)³³]. For poly(ECH-stat-PS), the reactivity ratios for ECH (r_{ECH}) and PS (r_{PS}) were determined to be $r_{ECH} = 0.906 \pm .043$ and $r_{PS} = 1.191 \pm 0.059$ and for poly(PO-*stat*-PS), the r_{PO} and r_{PS} were calculated to be $r_{PO}=0.905\pm0.082$ and $r_{PS}=$ 1.138 ± 0.108 , commensurate with a statistical copolymer that favors PS over epoxide addition. From DSC analysis, P(ECH-stat-PS) and P(PO-stat-PS) presented only one glass transition temperature (T_g) at -40 °C and -46 °C, respectively, consistent with a statistical copolymer of these two monomers (SI, Figure 3-12). SEC and diffusion ordered spectroscopy (DOSY) further corroborate the copolymer structure. SEC (SI, Figure 3-13) showed a single peak with M_n of 29.2 kg/mol and Đ of 1.56 for poly(ECH-stat-PS) (Table 3-1, entry 6) and M_n of 30.8 kg/mol and Đ of 1.21 for poly(PO-stat-PS) (Table 3-1, entry 7). It is unclear why the Đ is much higher for the ECH containing copolymer when compared with the PO containing copolymer. From the ¹H and ¹³C NMR spectra, there are no additional peaks due to an unexpected side reaction. Furthermore, the DOSY spectra (Figure 3-4, a and b) exhibit the same diffusion coefficient for all the protons pertaining to the polymers, suggesting only one polymer chain is present.



Scheme 3-2 Statistical (a) and block (b) copolymerization of PS and epoxides.



Figure 3-3 Total conversion as a function of normalized monomer concentration for (a) poly(PO-*stat*-PS) and (b) poly(ECH-*stat*-PS). A fit to this data results in the reactivity ratios for each monomer. The reactivity ratios of the monomer pairs are determined to be r_{PO} = 0.905 ± 0.082 and r_{PS} = 1.138 ± 0.108 for poly(PO-*stat*-PS) and r_{ECH} = 0.906 ± 0.043 and r_{PS} = 1.191 ± 0.059 for poly(ECH-*stat*-PS).



Figure 3-4 DOSY NMR of statistical copolymers (a and b) and block copolymers (c and d). The DOSY spectra reveal that there is only one diffusing species for both the statistical and block copolymers, indicating that both monomers share a common backbone.

We further synthesized block copolymers of PS and ECH or PO via sequential addition initiated with BnSAlMe₂ (**Scheme 3-2, b**) in the presence of NAl to obtain poly(ECH-*b*-PS) and poly(PO-*b*-PS), respectively. The synthetic method does not require any intermediate steps and epoxide, or PS can be directly polymerized from the living chain end of the other. DOSY of the copolymers revealed spectroscopic signals corresponding to PECH or PPO and PPS detected at a similar diffusion coefficient for both block copolymers, at 8.37×10^{-7} cm²/sec for P(ECH-*b*-PS) and 1.17×10^{-6} cm²/sec for P(PO-*b*-PS) (**Figure 3-4, c and d**). This finding suggests that both blocks are in the same polymer chain. Both copolymers were characterized by SEC where poly(ECH-*b*-PS) had an M_n= 29.9 kg/mol and D = 1.74 (**Table 3-1**, entry 8) and poly(PO-*b*-PS) had an M_n = 29.6 kg/mol and D = 1.32 (**Table 3-1**, entry 9) and (SI, **Figure 3-14**). For P(ECH-*b*-PS), two T_g at -29 °C and -40 °C were observed for PECH block and PS block, respectively (SI, **Figure 3-15**). For P(PO-*b*-PS), we observed two T_gs at -70 °C and -47 °C, in agreement with expected values (SI, **Figure 3-15 b**). Small angle X-ray scattering (SAXS) revealed much stronger scattering intensity than the statistical copolymer at low wavevector, Q <0.3 Å⁻¹, indicating weak phase separation behavior for both block copolymers (SI, **Figure 3-16**) consistent with the DSC results. Therefore, this is a facile method to produce functional block copolymers of PS and epoxide.

As mentioned, true statistical copolymers of episulfides and epoxides were difficult to achieve in the past due to episulfide's proclivity to homopolymerize when initiated by the thiolate ion. However, in this work, we were able to achieve statistical copolymers of these two disparate monomers suggesting that PS can add similarly as well to what we hypothesize to be a thiolate (from the PS) or oxyanion (from the epoxide) polymer chain end. We, therefore, wondered: does the initiating anion matter? To this end, we polymerized PS from a benzyl alcohol aluminum initiator (BnOAlMe₂) in the presence of NAl catalyst. The resultant PPS was characterized by ¹H and ¹³C NMR spectroscopy (SI, Figure 3-17) and M_n (SI, Figure 3-18), characterized by SEC. Both the ¹H and ¹³C NMR spectra were similar to the PPS initiated by the SAI. The M_n was found to be 31.7 kg/mol from SEC which compared favorably with the targeted M_n of 30 kg/mol with D = 1.24. The T_g was also determined for this polymer from DSC and found to be -42 °C (SI, Figure 3-19), consistent with the PPS initiated from BnSAlMe₂. The difference between the PPS initiated by BnOAlMe2 and BnSAlMe2 was the overall polymerization time. PS was > 99% converted after 48 hours with BnOAlMe₂ compared with 10 hours for BnSAlMe₂. It has been previously noted³⁴ that the electronegativity of the substituent

groups at the aluminum can have a significant effect on the propagation rate for polymerization of heterocycles (*i.e.*, lactones) and so the difference may be due to the difference in electronegativity between sulfur and oxygen. Ultimately, this result suggests that a PS polymerization initiated by either the oxyanion or the thiolate proceed by the same mechanism, but with the oxyanion-initiated polymerization proceeding more slowly. This may explain why we are able to achieve statistical copolymers of epoxides and PS. Work is ongoing to better understand this interaction



Scheme 3-3 BnOAlMe₂ initiated PS polymerization.

Inspired by the previous reports of PS containing ABA and star polymers,^{10, 11} we investigated (co)polymer architecture through initiator design and di-functional (d-H) (**Figure 3-3**a, compound 1) and tetra-functional (t-H) (**Figure 3-5**a, compound 4) initiators were synthesized. The d-H initiator was synthesized from 1,3 propane dithiol and the t-H from pentaerythritol tetrakis(3-mercaptopropionate) with trimethylaluminum at -78 °C. d-H initiator was characterized by ¹H and ¹³C NMR spectroscopy as well as ¹H – ¹H correlated spectroscopy (COSY). The NMR spectra of the d-H initiator were consistent with our suggested structure. (SI, **Figures 3-20** and **3-21**). The ¹H NMR spectrum of the t-H initiator (SI, **Figure 3-11a**) suggested a complex structure which might be due to the formation of polymeric compounds with trimethyl aluminum like dimeric or trimeric or larger complexes [(CH₃)₂AlS(ligand)]_n.



Figure 3-5 (a) Chemical reaction scheme for the synthesis of d-H initiator followed by PPS synthesis from d-H initiator and copolymerization form it. (b) chemical reaction scheme for the synthesis of t-H initiator followed by PPS synthesis from t-H initiator and copolymerization form it.

The d-H and t-H initiators were used to synthesize linear PPS from the d-H initiator and star-shaped PPS (**3-5 b**, compound 5) from the t-H initiator. The homopolymers were characterized by SEC (SI, **Figure 3-23**). The d-H PPS had $M_n = 34.5$ and D = 1.37 (**Table 3-1**, Entry 10), consistent with the targeted molecular weight of 30 kg/mol. To test whether the PPS formed from both ends of the d-H initiator, we conducted a kinetic study. The d-H initiator and an analogous mono-functional initiator (PrSAlMe₂) polymerized PS at a controlled monomer to initiator ratio at 50 °C. The reactions were monitored over time by ¹H NMR spectroscopy, and the -ln([PS]/[PS]₀) vs. time (s) was plotted to determine k_{obs}, as seen in **Figure 3-6**. From the slope of the fit, the rate constant was calculated to be $k_{obs} = 7.11 \pm 0.59 \times 10^{-5} \text{ s}^{-1}$ (PrSAlMe₂) and $(15.9 \pm 0.86) \times 10^{-5} \text{ s}^{-1}$ (d-H). The polymerization is approximately twice as fast for the d-H

initiator than for the mono-functional initiator, commensurate with propagation co-occurring at two ends. The t-H PPS had an $M_n = 88.7$ kg/mol and D = 1.51 (**Table 3-1**, Entry 12), in line with the targeted molecular weight of 80 kg/mol. Furthermore, the radius of gyration (R_g) measured by SEC for t-H PPS = 4.23 nm is smaller than PPS synthesized by BnSAlMe₂ ($R_g = 18.78$ nm), consistent with the branched architecture of the star polymer.



Figure 3-6 (top) Reaction scheme for the d-h or PrSAlMe₂ initiated polymerization of PS. (bottom) Plot of normalized PS concentration over time with PrSAlMe₂ initiator and NAl catalyst (red line) and plot of normalized PS concentration over time with d-H initiator and NAl catalyst (blue line). Monomer concentration was monitored via ¹H NMR spectroscopy, and the rate of reactions calculated. From the slope of the fit, the rate constant was calculated to be $k_{obs} = (7.11 \pm 0.59) \times 10^{-5} \text{ s}^{-1}$ (PrSAlMe₂) and (15.9 ± 0.86) × 10⁻⁵ s ⁻¹ (d-H). This experiment shows that the rate of polymerization is as twice as fast for d-H initiator in compare with PrSAlMe₂, proving that the initiation is happening from both heads of the initiator.

The d-H and t-H initiators were used to synthesize tri-block-copolymers (3-5 a,

compound 3) and star-block-copolymers (**Figure 3-5 b**, compound 6) of PS and PO through sequential addition. The resultant copolymers were characterized by ¹H and ¹³C NMR

spectroscopy and the spectroscopic peaks were commensurate with the anticipated polymer structure (SI, **Figure 3-24 and 3-25**). DOSY experiments, **Figure 3-7**, revealed a single diffusion coefficient for all polymer peaks for both the d-H and t-H initiated copolymers. Copolymers were further characterized by SEC (SI, **Figure 3-26**). For d-H P(PS-*b*-PO) (**Table 3-1**, entry 11), the $M_n = 29.8$ kg/mol and D = 1.39, which is consistent with the targeted M_n of 30 kg/mol. For t-H P(PS-*b*-PO) (Table 1, entry 13), the $M_n = 84.3$ kg/mol and D = 1.09. DSC (SI, **Figure 3-27**) of these polymers revealed two Tgs at -66 °C and -45 °C for d-H poly(PS-*b*-PO) and two Tgs at -65°C and -47 °C for t-H poly(PS-*b*-PO), which agrees with the block-copolymer architecture. Furthermore, SAXS reveals clear microphase separation for the block polymers synthesized with both the d-H and t-H initiators. (SI, **Figure 3-28**). Therefore, this polymerization method allows us to synthesize block copolymers of PS and epoxide and allows us to tune polymer architecture through initiator design.



Figure 3-7 DOSY NMR of (a) poly d-H (PS-b-PO) and (b) poly t-h (PS-b-PO). The results suggest both the epoxide and PS are in the same polymer chain.

Finally, we synthesized a block copolymer consisting of ethylene glycol (EG) and PS units to further demonstrate the utility of our synthetic platform. PEG-b-PS is an important polymer in

drug delivery applications and is often synthesized through a two-step process. Here, we reacted 5 kg/mol monomethyl ether-PEG (mPEG) with AlMe₃ in benzene to create a macroinitiator mPEGAlMe₂, as seen in **Figure 3-8** a. PS was then polymerized from the end of the mPEGAlMe₂ in benzene at 50 °C in the presence of NAl catalyst. The final PEG-b-PPS was characterized via ¹H NMR and ¹³C NMR spectroscopy (SI, Figure 3-29) as well as DOSY NMR, Figure 3-8 b. The ¹H and ¹³C NMR spectra were consistent with the anticipated block-copolymer and the DOSY NMR revealed a single diffusion coefficient, suggesting PEG and PPS units are in the same polymer chain. The mPEG and PEG-b-PPS was also characterized via SEC and the LS traces can be seen in Figure 3-8 c. A shift to a lower retention time can be seen upon polymerization of PPS from the mPEGAlMe₂ macroinitiator, consistent with the expected increase in the molecular weight. The SEC of mPEG revealed a M_n of 5.5 kg/mol and Đ of 1.24, matching data provided by the vendor. The SEC of the block-co-polymer revealed a M_n of 22.2 kg/mol and D = 1.18, commensurate with the targeted M_n. Finally, DSC (SI, Figure 3-30) revealed a single Tg at -41 °C, matching that of the PPS block, and a melting point (Tm) of 58 °C, consistent with the thermal data provided by the vendor. The T_g of the PEG block is not evident as it is most likely out of the temperature range accessible by our DSC, but the appearance of the T_m is strong evidence the PEG block is present. Therefore, we have demonstrated a facile method to produce PEG-b-PPS via our method. In summary, we presented a new methodology for (co)polymerization of PS with a recently reported SAl initiator. This method is living and produces polymers with controlled molecular weight up to 100 kg/mol and low D. We demonstrated statistical copolymerization of PS and epoxides to obtain unique, compositionally controlled copolymers. Polymer structure was characterized by various means such as ¹H and ¹³C NMR spectroscopy, DOSY, SEC, DSC, and SAXS. Further, the chemical flexibility of our SAI

initiators enabled us to impart architectures on the PS containing (co)polymers in the form of ABA copolymers and star (co)polymers. Finally, we synthesized a PEG-*b*-PPS from a PEG macroinitiator and characterized it by ¹H and ¹³C NMR spectroscopy, DOSY, DSC, and SEC. This facile and tunable aluminum initiator system opens the door for a more robust and controlled synthesis of PS-epoxide copolymers that can be applied in biomedical and other contexts.



Figure 3-8 a) Scheme for synthesis of PEG-*b*-PPS. b) DOSY NMR PEG-*b*-PPS c) SEC traces (LS) of PEG (right, blue curve) and PEG-*b*-PPS (left, red curve). The M_n and D were determined to be, respectively, 5.5 kg/mol and 1.24 (PEG) and 22.2 kg/mol and 1.18 PEG-*b*-PPS.



Figure 3-9 ¹H NMR and ¹³C NMR spectra of BnSPPS. a) ¹H NMR (500 MHz, CDCl₃) δ 2.91-2.80 (m, $-S-CH_2-CH(CH_3)-S-$), 2.65-2.58 (m, $-S-CH_2-CH(CH_3)-S-$), 1.39 (m, $-S-CH_2-CH(CH_3)-S-$). b) ¹³C NMR (126 MHz, CDCl₃) δ 41.14 ($-S-CH_2-CH(CH_3)-S$), 38.18 ($-S-CH_2-CH(CH_3)-S$), 20.63 ($-S-CH_2-CH(CH_3)-S-$).



Figure 3-10 DSC analysis of targeted 30k PPS with BnSAlMe₂. The data from the second heating curve were collected which reveals one T_g at -41 °C.



Figure 3-11 EIS-MS characterization of the targeted 5kg/mol PPS.



Figure 3-12 DSC analysis of (a) poly(ECH-*stat*-PS) and (b) poly(PO-*stat*-PS). The data from the second heating curve were collected which reveals one Tg at -40 °C for poly(ECH-*stat*-PS) and one Tg at -46 °C for poly(PO-*stat*-PS).



Figure 3-13 SEC traces of (a) poly(ECH-*stat*-PS) and (b) poly(PO-*stat*-PS). For poly(ECH-stat-PS), the M_n is determined to be 29.2 kg/mol with D of 1.56. And for or poly(PO-stat-PS), the M_n is determined to be 30.8 kg/mol with D of 1.21.



Figure 3-14 SEC traces of (a) P(ECH-*b*-PS) and (b) P(PO-*b*-PS). For poly(ECH-*b*-PS), the M_n is determined to be 29.9 kg/mol with \tilde{D} of 1.74. And for poly(PO-*b*-PS), the M_n is determined to be 29.6 kg/mol with \tilde{D} of 1.32.



Figure 3-15 DSC analysis of (a) poly(ECH-*b*-PS) and (b) poly(PO-*b*-PS). The data from the second heating curve were collected which reveals two Tg at -40 °C and -29 °C for PPS and PECH blocks, respectively. For poly(PO-b-PS) two Tg at -70 °C and -47 °C for PPO and PPS blocks, respectively.



Figure 3-16 SAXS data for the synthesized copolymers. The block copolymer and statistical copolymer all have very weak phase separation as indicated by the broad shoulder peak at $Q\sim0.02$ Å -1 for poly(ECH-*b*-S), $Q\sim0.07$ Å -1 for poly(PO-*stat*-PS), and $Q\sim0.033$ Å -1 for poly(PO-*b*-PS).


Figure 3-17 ¹H NMR and ¹³C NMR spectra of BnOPPS. a) ¹H NMR (500 MHz, CDCl₃) δ 2.91-2.80 (m, $-S-CH_2-CH(CH_3)-S-$), 2.65-2.58 (m, $-S-CH_2-CH_2-CH_3)-S-$), 1.39 (m, $-S-CH_2-CH(CH_3)-S-$). b) ¹³C NMR (126 MHz, CDCl₃) δ 41.14 ($-S-CH_2-CH_2-CH_3-S$), 38.18 ($-S-CH_2-CH(CH_3)-S$), 20.63 ($-S-CH_2-CH(CH_3)-S-$).



Figure 3-18 SEC trace of targeted 30k BnOPPS. the M_n is determined to be 31.6 kg/mol with D of 1.32.



Figure 3-19 DSC trace of BnOPPS. The data from the second heating curve were collected which reveals one T_g at -42 °C.



Figure 3-20 ¹H NMR and ¹³C NMR spectra of d-H initiator. (a) ¹H NMR (500 MHz, CDCl₃) δ 1.7-3.41 (b, 2(CH₃)Al-CH₂CH₂CH₂S-Al(CH₃)₂, 6H), -0.92-0.24 (b, 2(CH₃)Al-CH₂CH₂CH₂S-Al(CH₃)₂, 6H). Peaks at 0.88 and 1.26 in ¹H NMR spectrum, are corresponded to hexane. (b) ¹³C NMR (126 MHz, CDCl₃) δ 29.65 2(CH₃)Al-CH₂CH₂CH₂S-Al(CH₃)₂, 27.73 2(CH₃)Al-CH₂CH₂CH₂CH₂CH₂S-Al(CH₃)₂, 11.312(CH₃)Al-CH₂CH₂CH₂S-Al(CH₃)₂. Peaks at 14.14, 22.53, and 33.8 in ¹³C NMR spectra are corresponded to hexane. Broadening effects of the peaks are observed due to oligomerization in ¹H NMR spectrum.



Figure 3-21¹H–¹H correlation spectrum for d-H initiator. Only one half of the spectrum is shown for clarity. The spectrum suggests that there are three distinct species: single d-H initiator, dimerized, and trimerized form of d-H initiator, connect the peaks on the X- and Y-axes that are correlated with one another. The scheme below the diagonal represents the chemical structure of the species present. The peak assignments for the spectra are labeled here. Detailed peak assignments are listed in the methods section.



Figure 3-22 ¹H NMR and ¹³C NMR spectra of t-H initiator. a) ¹H NMR (500 MHz, CDCl₃) δ 4.21-1.42 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), -0.36 to -1.09 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), b) ¹³C NMR (126 MHz, CDCl₃) 198.53 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 42.42-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 31.61-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 29.61, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 25.10 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 9.81-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-).Peaks at 14.14, 22.35, and 31.87 in ¹³C NMR spectra are corresponded to hexane. Broadening effects of the peaks are observed due to oligomerization in ¹H NMR spectrum.



Figure 3-23 SEC traces of (a) d-h PPS and (b) t-H PPS. For d-h PPS), the M_n is determined to be 34.5 kg/mol with D of 1.37. And for d-h PPS, the M_n is determined to be 88.7 kg/mol with D of 1.51.



Figure 3-24 ¹H NMR and ¹³C NMR spectrum of d-H poly(PS-*b*-PO). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.72–3.2 (bm, –O–C<u>H₂</u>–C<u>H</u>(CH₃)–O–), 2.91-2.54 (bm, –S–C<u>H₂</u>–C<u>H</u>(CH₃)–S–), 1.31 (m, –S–CH₂–CH(C<u>H₃</u>)–S–), 1.11 (m, –O–CH₂–CH(C<u>H₃</u>)–O–). (b) ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (–O–CH₂–<u>C</u>H(CH₃)–O–), 73.35 (–O–<u>C</u>H₂–CH(CH₃)–O–), 40.6 (–S–CH₂–<u>C</u>H(CH₃)–S–), 37.9 (–S–<u>C</u>H₂–CH(CH₃)–S–), 20.98 (–S–CH₂–CH(<u>C</u>H₃)–S–), 16.83 (–O–CH₂–CH(<u>C</u>H₃)–O–).



Figure 3-25 ¹H NMR and ¹³C NMR spectrum of t-H poly(PS-*b*-PO). (a) ¹H NMR (500 MHz, CDCl₃) δ 2.97-2.81 (m, -S-CH₂-CH(CH₃)-S-), 2.71-2.57 (m, -S-CH₂-CH₂(CH₃)-S-), 1.40 (m, -S-CH₂-CH(CH₃)-S-). (b) ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (-O-CH₂-CH(CH₃)-O-), 73.35 (-O-CH₂-CH(CH₃)-O-), 40.6 (-S-CH₂-CH(CH₃)-S-), 37.9 (-S-CH₂-CH(CH₃)-S-), 20.98 (-S-CH₂-CH(CH₃)-S-), 16.83 (-O-CH₂-CH(CH₃)-O-).



Figure 3-26 SEC traces of (a) d-H poly(PS-*b*-PO) and (b) t-H poly(PS-*b*-PO). For d-H poly(PSb-PO), the M_n is determined to be 29.8 kg/mol with D of 1.39. And for t-H poly(PS-b-PO, the M_n is determined to be 84.0 kg/mol with D of 1.09.



Figure 3-27 DSC analysis of (a) d-H poly(PS-*b*-PO) and (b) t-H poly(PS-*b*-PO). The data from the second heating curve were collected which reveals two T_{gs} at -66 °C and -45 for d-H poly(PS-*b*-PO) corresponded to PECH and PPS blocks. For t-H poly(PS-*b*-PO), DSC reveals two Tgs at -65 °C and -47 for d-H poly(PS-*b*-PO) corresponded to PECH and PPS blocks.



Figure 3-28 SAXS data for the synthesized copolymers. The phase behavior of the d-H poly(PS*b*-PO) and t-H poly(PS-*b*-PO) are more obvious at Q~0.018 Å -1 and Q~0.022 Å -1.



Figure 3-29 ¹H NMR and ¹³C NMR spectrum of PEG-*b*-PPS a) ¹H NMR (500 MHz, CDCl₃) δ 3.65-3.48 (b, $-O-\underline{CH}_2-\underline{CH}_2-O-$), 2.92-2.78 80 (m, $-S-\underline{CH}_2-CH(CH_3)-S-$), 2.66-2.59 (m, $-S-CH_2-\underline{CH}(CH_3)-S-$), 1.38 (m, $-S-CH_2-CH(C\underline{H}_3)-S-$). b) ¹³C NMR (126 MHz, cdcl₃) δ 70.55 ($-O-\underline{CH}_2-\underline{CH}_2-O-$), 41.26 ($-S-CH_2-\underline{CH}(CH_3)-S-$), 38.38 ($-S-\underline{CH}_2-CH(CH_3)-S-$), 20.79 ($-S-CH_2-CH(\underline{CH}_3)-S-$).



Figure 3-30 DSC analysis of PEG-*b*-PPS. The data from the second heating curve were collected which reveals one T_g at -41 °C for PPS block and another T_m at 58 °C.



Figure 3-31 ¹H NMR and ¹³C NMR spectrum of BnSAlMe₂. a) ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.21 (m, 5H, <u>Ph</u>CH₂S-Al(CH₃)₂), 3.91 (s, 2H, PhC<u>H₂</u>S-Al(CH₃)₂), -0.43 (s, 6H, PhCH₂SAl(C<u>H₃</u>)₂). b) ¹³C NMR (126 MHz, CDCl₃) δ 141.46, 128.56, 127.97, 126.89 (<u>Ph</u>CH₂S-Al(CH₃)₂), 32.00 (Ph<u>C</u>H₂S-Al(CH₃)₂), 28.78 (PhCH₂S-Al(<u>C</u>H₃)₂).



Figure 3-32 ¹H NMR and ¹³C NMR spectrum of PrSAlMe₂. a) ¹H NMR (500 MHz, CDCl₃) δ 2.62 (m, 2H, CH₃CH₂CH₂S-Al(CH₃)₂), 1.65 (dq, 2H, CH₃CH₂CH₂S-Al(CH₃)₂), 1.04-0.95 (m, 3H, CH₃CH₂CH₂S-Al(CH₃)₂), -0.49 (S, 6H, CH₃CH₂CH₂S-Al(CH₃)₂). b) ¹³C NMR (126 MHz, CDCl₃) δ 30.33 (CH₃CH₂CH₂S-Al(CH₃)₂), 25.97 (CH₃CH₂CH₂S-Al(CH₃)₂), 13.15 (CH₃CH₂CH₂S-Al(CH₃)₂), -9.21 (CH₃CH₂CH₂S-Al(CH₃)₂).



Figure 3-33 1H NMR and ¹³C NMR spectra of poly(ECH-stat-PS). a) ¹H NMR (500 MHz, CDCl₃) δ 3.80-3.29 (bm, -O-CH2-CH(CH2Cl)-O-), 3.16-2.51 (bm, -S-CH2-CH(CH3)-S-), 1.63-1.54 (m, -O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-), 1.40-1.33 (m, -S-CH2-CH(CH3)-S-), 1.37-1.17 O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-). b) ¹³C NMR (126 MHz, CDCl3) 79.37(-O-CH2-CH(CH2Cl)-O-), 75.58 (-O-CH2-CH(CH2Cl)-O-), 44.72 (-O-CH2-CH(CH2Cl)-O-), 41.16 (-S-CH2-CH(CH3)-S-) , 38.39 (-O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-), 20.63 (-S-CH2-CH(CH3)-S-), 20.85 (-O-CH2-CH(CH2Cl)-O- and -S-CH2-CH(CH3)-S-), 20.63 (-S-CH2-CH(CH3)-S-), 18.59 (-S-CH2-CH(CH3)-S-).



Figure 3-34 ¹H NMR and ¹³C NMR spectrum of poly(PO-*stat*-PS). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.83-3.24 (bm, $-O-C\underline{H}_2-C\underline{H}(CH_3)-O-$), 3.10-2.41 (bm, $-S-C\underline{H}_2-C\underline{H}(CH_3)-S-$, $-O-CH_2-C\underline{H}(CH_3)-O-$ and $-S-CH_2-C\underline{H}(CH_3)-S-$), 1.32-1.42 (m, $-S-CH_2-CH(C\underline{H}_3)-S-$), 1.30-1.19 (bm, $-O-C\underline{H}_2-CH(CH_3)-O-$ and $-S-C\underline{H}_2-CH(CH_3)-S-$), 1.17-1.04 (m, $-O-CH_2-CH(C\underline{H}_3)-O-$). (b) ¹³C NMR (126 MHz, CDCl₃) δ 75.85 ($-O-CH_2-\underline{C}H(CH_3)-O-$), 73.34 ($-O-\underline{C}H_2-CH(CH_3)-O-$), 72.90 ($-O-CH_2-\underline{C}H(CH_3)-O-$ and $-S-CH_2-\underline{C}H(CH_3)-S$), 41.23 ($-S-CH_2-\underline{C}H(CH_3)-S-$), 38.10 ($-S-\underline{C}H_2-CH(CH_3)-S-$), 20.8 ($-O-\underline{C}H_2-CH(CH_3)-O-$) and $-S-\underline{C}H_2-CH(CH_3)-O-$).



Figure 3-35 ¹H NMR and ¹³C NMR spectrum of poly(ECH-*b*-PS). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.77-3.55 (bm, $-O-C\underline{H}_2-C\underline{H}(C\underline{H}_2Cl)-O-$), 2.91-2.80 (m, $-S-C\underline{H}_2-CH(CH_3)-S-$), 2.65-2.58 (m, $-S-CH_2-C\underline{H}(CH_3)-S-$), 1.35 (m, $-S-CH_2-CH(C\underline{H}_3)-S-$). (b) ¹³C NMR (126 MHz, CDCl₃) δ 78.97 ($-O-CH_2-C\underline{H}(CH_2Cl)-O-$), 69.51 ($-O-CH_2-CH(CH_2Cl)-O$), 43.47 ($-O-CH_2-CH(C\underline{H}_2Cl)-O-$), 41.17 ($-S-CH_2-C\underline{H}(CH_3)-S-$), 38.24 ($-S-C\underline{H}_2-CH(CH_3)-S-$), 20.86 ($-S-CH_2-CH(C\underline{H}_3)-S-$).



Figure 3-36 ¹H NMR and ¹³C NMR spectrum of poly(PO-*b*-PS). (a) ¹H NMR (500 MHz, CDCl₃) δ 3.72–3.2 (bm, –O–C<u>H₂</u>–C<u>H</u>(CH₃)–O–), 2.91-2.54 (bm, –S–C<u>H₂</u>–C<u>H</u>(CH₃)–S–), 1.31 (m, –S–CH₂–CH(C<u>H₃</u>)–S–), 1.11 (m, –O–CH₂–CH(C<u>H₃</u>)–O–). (b) ¹³C NMR (126 MHz, CDCl₃) δ 75.26 (–O–CH₂–<u>C</u>H(CH₃)–O–), 73.35 (–O–<u>C</u>H₂–CH(CH₃)–O–), 40.6 (–S–CH₂–<u>C</u>H(CH₃)–S–), 37.9 (–S–<u>C</u>H₂–CH(CH₃)–S–), 20.98 (–S–CH₂–CH(<u>C</u>H₃)–S–), 16.83 (–O–CH₂–CH(<u>C</u>H₃)–O–).



Figure 3-37 ¹H NMR and ¹³C NMR spectrum of d-H PPS. (a) ¹H NMR (500 MHz, CDCl₃) δ 2.91-2.80 (m, -S-CH₂-CH(CH₃)-S-), 2.65-2.58 (m, -S-CH₂-CH₂(CH₃)-S-), 1.39 (m, -S-CH₂-CH(CH₃)-S-). (b) ¹³C NMR (126 MHz, CDCl₃) δ ¹³C NMR (126 MHz, CDCl₃) δ 41.14 (-S-CH₂-CH(CH₃)-S), 38.18 (-S-CH₂-CH(CH₃)-S), 20.63 (-S-CH₂-CH(CH₃)-S-).



Figure 3-38 ¹H NMR and ¹³C NMR spectrum of t-H PPS. (a) ¹H NMR (500 MHz, CDCl₃) δ 2.91-2.80 (m, -S-CH₂-CH(CH₃)-S-), 2.65-2.58 (m, -S-CH₂-CH₂(CH₃)-S-), 1.39 (m, -S-CH₂-CH(CH₃)-S-). (b) ¹³C NMR (126 MHz, CDCl₃) δ ¹³C NMR (126 MHz, CDCl₃) δ 41.14 (-S-CH₂-CH(CH₃)-S), 38.18 (-S-CH₂-CH(CH₃)-S), 20.63 (-S-CH₂-CH(CH₃)-S-).



Figure 3-39 DSC analysis of (a) d-H PPS and (b) t-H PPS. The data from the second heating curve were collected which reveals one T_g at -41 °C for both these.



Figure 3-40 ¹H NMR and ¹³C NMR spectrum of BnOAlMe₂. a) ¹H NMR (500 MHz, CDCl₃) δ 7.47 – 7.38 (m, 5H, <u>Ph</u>CH₂O-Al(CH₃)₂), 3.33 (s, 2H, PhC<u>H₂O-Al(CH₃)₂), 0.15 - 0.6 (s, 6H, PhCH₂OAl(C<u>H₃)₂)</u>. b) ¹³C NMR (126 MHz, CDCl₃) δ 138.64, 137.57, 130.04, 126.69 (<u>Ph</u>CH₂O-Al(CH₃)₂), 50.76 (Ph<u>C</u>H₂O-Al(CH₃)₂), -7.71 (PhCH₂O-Al(<u>C</u>H₃)₂).</u>

BIBLIOGRAPHY

BIBLIOGRAPHY

(1) Ford, C. A.; Spoonmore, T. J.; Gupta, M. K.; Duvall, C. L.; Guelcher, S. A.; Cassat, J. E., Diflunisal-loaded poly(propylene sulfide) nanoparticles decrease S. aureus-mediated bone destruction during osteomyelitis. *Journal of Orthopaedic Research* **2021**, 39 (2), 426-437.

(2) Reddy, S. T.; Rehor, A.; Schmoekel, H. G.; Hubbell, J. A.; Swartz, M. A., In vivo targeting of dendritic cells in lymph nodes with poly(propylene sulfide) nanoparticles. *J. Controlled Release* **2006**, 112 (1), 26-34.

(3) Hirosue, S.; Kourtis, I. C.; van der Vlies, A. J.; Hubbell, J. A.; Swartz, M. A., Antigen delivery to dendritic cells by poly(propylene sulfide) nanoparticles with disulfide conjugated peptides: Cross-presentation and T cell activation. *Vaccine* **2010**, 28 (50), 7897-7906.

(4) Bearinger, J. P.; Stone, G.; Hiddessen, A. L.; Dugan, L. C.; Wu, L.; Hailey, P.; Conway, J. W.; Kuenzler, T.; Feller, L.; Cerritelli, S.; Hubbell, J. A., Phototocatalytic lithography of poly(propylene sulfide) block copolymers: toward high-throughput nanolithography for biomolecular arraying applications. *Langmuir : the ACS journal of surfaces and colloids* **2009**, 25 (2), 1238-1244.

(5) Feller, L.; Bearinger, J. P.; Wu, L.; Hubbell, J. A.; Textor, M.; Tosatti, S., Micropatterning of gold substrates based on poly(propylene sulfide-bl-ethylene glycol), (PPS-PEG) background passivation and the molecular-assembly patterning by lift-off (MAPL) technique. *Surf. Sci.* **2008**, 602 (13), 2305-2310.

(6) Vo, C. D.; Kilcher, G.; Tirelli, N., Polymers and Sulfur: what are Organic Polysulfides Good For? Preparative Strategies and Biological Applications. *Macromol. Rapid Commun.* **2009**, 30 (4-5), 299-315.

(7) Du, F.; Qiao, B.; Nguyen, T. D.; Vincent, M. P.; Bobbala, S.; Yi, S.; Lescott, C.; Dravid, V. P.; Olvera de la Cruz, M.; Scott, E. A., Homopolymer self-assembly of poly(propylene sulfone) hydrogels via dynamic noncovalent sulfone–sulfone bonding. *Nature Communications* **2020**, 11 (1), 4896.

(8) Boileau, S.; Champetier, G.; Sigwalt, P., POLYMERISATION ANIONIQUE DU SULFURE DE PROPYLENE. *Makromolekulare Chemie* **1963**, *69*, 180-192.

(9) Rumyantsev, M., Living polymerizations of propylene sulfide initiated with potassium xanthates characterized by unprecedentedly high propagation rates. *Polymer Chemistry* 2021, 12 (9), 1298-1309.

(10) Rehor, A.; Tirelli, N.; Hubbell, J. A., A New Living Emulsion Polymerization Mechanism: Episulfide Anionic Polymerization. *Macromolecules* **2002**, 35 (23), 8688-8693. (11) van der Vlies, A. J.; O'Neil, C. P.; Hasegawa, U.; Hammond, N.; Hubbell, J. A., Synthesis of Pyridyl Disulfide-Functionalized Nanoparticles for Conjugating Thiol-Containing Small Molecules, Peptides, and Proteins. *Bioconjugate Chem.* **2010**, 21 (4), 653-662.

(12) Suzuki, A.; Nagai, D.; Ochiai, B.; Endo, T., Star-Shaped Polymer Synthesis by Anionic Polymerization of Propylene Sulfide Based on Trifunctional Initiator Derived from Trifunctional Five-Membered Cyclic Dithiocarbonate. *Macromolecules* **2004**, 37 (24), 8823-8824.

(13) Napoli, A.; Valentini, M.; Tirelli, N.; Müller, M.; Hubbell, J. A., Oxidation-responsive polymeric vesicles. *Nature Materials* **2004**, **3** (3), 183-189.

(14) Vasdekis, A. E.; Scott, E. A.; O'Neil, C. P.; Psaltis, D.; Hubbell, J. A., Precision Intracellular Delivery Based on Optofluidic Polymersome Rupture. *ACS Nano* **2012**, 6 (9), 7850-7857.

(15) Lee, Y.; Koo, H.; Jin, G.-w.; Mo, H.; Cho, M. Y.; Park, J.-Y.; Choi, J. S.; Park, J. S., Poly(ethylene oxide sulfide): New Poly(ethylene glycol) Derivatives Degradable in Reductive Conditions. *Biomacromolecules* **2005**, 6 (1), 24-26.

(16) Napoli, A.; Tirelli, N.; Kilcher, G.; Hubbell, A., New Synthetic Methodologies for Amphiphilic Multiblock Copolymers of Ethylene Glycol and Propylene Sulfide. *Macromolecules* **2001**, *34* (26), 8913-8917.

(17) Frey, M.; Vincent, M.; Bobbala, S.; Burt, R.; Scott, E., Mapping the supramolecular assembly space of poly(sarcosine)-b-poly(propylene sulfide) using a combinatorial copolymer library. *Chem. Commun.* **2020**, 56 (49), 6644-6647.

(18) Wang, C.-H.; Fan, Y.-S.; Zhang, Z.; Chen, Q.-B.; Zeng, T.-Y.; Meng, Q.-Y.; You, Y.-Z., Synthesis of dual-responsive polymer via convertible RAFT and ring-opening polymerizations in one-pot. *Appl. Surf. Sci.* **2019**, 475, 639-644.

(19) Tang, Y.; Pina-Hernandez, C.; Niu, Q.; Nie, J.; Cabrini, S., A novel high-refractive index episulfide-thiol polymer for nanoimprinting optical elements. *Journal of Materials Chemistry C* **2018**, 6 (32), 8823-8831.

(20) Bell, J. P.; Don, T.-M.; Voong, S.; Fernandez, A.; Ku, W., Synthesis and properties of epoxy-episulfide resins. *Die Angewandte Makromolekulare Chemie* **1996**, *240* (1), 67-81.

(21) Zhang, C.-J.; Zhu, T.-C.; Cao, X.-H.; Hong, X.; Zhang, X.-H., Poly(thioether)s from Closed-System One-Pot Reaction of Carbonyl Sulfide and Epoxides by Organic Bases. *Journal of the American Chemical Society* **2019**, 141 (13), 5490-5496.

(22) Nakano, K.; Tatsumi, G.; Nozaki, K., Synthesis of Sulfur-Rich Polymers: Copolymerization of Episulfide with Carbon Disulfide by Using [PPN]Cl/(salph)Cr(III)Cl System. *Journal of the American Chemical Society* **2007**, 129 (49), 15116-15117. (23) Culvenor, C. C. J.; Davies, W.; Heath, N. S., 67. The preparation and reactions of aliphatic and alicyclic ethylene sulphides. *Journal of the Chemical Society (Resumed)* **1949**, 2 (1), 282-287.

(24) Gurgiolo, A. E. COPOLYMERS OF PROPYLENE OXIDE ANDALKYLENE SULFIDES. 3000865, *Synthesis* **1958** (10), 81-89.

(25) Steven A Ballard, R. C. M., John L Van Winkle Liquid Sulfoalkylene-Oxyalkylene Copolymers. 2484370, *Synthesis* **1946** (19), 118-122.

(26) Safaie, N.; Rawal, B.; Ohno, K.; Ferrier, R. C., Aluminum-Based Initiators from Thiols for Epoxide Polymerizations. *Macromolecules* **2020**, 53 (19), 8181-8191.

(27) Imbrogno, J.; Ferrier, R. C.; Wheatle, B. K.; Rose, M. J.; Lynd, N. A., Decoupling Catalysis and Chain-Growth Functions of Mono(μ-alkoxo)bis(alkylaluminums) in Epoxide Polymerization: Emergence of the N–Al Adduct Catalyst. *ACS Catalysis* **2018**, 8 (9), 8796-8803.

(28) Nicol, E.; Nicolai, T.; Durand, D., Dynamics of Poly(propylene sulfide) Studied by Dynamic Mechanical Measurements and Dielectric Spectroscopy. *Macromolecules* **1999**, 32 (22), 7530-7536.

(29) Zhang, Y.; Miyake, G. M.; Chen, E. Y.-X., Alane-Based Classical and Frustrated Lewis Pairs in Polymer Synthesis: Rapid Polymerization of MMA and Naturally Renewable Methylene Butyrolactones into High-Molecular-Weight Polymers. *Angew. Chem. Int. Ed.* **2010**, 49 (52), 10158-10162.

(30) Zhang, Y.; Miyake, G. M.; John, M. G.; Falivene, L.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X., Lewis pair polymerization by classical and frustrated Lewis pairs: acid, base and monomer scope and polymerization mechanism. *Dalton Transactions* **2012**, 41 (30), 9119-9134.

(31) Chen, E. Y.-X., Polymerization by Classical and Frustrated Lewis Pairs. In *Frustrated Lewis Pairs II: Expanding the Scope*, Erker, G.; Stephan, D. W., Eds. Springer Berlin Heidelberg: Berlin, Heidelberg, *Synthesis* **2013**; 32 (7), 239-260.

(32) Watanabe, Y.; Aida, T.; Inoue, S., First example of photoinduced copolymerizability enhancement: copolymerization of epoxide and episulfide initiated with zinc N-substituted porphyrin under visible light irradiation. *Macromolecules* **1991**, 24 (13), 3970-3972.

(33) Lynd, N. A.; Ferrier, R. C.; Beckingham, B. S., Recommendation for Accurate Experimental Determination of Reactivity Ratios in Chain Copolymerization. *Macromolecules* **2019**, 52 (6), 2277-2285.

(34) Duda, A.; Penczek, S., Kinetics of ε-caprolactone polymerization on dialkylaluminum alkoxides. *Makromolekulare Chemie. Macromolecular Symposia* **1991**, 47 (1), 127-140.

Chapter 4. Two-steps Solvent Free Synthesis Method for Preparation of Star-shaped Cross-linked Polyether Membranes Containing Different Amines via SAI Initiator

4.1 Introduction

Much of the recent membrane research is heavily invested in multifunctional films for applications in gas and molecule separation^{1–3}, catalysis^{4,5}, drug delivery^{6,7}, sensing^{8,9}, and many more. The mechanical integrity, thermal stability, and low resistance with low energy consumption make membranes desirable candidates in electrochemical applications, especially in CO_2 separation^{10–15}. Different polymeric membrane materials like perfluoro polymer, polyimides, polyamides have been used for CO_2 separation from the gas mixture^{13,16–19}. Mostly, the concern about these membranes is related to their low permeability and selectivity^{20,21}. The addition of the polar groups into the membrane matrix, such as ether oxygen (R-O-R), cyano (-C-N), carbonate (CO_3^{2-}), and ester (-COOR) groups helps to increase the selectivity of the membrane for CO_2 separation²². Thus, from that idea, multiple polymer membranes have been reported previously, which help to enhance membrane selectivity and permeability. ^{23–25}

Among them, polyethylene glycol (PEG) is an attractive polymeric tool for the gas separation processes due to the presence of polar ether linkage in their backbone, which enables favorable interaction with CO₂^{24,26,27}. However, the widely used PEG has a crystalline nature, which reduces the mechanical stability of the membrane²⁶. Therefore, controlling the physical and chemical properties of polyether's-based membranes for CO₂ separation is still crucial. The cross-linking strategy is considered one of the ideal methods to decrease crystallization properties²⁸. In a series of works by Dr. Freeman, the cross-linked PEO membranes demonstrate excellent CO₂ permeability and selectivity, including cross-linked PEG ²⁹, cross-linked poly(ethylene glycol diacrylate)^{30 31,32}, and cross-linked poly(propylene glycol diacrylate).

137

Moreover, combining different epoxide monomers into a single polymer backbone is another interesting method to achieve a tunable copolymeric structure to improve the permeability by reducing the crystallization of the membrane ³³. In a recent work by Lynd ³⁴, they used 1,4 butanediol-diglycidyl ether as a crosslinker to prepare a wide range of copolymers, such as n-butyl glycidyl ether and allyl glycidyl ether, epichlorohydrin, and glycidol which exhibited high selectivity for CO₂ separation.

The architecture of the membrane also has a significant impact on the efficiency of gas separation. Yin et al. ²⁷ suggested that the star-shaped polymers with a three-dimensional structure are suitable for gas separation applications since the intermolecular packing of the star-like polymer may be different from the inter-segmental packing of linear polymer chains. They suggested that the star-shaped polymers had lower glass transition temperatures (Tg) and higher chain flexibility. In another study by Zhao et al.,³⁵ denoted that the decrease of chain flexibility and the increase of inter-segment distance have the opposite effects on gas permeation performance. In addition, fabricated membranes with different amine (primary, secondary and tertiary) showed that the fixed site carriers facilitate the transport properties (reactive diffusion pathway for CO₂ transport). Furthermore, quaternary amine-based anion exchange membrane also studied for CO₂ transport, where hydroxide ions act as a mobile carrier helping to improve the selectivity and permeability³⁶⁻³⁸.

This research aims to develop a new and straightforward one-step method to prepare a membrane with specific architecture functionalized with different amines. There are three key elements to address in the strategy for cross-linked membrane synthesis, specifically for CO_2 separation. First, we need a specific star shape structure to facilities cross-linking due to the vicinity and flexibility of the polymer arms. Second, the presence of PO and ECH is a copolymer

138

composition that provides control over glass transition temperature (Tg) in the membrane structure since polypropylene oxide (PPO), and poly epichlorohydrin (PECH) differs significantly in the T_g . And finally, the Cl group of ECH can further react with an amine to improve the charged nature of the membrane for CO₂ separation.

4.2 Experimental section

4.2.1 Materials

Trimethylaluminum solution (TMA) (AlMe₃, 2.0 M in hexane), triethylamine (TEA) (\geq 99.5%), diethylamine (DEA) (40% in water), trimethylamine (TMA) (40% in EtOH), dimethylamine solution (DMA) (2.0 M in THF), pentaerythritol tetrakis(3-mercaptopropionate) (99%), and NaOH (ACS reagent, \geq 97.0%, pellets) were purchased from Sigma-Aldrich. Propylene oxide (PO, Sigma-Aldrich, GC, \geq 99.5%), epichlorohydrin (ECH, Sigma-Aldrich, \geq 99%), and poly(ethylene glycol) diglycidyl ether (Sigma-Aldrich, average M_n 500) were all used as received. CDCl₃ (Cambridge Analytica) was used without any further purification inside a glovebox.

4.2.2 Synthesis of Trimethylaluminum and Triethylamine Adduct (NAI)

In a reaction vial with a stir bar, 6.35 mL of anhydrous hexanes and 2.0 M AlMe₃ in hexane (6.35 mL, 12.7 mmol) were added and cooled to -78 °C. Then, triethylamine (1.5 mL, 10.7 mmol) was added dropwise to the vial. The solution was set to stir and warm to room temperature overnight. To crystallize the desired product, the solution was then directly cooled to -40 °C, and the resultant crystals were washed three times with anhydrous hexanes (3 × 5 mL) and dried in vacuo. ¹H NMR (500 MHz, CDCl₃) δ 2.80 (q, 6H, ₃(CH₃C<u>H₂)N:Al(CH₃)₃), 1.18 (t,</u>

9H, ₃(C<u>H</u>₃CH₂)N:Al(CH₃)₃), -0.89 (s, 9H, ₃(CH₃CH₂)N:Al(C<u>H</u>₃)₃). ¹³C NMR (126 MHz, CDCl₃) δ 64.54 ₃(CH₃<u>C</u>H₂)N:Al(CH₃)₃), 47.78 ₃(<u>C</u>H₃CH₂)N:Al(CH₃)₃, 9.20 ₃(CH₃CH₂)N:Al(<u>C</u>H₃)₃).

4.2.3 Synthesis of Tetra-headed Initiator (t-H)

To a solution of AlMe₃ (12.7 mmol, 12.7 mL) and anhydrous hexane (12.7 mL) at -78 °C, pentaerythritol tetrakis(3-mercaptopropionate) (12.7 mmol, 6.20 g, 4.85 ml) was added dropwise. The reaction mixture was stirred and warmed up to room temperature overnight. The resultant yellow powders were washed three times with anhydrous hexanes and dried in *vacuo*.¹H NMR (500 MHz, CDCl₃) δ 4.21-1.42 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), -0.36 to -1.09 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), -0.36 to -1.09 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 42.42-[C-<u>C</u>H₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 31.61-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 25.10 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 9.81-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-).

4.2.4 Membrane Preparation

Membrane polymeric solutions were all initially prepared in a 20 mL vial with the t-H initiator, NAl, epoxide monomers, and diglycidyl ether cross-linker. Under a nitrogen atmosphere in the glove box, the reaction mixture was heated to 50 °C until viscosity visibly increased (typically after 2-3 h). The resultant viscous solution was poured uniformly onto the quartz glass plate and placed directly on the top of the hotplate at 80 °C overnight under a nitrogen atmosphere. The film was peeled off from the glass plate with addition of water. To remove impurities from the membrane matrix, the membranes were washed with DI water and kept in DI water overnight, and dried in a vacuum oven overnight at 50 °C. The obtained membrane is transparent and homogenous with a thickness of approximately 200-300 µm. The solid films obtained by this

process were shows three-dimensional networks as suggested in the recently published work by Lynd group. ³⁴

4.2.5 Functionalization of the Membranes

For the functionalization of membranes (amine grafted membrane and quaternized amine grafted anion exchange membrane), post-modification method has been opted because of the crosslinked (insoluble in desired solvents) nature of it. The synthesized membranes were cut in varied sizes (2 x 2 cm²) and dipped into a different amine solution. For preparing tertiary amine grafted membrane, we dipped the membranes in DMA and DEA solutions, whereas for making quaternized anion exchange membrane, we dipped membranes in the TMA and TEA amine solution for 48-72 h respectively at RT. To remove the excess amine from the membranes surface membranes kept in the DI water overnight, moved in the vacuum oven at 50 °C to dry these overnight.

4.2.6 Structure Characterization

¹H NMR spectroscopy was performed on a 500 MHz Varian NMR spectrometer at room temperature, and chemical shifts are reported in parts per million (ppm) and are referenced using the residual ¹H peak from the deuterated solvent to characterize the structure of the pristine membrane before poring the viscous material in the quartz glass. FTIR spectra were measured on a Thermo Nicolet iS5 (Thermo Nicolet, USA) spectrometer for pristine membranes and fabricated ones to further characterize the structures.

4.2.7 Thermal Characterization

Differential scanning calorimetry (DSC) was performed on a TA250 series analyzer (TA Instruments). A membrane (5–6 mg) was loaded in an aluminum pan and crimped with an

141

aluminum hermetic lid. The sample was heated from -90 °C to a maximum of 50 °C with heating and cooling rates of 1 °C/min under a N₂ atmosphere. Data from the second heating curve were collected. Thermogravimetric analysis (TGA) was performed on TGA 500 (TA Instruments, USA) under a N₂ atmosphere with a heating rate of 10 °C/min. Approximately 5 mg of the membrane sample was loaded in an aluminum pan and heated to a maximum of 500 °C.

4.2.8 Water Uptake and Swelling Ratio

The samples the most optimized PPO:PECH 90:10 and their derivatives (amine attached) were immersed in deionized water at RT to investigate the water uptake (WU) for 24 h. For swelling ratio measurements, the samples were immersed in DI water for 48 h at 50 °C. The membranes' water uptake and swelling ratio were determined by the change of weight and length between dried and hydrated membranes, respectively based on the following equations.

WU = w wet - w dry w drySR = l wet - l dry l dry

4.2.9 Resistance Characterization

The most optimized PPO:PECH 90:10 and their derivatives (amine attached) were soaked overnight in 0.1 M NaOH and rinsed with DI water prior to measurement. The membranes were loaded in a Biologic Controlled Environment Sample Holder (CESH), consisting of two parallel anodized aluminum plates, a fixed bottom disc of 47 mm diameter on which a gold electrode (1/4 inch) is installed, and an upper metallic plate, moveable vertically versus the bottom plate. Electrochemical impedance spectroscopy measurements were performed with a Biologic VSP Potentiostat. The ionic conductivity was obtained by electrical measurements using a four-probe

testing cell by the Nyquist plot fitting simulation method. The ion conductivity (σ) of the membranes was calculated using the following equation.

 $\sigma = l RA$

Where R (Ω) is the membrane impedance, *l* (cm) is the distance between reference electrodes, A (cm) is the thickness of the membranes, respectively.

4.2.10 Rheology Characterization

The viscoelastic properties of cross-linked polyether films (the most optimized PPO:PECH 90:10 and mine modified membranes) were determined with MCR 302 rheometer from Anton Paar instrument rotational rheometer equipped with 8 mm diameter stainless steel parallel plate geometry. Oscillatory rheological measurements were conducted to measure the moduli of the films as a function of shear strain amplitude and as a function of frequency. The film sample was fixed between the upper parallel plate and stationary surface, with the gap size set according to individual film thickness (100–200 μ m). All tests were performed in triplicate at 23 ± 0.1 °C.

4.2.11 Alkaline stability

PPO-PECH-TMA and PPO-PECH-TMA were soaked in the 2 M NaOH for 216 h at 50 °C and the conductivity were measured by EIS.

4.3 Results and discussion

Herein, we investigated the use of the thio-aluminum based (SAI) initiator to prepare crosslinked polyether-based membranes. We have previously used the SAI initiator in the presence of NAI, as a Lewis pair catalyst, to synthesize linear copolymers consisting of different epoxides with molecular weight control and relatively low polydispersity [39]. To further expand the generality of this synthetic technique and achieve higher molecular weight in a shorter reaction time, we prepared the tetra functional (t-H) initiator from the reaction of pentaerythritol tetrakis(3-mercaptopropionate) with TEA solution (**Scheme 4-1a**). We further characterized the t-H initiator by ¹H NMR and ¹³C NMR spectroscopy (SI, **Figure 4-5**) The t-H initiator allows us to polymerize four arm star polymers, which may enhance the mechanical properties of crosslinked polyether-based membranes.



Scheme 4-1 Synthesis of cross-linked polyether membrane using the star shape initiator (PPO-PECH)

Membranes were prepared from the copolymerization of epichlorohydrin (ECH), propylene oxide (PO) and a crosslinker from t-H initiator. **Scheme 4-1,b** represents a general scheme for membrane preparation. ECH was chosen for these membranes because it is an inexpensive epoxide monomer containing a functional chloromethyl group, which can be easily modified with amine groups. PO was chosen as a comonomer to tune the ratio of ECH and due to its low T_g and non-crystalizing nature of it. The t-H initiator and NAI were first weighed in a scintillation vial, followed by the addition of the epoxide monomers in different ratios and a diglycidyl ether as a cross-linker. All the obtained membranes exhibited transparency with the light-yellow color. Further, cross-linked nature of the membranes was confirmed by the solubility test in different solvents (DCM, CHCl₃, DMSO, DMAc, and DI water). None of the membranes dissolved in any of the solvents, which supports the cross-linked characteristic of them. Different ratios of PO:ECH were used to tune the chemical and physical properties of the membrane. Reaction conditions and characteristics of the resultant cross-linked films are summarized in **Table 4-1**.

Entry	PO:ECH ^a	Time (h)	T _g (°C) ^b				
1	40:60	5	-				
2	50:50	4.5	-38				
3	60:40	4	-39				
4	70:30	3	-43				
5	80:20	3	-44				
6	90:10	3	-45				
^a reaction condition: membranes were prepared by using 12 mg of t-H initiator, 24 mg of NAl,							
and diglycidyl ether (0.2 ml) as a cross-linker with different ratios of PO and ECH ^b measured							
from second heating curve of DSC.							

Table 4-1 Characterization of t-H-Initiated Cross-linked Membranes.

The structural properties of the membrane were characterized by FTIR spectroscopy and DSC. (**Table 4-1**, entries 1-6). The spectrum of PPO-PECH with the ratio of 90:10 (PO :ECH) showed all the functional groups in the membrane matrix (**Figure 4-1**, yellow line). Peaks present at 1620, 1611, 1110, and 750 cm⁻¹suggest the presence of C=O, C-O, C-S, and C-Cl, respectively. From the DSC measurements (**Table 4-1**, entries 1-6), we observed a decrease in T_g due to continuous decrement of ECH content, which is consistent with the lower T_g of PPO compared with PECH. The DSC figure of membranes is presented in the SI, Figure 4-6, showing the shift from -38 °C for membrane having 50:50 of PO:ECH to -45 °C for membrane having 90:10 of PO:ECH. This is noteworthy because low T_g values have been shown to mitigate physical aging and promote high permeabilities in membrane materials. The prepared membrane of PO:PECH with the ratio of 90:10 (**Table 4-1**, entry 6) showed the desirable mechanical

robustness as well as the lowest T_g. Therefore, we opted to further modify this membrane with various amines. The chemical structure of the membrane with the ratio of 90:10 was studied by ¹H NMR spectroscopy, depicted in the SI, **Figure 4-7**), showing all the corresponding ¹H NMR peaks.



Scheme 4-2 Synthesis of amine modified cross-linked PPO-PECH Membranes Using the t-H Initiator. Image of the representative cross-linked polyether membrane demonstrating optical transparency and flexibility is presented.

4.3.1 Synthesis and Characterization of Modified Cross-linked Membranes

We have chosen the post-modification solvent dip method to functionalize the membranes because of the membrane's cross-linked nature. The 90:10 PO:ECH membrane was dipped in TMA, TEA, DMA, and DEA solution for 48-72 h at room temperature where the free Cl group of the pristine membrane reacted with these amines to form quarternized (TMA and TEA) (Table 2, entries 2 and 4), and tertiary amines (DMA and DEA) (Table 2, entries 3 and 5) tethered to the polymer backbone . To remove the excess amine from the membrane surface, membranes were kept in DI water for 24 h and dried in a vacuum oven for 24 hr. **Scheme 2** represents a general method for the post-modification of the membranes.

Entry	Sample ^a	Tg	WU	SR	G' ^d	Conductivity ^e
		(°C)°	(%)	(%)	(MPa)	(S/cm)
1	PPO-PECH ^b	-45	11.3	5.5	0.12	0.08 x 10 ⁻³
2	PPO-PECH-TMA	-38	38.6	26.1	0.07	1.40 x 10 ⁻³
3	PPO-PECH-DMA	-39	30.3	18.8	0.05	0.58 x 10 ⁻³
4	PPO-PECH-TEA	-43	34.3	23.2	0.06	0.21 x 10 ⁻³
5	PPO-PECH-DEA	-44	28.9	15.4	0.06	0.15 x 10 ⁻³

Table 4-2 Characterization of amine modified t-H-Initiated Cross-linked Membranes.

^a reaction condition: amine solution (20 ml) at RT. ^b pristine membrane. ^c measured from second heating curve of DSC. ^d The plateau shear modulus was measured by rheometry. ^e calculated by EIS.

4.3.2 Structural characterization

FT-IR spectroscopy was utilized to provide information about amine attachment to the membrane structure. **Figure 4-1** depicted FT-IR spectra of PPO-PECH (yellow color) showing stretching frequencies around 1102, 903, and 611 cm⁻¹ suggesting the presence of C-O, C-C-O and C-Cl in the pristine membrane matrix. Whereas amine tethered PPO-PECH membranes, PPO-PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, PPO-PECH-DMA presented an extra characteristic frequency of C-N at 1253 cm¹ (showed by vertical dashed line) followed by PPO-PECH peaks, suggesting the successful amine attachment with the polyether backbone in the membrane structure.



Figure 4-1 FTIR spectrum of PPO-PECH (yellow color), PPO-PECH-TEA (green color), PPO-PECH-DEA (red color), PPO-PECH-TMA (blue color), and PPO-PECH-DMA (purple color). The C-N characteristic starching frequency of amin modified membranes are represented by a vertical line that is not presented in the pristine membrane.

4.3.3 Thermal characterization

The thermal stability of the amine-modified membranes was measured by TGA under air atmosphere as shown in Figure 4-2, a. to investigate the successful amine modification. According to the TGA curves, all membranes showing three stages degradation profile. The pristine membrane showed the weight losses due to water loss, functional group (C-O, C-Cl) breakage, and backbone decomposition. For the amine tethered membranes, the first slight stage for weight loss below 100-200 °C is due to adsorbed humidity or residual solvent evaporation in the membranes. The second weight loss at 200–380 °C is associated with the degradation of functional amine groups. The third weight loss above 400 °C is related to the decomposition of the polymer backbone. Moreover, quaternary membranes, PPO-PECH-TMA and PPO-PECH- TEA showed more weight loss in the second stage than the pristine and secondary amine (PPO-PECH-DEA, and PPO-PECH-DMA) grafted membranes due to their charge nature. **Figure 4-2**, **b**, presents a DSC analysis of the PPO-PECH and amine modified membranes. The T_g corresponded to PPO-PECH comes at -45 °C and it shifted to the lower T_gs for the amine grafted membranes matrix. All the resultant T_g's of the amine modified cross-linked films were generally less than -50 °C. This is noteworthy because low T_g values have been shown to mitigate physical aging and promote high permeabilities in membrane materials. There were also no signs of melting or crystallization in any of the films.

4.3.4 Water uptake and swelling ratio

Sufficient bound and free water is essential for hydration and ion conduction in membranes, which is originated from the quaternary amines group and other functional groups. However, too much absorbed water could give rise to the decline of conductivity and mechanical strength for hydrated membranes, due to the dilution effect and excessive swelling. Therefore, we have used PPO-PECH (90:10) where less amount of PECH as compared to PPO helps to balance the ionic conductivity and dimensional stability.

As depicted in SI Figure 4-8, both the water uptake and the swelling ratio increases after the secondary and tertiary amines are attached to the membrane. Secondary amines attached membrane show less water uptake than tertiary amines of the hydrophilic nature of these, respectively (**Table 4-2**, entries 1-5). Moreover, the tertiary amines attached to the polyether backbone membrane will act as a quaternary anion exchange membrane, helping to transport the hydroxide and chloride ions. This observation suggests the conducting nature of the quartenized membranes compared to the PPO-PECH-DMA, PPO-PECH-DMA DEA, and pristine membranes.

149



Figure 4-2 DSC measurements (a) and TGA characterization of (b) PPO-PECH (yellow color), and amine modified membranes PPO-PECH-TEA (green color), PPO-PECH-DEA (red color), PPO-PECH-TMA (blue color), and PPO-PECH-DMA (purple color).

4.3.5 Conductivity

The ionic conductivity is an essential property for the membranes which plays a key role in the different applications. The hydroxide ion conductivity is significantly influenced by the water uptake and swelling ratio of the membranes. The ionic conductivity of the amine tethered membranes values at RT are also included in **Table 4-2**, entries 1-6. As shown in Figure 4-3, all amine grafted membranes showed higher conductivity in comparison with the PPO-PECH membrane. PPO-PECH-DMA and PPO-PECH-DEA showed comparable conductivity as compared to the pristine membrane.

The minor difference in the conductivity of the PPO-PECH-DMA (0.58 x 10⁻³ S/cm) and PPO-PECH-DEA (0.21 x 10⁻³ S/cm) in comparison with the pristine membrane stem from the absence of the ionic channels (counter ions) in the PPO-PECH-DMA and PPO-PECH-DEA membranes. On the other hand, the quartenized membranes, PPO-PECH-TEA and PPO-PECH-TMA, have higher conductivity in comparison with the pristine membrane and PPO-PECH-

DMA and PPO-PECH-DEA. Because these quartenized membranes contain labile hydroxide counter ion, helping to create a better transport pathway owing to the enhancement of the mobility of anions. In addition, the membrane containing TMA (1.40 x 10⁻³ S/cm) showed higher conductivity due to the more basic nature of TMA than TEA. This fact explains more conductivity of PPO-PECH-DMA than PPO-PECH-DEA due to more basic characteristics of DMA. It is noted that the design of a copolymer with high conductivity improves the performance of membranes in fuel cell applications. It is clear from the data shown in <u>Table</u> 2 and <u>Figure 3</u> that the OH⁻ conductivity of quartenized membranes has a direct correlation with water uptake and swelling ratio of the membrane which are dependent on both the polymer backbone and the nature of the amine.

4.3.6 Rheology

Further evidence of compositional control of structure–property relationships in the network polyether materials was evident in the rheological properties of the resultant films. We have used the rheology data to determine the mechanical stability of the pristine and modified membranes as **Figure 4** presents the shear modulus (G') vs different membrane names. For the pristine membrane the shear modulus comes nearby 0.12 MPa whereas for the charged membranes it decreases (form 0.07-0.05 MPa) due to the successful amine attachment to the membrane matrix.



Figure 4-3 conductivity measurement of PPO-PECH and amine modified membranes PPO-PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA.



Figure 4-4 rheology measurements of PPO-PECH and amine tethered membranes PPO-PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA.

In summary, a novel star-shaped with a Cl-bearing monomer ether-based backbone was synthesized and readily fabricated with different amines for CO₂ transport. Star shape structure of the initiator facilities cross-linking due to vicinity of the arms and helps to improve the mechanical stability of the membrane. The monomer ratio in the polymer backbone PO:ECH was controlled ranging from 40:60 to 90:10, respectively. Further the physical and chemical characteristic of these membranes studied by FT-IR, DSC and TGA and the optimized PPO- PECH membrane with the ratio of PO:ECH (90:10) have further modified with different amines. The post-modification of the PPO-PECH with TMA, DMA, TEA, and DEA was opted for amin grafting to the polyether backbone achieving amine tethered cross-linked polyether films with uniform and complete incorporation of comonomers into polymer films with thermal stability, optical transparency, and flexibility. The low T_g of amine grafted PPO-PECH membrane (below - 54 °C) considered to play an important role in the permeability of the membranes. This unique amine modified membranes are the great candidates for CO₂ transport because of favorable C-O interaction in the polymer backbone with CO₂ as well as amine presence in the structure facilitates the CO₂ selectivity and permeability. These features signify great potential for these membranes in the practical applications for CO₂ separation.



4.4 Supporting information

Figure 4-5 ¹H NMR and ¹³C NMR spectra of t-H initiator. a) ¹H NMR (500 MHz, CDCl₃) δ 4.21-1.42 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), -0.36 to -1.09 (24 H, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), b) ¹³C NMR (126 MHz, CDCl₃) 198.53 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 42.42-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 31.61-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 29.61, -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 25.10 -[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-), 9.81-[C-CH₂COOCH₂CH₂S-Al(CH₃)₂]₄-). Peaks at 14.14, 22.35, and 31.87 in ¹³C NMR spectra are corresponded to hexane. Broadening effects of the peaks are observed due to oligomerization in ¹H NMR spectrum.



Figure 4-6 DSC measurement of star shape membrane with different ratios of PO:ECH ranging from 50:50 to 90:10.



Figure 4-7 ¹H NMR spectroscopy of the polymeric solution with the ratio of PPO-PECH with ratio of PO:ECH (90:10). All the corresponding peaks are assigned.



Figure 4-8 water uptake and the swelling ratio of PPO-PECH and amine modified membranes PPO-PECH-TEA, PPO-PECH-DEA, PPO-PECH-TMA, and PPO-PECH-DMA. Red circle is corresponded to water uptake (WU) and blue dimond is corresponded to welling ratio (SR).
BILBIOGRAPHY

BIBLIOGRAPHY

(1) Friess, K.; Izák, P.; Kárászová, M.; Pasichnyk, M.; Lanč, M.; Nikolaeva, D.; Luis, P.; Jansen, J. C. A Review on Ionic Liquid Gas Separation Membranes. *Membranes* **2021**, 11 (2). 1093-1099.

(2) Uliana, A. A.; Bui, N. T.; Kamcev, J.; Taylor, M. K.; Urban, J. J.; Long, J. R. Ion-Capture Electrodialysis Using Multifunctional Adsorptive Membranes. *Science* **2021**, 372 (6539), 296–299.

(3) Choi, O.; Kim, Y.; Jeon, J.-D.; Kim, T.-H. Preparation of Thin Film Nanocomposite Hollow Fiber Membranes with Polydopamine-Encapsulated Engelhard Titanosilicate-4 for Gas Separation Applications. *J. Memb. Sci.* **2021**, 620 (77), 118946-118951.

(4) Zhang, Y.; Chen, Y.; Kang, Z. W.; Gao, X.; Zeng, X. ... Eggshell Membrane-Assisted Synthesis of Magnetic CuFe2O4 Nanomaterials with Multifunctional Properties (adsorptive, Catalytic, Antibacterial) for Water *Colloids Surf. A Physicochem. Eng. Asp.* **2021**, 12 (2), 4-9.

(5) Pourjavadi, A.; Safaie, N.; Hosseini, S. H. Graphene Oxide/poly (vinyl Imidazole) Nanocomposite: An Effective Support for Preparation of Highly Loaded Heterogeneous Copper Catalyst. *Applied* **2015**, 22 (8), 14-29.

(6) Guo, B.; Fan, R.; Shen, S.; Xue, Y.; Zhu, Z.; Xu, R. X. A Photo-Responsive Membrane for Tailored Drug Delivery with Spatially and Temporally Controlled Release. *J. Mater. Chem. B Mater. Biol. Med.* **2021**, 52 (7), 810-821.

(7) Hedge, O. J.; Höök, F.; Joyce, P.; Bergström, C. A. S. Investigation of Self-Emulsifying Drug-Delivery System Interaction with a Biomimetic Membrane under Conditions Relevant to the Small Intestine. *Langmuir* **2021**, 37 (33), 10200–10213.

(8) Feng, W.; Yang, X.; He, Z.; Liu, M. Hydrogen Sulfide Gas Sensor Based on TiO2–ZnO Composite Sensing Membrane-Coated No-Core Fiber. *J. Phys. D Appl. Phys.* **2021**, 54 (13), 135105-135110.

(9) Chen, H.; Yang, X.; Feng, W. Cadmium-Ion Detection: A Comparative Study for a SnO 2, MoS 2, SnO 2/MoS 2, SnO 2-MoS 2 Sensing Membrane Combination with a Fiber-Optic Mach--Zehnder Interferometer. *Appl. Opt.* **2021**, 60 (4), 799–804.

(10) Salvatore, D. A.; Gabardo, C. M.; Reyes, A.; O'Brien, C. P.; Holdcroft, S.; Pintauro, P.; Bahar, B.; Hickner, M.; Bae, C.; Sinton, D.; Sargent, E. H.; Berlinguette, C. P. Designing Anion Exchange Membranes for CO2 Electrolysers. *Nature Energy* **2021**, *6* (4), 339–348.

(11) Alam, K. S.; Fatema-Tuj-Johora, M.; Khan, G. M. A. Fundamental Aspects and Developments in Cellulose-Based Membrane Technologies for Virus Retention: A Review. *Journal of Environmental Chemical Engineering* **2021**, 9 (6), 106401-106421.

(12) Vermaak, L.; Neomagus, H. W. J. P.; Bessarabov, D. G. Recent Advances in Membrane-Based Electrochemical Hydrogen Separation: A Review. *Membranes* **2021**, 11 (2), 1031-1044.

(13) Scholes, C. A.; Stevens, G. W.; Kentish, S. E. Membrane Gas Separation Applications in Natural Gas Processing. *Fuel* **2012**, 96, 15–28.

(14) Deng, L.; Hägg, M.-B. Carbon Nanotube Reinforced PVAm/PVA Blend FSC Nanocomposite Membrane for CO2/CH4 Separation. *Int. J. Greenhouse Gas Control* 2014, 26 (3), 127–134.

(15) Zhang, X.; Singh, B.; He, X.; Gundersen, T.; Deng, L.; Zhang, S. Post-Combustion Carbon Capture Technologies: Energetic Analysis and Life Cycle Assessment. *Int. J. Greenhouse Gas Control* **2014**, 27 (10), 289–298.

(16) Han, Y.; Ho, W. S. W. Polymeric Membranes for CO2 Separation and Capture. *J. Memb. Sci.* **2021**, 628 (71), 119244-1192456.

(17) Wu, J.; Japip, S.; Chung, T. S. Polymeric Membranes for H2 and N2 Separation. *Polymeric Membranes for Water Purification and Gas Separation* **2021**, 113 (32), 243–334.

(18) Seong, J. G.; Lee, W. H.; Lee, J.; Lee, S. Y.; Do, Y. S.; Bae, J. Y.; Moon, S. J.; Park, C. H.; Jo, H. J.; Kim, J. S.; Lee, K.-R.; Hung, W.-S.; Lai, J.-Y.; Ren, Y.; Roos, C. J.; Lively, R. P.; Lee, Y. M. Microporous Polymers with Cascaded Cavities for Controlled Transport of Small Gas Molecules. *Sci Adv* **2021**, *7* (40), 9062-9069.

(19) Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. Energy-Efficient Polymeric Gas Separation Membranes for a Sustainable Future: A Review. *Polymer* **2013**, 54 (18), 4729–4761.

(20) Robeson, L. M. Correlation of Separation Factor versus Permeability for Polymeric Membranes. *J. Memb. Sci.* **1991**, 62 (2), 165–185.

(21) Robeson, L. M. The Upper Bound Revisited. J. Memb. Sci. 2008, 320 (1), 390–400.

(22) Lin, H.; Freeman, B. D. Materials Selection Guidelines for Membranes That Remove CO2 from Gas Mixtures. *J. Mol. Struct.* **2005**, 739 (1), 57–74.

(23) Husken, D.; Visser, T.; Wessling, M.; Gaymans, R. J. CO2 Permeation Properties of Poly(ethylene Oxide)-Based Segmented Block Copolymers. *J. Memb. Sci.* **2010**, 346 (1), 194–201.

(24) Lin, H.; Van Wagner, E.; Freeman, B. D.; Toy, L. G.; Gupta, R. P. Plasticization-Enhanced Hydrogen Purification Using Polymeric Membranes. *Science* **2006**, 311 (5761), 639– 642.

(25) Zhao, H.-Y.; Cao, Y.-M.; Ding, X.-L.; Zhou, M.-Q.; Yuan, Q. Effects of Cross-Linkers with Different Molecular Weights in Cross-Linked Matrimid 5218 and Test Temperature on Gas Transport Properties. *J. Memb. Sci.* **2008**, 323 (1), 176–184.

(26) Kusuma, V. A.; Freeman, B. D.; Borns, M. A.; Kalika, D. S. Influence of Chemical Structure of Short Chain Pendant Groups on Gas Transport Properties of Cross-Linked Poly(ethylene Oxide) Copolymers. *J. Memb. Sci.* **2009**, 327 (1), 195–207.

(27) Yin, Y.; Yang, L.; Yoshino, M.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K.-I. Synthesis and Gas Permeation Properties of Star-like Poly(ethylene Oxide)s Using Hyperbranched Polyimide as Central Core. *Polym. J.* **2004**, 36 (4), 294–302.

(28) Zhao, H.-Y.; Cao, Y.-M.; Ding, X.-L.; Zhou, M.-Q.; Liu, J.-H.; Yuan, Q. Poly(ethylene Oxide) Induced Cross-Linking Modification of Matrimid Membranes for Selective Separation of CO2. *J. Memb. Sci.* **2008**, 320 (1), 179–184.

(29) Lin, H.; Van Wagner, E.; Swinnea, J. S.; Freeman, B. D.; Pas, S. J.; Hill, A. J.; Kalakkunnath, S.; Kalika, D. S. Transport and Structural Characteristics of Crosslinked Poly(ethylene Oxide) Rubbers. *J. Memb. Sci.* **2006**, 276 (1), 145–161.

(30) Lin, H.; Freeman, B. D. Gas Permeation and Diffusion in Cross-Linked Poly(ethylene Glycol Diacrylate). *Macromolecules* **2006**, 39 (10), 3568–3580.

(31) Lin, H.; Freeman, B. D. Gas and Vapor Solubility in Cross-Linked Poly(ethylene Glycol Diacrylate). *Macromolecules* **2005**, 38 (20), 8394–8407.

(32) Lin, H.; Kai, T.; Freeman, B. D.; Kalakkunnath, S.; Kalika, D. S. The Effect of Cross-Linking on Gas Permeability in Cross-Linked Poly(Ethylene Glycol Diacrylate). *Macromolecules* **2005**, 38 (20), 8381–8393.

(33) Raharjo, R. D.; Lin, H.; Sanders, D. F.; Freeman, B. D.; Kalakkunnath, S.; Kalika, D. S. Relation between Network Structure and Gas Transport in Crosslinked Poly(propylene Glycol Diacrylate). *J. Memb. Sci.* **2006**, 283 (1), 253–265.

(34) Rodriguez, C. G.; Chwatko, M.; Park, J.; Bentley, C. L.; Freeman, B. D.; Lynd, N. A. Compositionally Controlled Polyether Membranes via Mono(μ-Alkoxo)bis(alkylaluminum)-Initiated Chain-Growth Network Epoxide Polymerization: Synthesis and Transport Properties. *Macromolecules* **2020**, 53 (4), 1191–1198.

(35) Zhao, H.; Ding, X.; Yang, P.; Li, L.; Li, X.; Zhang, Y. A Novel Multi-Armed and Starlike Poly(ethylene Oxide) Membrane for CO2 Separation. *J. Memb. Sci.* **2015**, 48 (9), 258–263. (36) Merkel, T. C.; Pinnau, I.; Prabhakar, R.; Freeman, B. D. Gas and Vapor Transport Properties of Perfluoropolymers. *Materials science of membranes for gas and vapor separation* **2006**, 1 (1) 89-104.

(37) Okamoto, Y.; Chiang, H.-C.; Fang, M.; Galizia, M.; Merkel, T.; Yavari, M.; Nguyen, H.; Lin, H. Perfluorodioxolane Polymers for Gas Separation Membrane Applications. *Membranes* **2020**, 10 (12) 394-407.

(38) Park, H. B.; Jung, C. H.; Lee, Y. M.; Hill, A. J.; Pas, S. J.; Mudie, S. T.; Van Wagner, E.; Freeman, B. D.; Cookson, D. J. Polymers with Cavities Tuned for Fast Selective Transport of Small Molecules and Ions. *Science* **2007**, 318 (5848), 254–258.

(39) Safaie, N.; Rawal, B.; Ohno, K.; Ferrier, R. C., Jr. Aluminum-Based Initiators from Thiols for Epoxide Polymerizations. *Macromolecules* **2020**, 31 (7) 6168-6190.

Chapter 5. Development and Characterization of Crosslinked Amine Modified Membranes for CO₂ separation and capture

5.1 Introduction

System compactness, energy efficiency, operational simplicity, and ability to overcome thermodynamic limitations have driven rapid growth and advances in the membrane market ^{1,2}. Membranes have been used for applications including fuel cell ^{2–6}, water desalination ^{7–11}, redox batteries ^{12–16}, and CO₂ separation ^{17–20}. Over the past decade, issues relating to climate change have enhanced focus on CO₂ separation and capture technologies resulting in innovative designs for CO₂ selective membranes. Precisely, membranes that allow separation from other gases or directly capture CO₂ from the air have been increasingly studied. These studies have led to an enhanced fundamental understanding of membrane design ^{21–25}.

For nearly 50 years, polymeric membranes have enjoyed the most significant share of the gas-separation membrane market because of the polymer membrane's lower cost and superior processability ²⁶. Generally, gas transport through polymeric membranes follows the solution-diffusion mechanism, in which permeability is the product of gas solubility and diffusivity ^{27,28}. The critical shortcoming of solution-diffusion membranes is the trade-off between permeability and selectivity, governed by Robeson's upper bound ^{29,30}. However, the transport mechanism is different inside facilitated transport membranes (FTMs); both high permeability and selectivity can be obtained simultaneously. The advantage of facilitated transport membranes becomes even more favorable when applied for CO₂ capture from low CO₂ pressure streams, e.g., flue gas in coal-fired power plants ¹.

Facilitated transport membranes containing amines have shifted the paradigm in CO₂ membrane design. FTMs generally include amines with various substitutions either attached

('fixed') to the membrane backbone or dissolved ('free') in the membrane matrix ^{31,32}. These amines are further broken down into two categories, hindered and unhindered. Hindered amines have a tertiary carbon attached to a primary amine or secondary or tertiary carbon atom attached to a secondary amine ^{33,34}. The reaction between CO₂ and fixed carriers is an intermediate that deprotonates with another amine to form a carbamate. In this case, if the amino group is sterically hindered, the rotation of the C–N bond in the carbamate product is restricted, and hence the carbamate product is destabilized by the surrounding bulky substituents ³⁵ 1,32,36–38</sup>. In the presence of water, the hindered carbamate can be easily hydrolyzed, resulting in the formation of bicarbonate and the regeneration of a free amino group, hereby doubling the CO₂ loading capacity ³⁹ 40–424344. Zhao and Ho grafted *sec*-butyl, isopropyl, and *tert*-butyl groups on the primary amino sites in PAA. A moderately hindered PAA, poly(*N*-isopropylallylamine) exhibited a high CO₂ permeability of 297 Barrer, nearly 5.5 times more permeable than the unhindered PAA ⁴⁵.

Polyether-based membranes are particularly attractive for CO₂ separations. The high mobility of C-O polymeric chain and favorable interaction between the C-O bond and CO₂ make it desirable for CO₂ application ^{46,47}. In addition, it has been observed that crosslinking of polyether and its derivatives (like polyethylene glycol) can enhance the membrane's permeability due to the flexibility of the chains ⁴⁸. In the recent work in 2020 by Lynd ⁴⁹, they presented a chain-growth network polymerization of epoxides to address the need for new synthetic concepts using mono(μ-alkoxo)- bis(alkylaluminum) (MOB) ^{50,51} initiators were further crosslinked to result in a thin film for CO₂ separation.

Inspired from the previous studies, we prepared facilitated transport membranes combining the enhanced selectivity and permeability of ether-based membranes with the increased loading capacity and transport properties of amines tethered membranes. Specifically, we synthesized robust, crosslinked polyether membranes containing functional chloromethyl groups at a controlled ratio. This one-pot solvent-free synthesis of the membrane was achieved by the reaction of MOB in the presence of epoxides monomer and poly (ethylene glycol) glycidyl ether as a crosslinker. The membranes were modified *via* post-polymerization with various amines to understand how the structure of the tethered amines affected the physicochemical properties of the membranes. Furthermore, the effect of a steric hindrance for different primary amines (hindered and unhindered amines) has been explored for CO₂ transport. The chemical structure, thermal properties, and single-gas permeation of the resultant membranes are investigated here by various characterization techniques.

5.2 Experimental section

5.2.1 Material

Trimethylaluminum solution (TMA) (AlMe₃, 2.0 M in hexane), 1-Methoxy-2-ethanol (anhydrous, 99.8%), (40% in EtOH), dimethylamine solution (DMA) (2.0 M in THF), nbutylamine (99%) (n-BuA), isobutyl amine (99%) (iso-BuA), tert-Butylamine (99%) (t-BuA) were purchased from Sigma-Aldrich. Propylene oxide (PO, Sigma-Aldrich, GC, \geq 99.5%), epichlorohydrin (ECH, Sigma-Aldrich, \geq 99%), and poly(ethylene glycol) glycidyl ether (Sigma-Aldrich, average M_n 500) were all used as received. CDCl₃ (Cambridge Analytica) was used without any further purification inside a glovebox. All the air and sensitive reaction were carried out in the glovebox. 5.2.2 Synthesis of Bis(µ-oxo)alkylaluminum [(CH₃)₂NCH₂CH₂(µ2-

OAl(CH₃)₂·Al(CH₃)₃](MOB)

A reaction vial was charged with a stir bar and trimethylaluminum (12.7 mmol, 12.7 mL) and cooled to -78 °C. 1-Methoxy-2-ethanol (12.7 mmol, 0.966 g) was added dropwise into the reaction vial containing trimethylaluminum. The solution was set to stir and warm to room temperature overnight. The solution was then directly cooled to -40 °C to crystallize the desired product. The resultant crystals were washed three times with anhydrous hexanes and dried in vacuo. ¹ H NMR (CDCl₃, 500 MHz) δ : -0.95 ([(CH₃)₂NCH₂CH₂(µ₂- O)Al(CH₃)₂·Al(CH₃)₃], -0.74 3.46 ([(CH₃)₂NCH₂CH₂(µ₂-O)Al(CH₃)₂·Al(CH₃)₂)·Al(CH₃)₃], 2.58 (s, CH₃=N-), 2.92 (t, $-N-CH_2-CH_2-O-$), 3.98 (t, $-N-CH_2-CH_2-O-$). ¹³ C NMR (CDCl₃, 100 MHz) δ : 45.2 ([(CH₃)₂NCH₂CH₂(µ₂-O)Al(CH₃)₂·Al(CH₃)₃], 55.11 (CH₃-N-), 58.84 ($-N-CH_2-CH_2-O-$), 67.30 ($-N-CH_2-CH_2-O-$). ¹H and ¹³C NMR spectrum are presented in the **SI, Figure 5-6.**

5.2.3 Synthesis of crosslinked membranes

Polymeric membrane solution prepared in a 20 mL vial with the initiator (14 mg), propylene oxide (0.74 ml), epichlorohydrin (0.11 ml), and diglycidyl ether (0.1 ml) as a cross-linker. Under a nitrogen atmosphere in the glove box, the reaction mixture was heated to 60 °C until viscosity visibly increased (5 hrs). The resultant viscous solution was casted uniformly onto the quartz glass plate and placed directly on the top of the hotplate at 80 °C overnight under a nitrogen atmosphere. The film was peeled off from the glass plate with addition of water. To remove impurities from the membrane matrix, the membranes were washed with DI water and kept in DI water overnight, and dried in a vacuum oven overnight at 40 °C. The obtained membrane is transparent and homogenous with a thickness of approximately 200-300 µm.

5.2.4 Crosslinked membrane functionalization

To synthesize the different amine grafted membranes, post- modification method has been opted because of the crosslinked nature of it (insoluble in desired solvents). The synthesized membranes were cut in varied sizes (2 x 2 cm²) and dipped into a different amine solution including MeA, nBu-A, iso-BuA, t-BuA for 48-72 h at RT. To remove the excess amine from the membranes, the membranes kept in the DI water.

5.2.5 Structure Characterization

The structure of the MOB was determined by 13C NMR spectroscopy on a 126 MHz Varian NMR spectrometer, as well as 1H NMR spectroscopy on a 500 MHz Varian NMR spectrometer at room temperature. 1H NMR spectroscopy of pristine membrane was performed on the same instrument and referenced using the residual 1H peak from the deuterated solvent before poring the viscous material in the quartz glass. FTIR spectra were measured on a Shimadzu IRAffinity-1 spectrometer equipped with MIRacle ATR attachment. The spectra were recorded between the wavelength of 500-4000 cm-1 in absorption mode for the pristine membranes and fabricated ones to further characterize the structures.

5.2.6 Thermal Characterization

Differential scanning calorimetry (DSC) was performed on a TA250 series analyzer (TA Instruments). A membrane (5–6 mg) was loaded in an aluminum pan and crimped with an aluminum hermetic lid. The sample was heated from –90 °C to a maximum of 50 °C with heating and cooling rates of 1 °C/min under a N₂ atmosphere. Data from the second heating curve were collected. Thermogravimetric analysis (TGA) was performed on TGA 500 (TA Instruments, USA) under a N₂ atmosphere with a heating rate of 10 °C/min. Approximately 5

mg of the membrane sample was loaded in an aluminum pan and heated to a maximum of 500 °C.

5.2.7 Rheology Characterization

The shear modulus of the pristine and amine modified membranes were determined with a MCR 302 rheometer from Anton Paar equipped with 8 mm diameter stainless steel parallel plate geometry. Oscillatory rheological measurements were conducted to measure the moduli of the films as a function of shear strain amplitude and as a function of frequency. The film sample was fixed between the upper parallel plate and stationary surface, with the gap size set according to individual film thickness (100–200 μ m). All tests were performed in triplicate at 23 ± 0.1 °C.

5.3 Results and discussion

MOB initiators were utilized for the synthesis of cross-linked, functional polyether membranes. In the recent work by Lynd and Freeman, MOB initiators were shown to exhibit tolerance of chemical functionality, provide control of molecular weight, and access to high reaction rates under some conditions. They also reported a cross-linked polyether membranes with a range of epoxide substrates using MOB that exhibited tolerance toward chemical functionality. This series of cross-linked polyether-based films demonstrated relatively high CO2 permeability and permselectivity under both dry and humidified conditions. Motivated by these results, we prepared the crosslinked-propylene oxide (PO) and epichlorohydrin (ECH) membrane to further investigate the effect of amine functionalization on the selectivity and permeability of polymeric ether-based cross-linked membranes. ECH was chosen for these membranes because it is an inexpensive epoxide monomer containing a functional chloromethyl group, which can be easily modified with amine groups. PO was chosen as a comonomer to tune the ratio of ECH and due to its low Tg and non-crystalizing nature of it. Therefore, crosslinked membranes were prepared solvent free by only adding PO, ECH, and poly(ethylene glycol) glycidyl ether crosslinker to a scintillation vial charged with MOB initiator. When the crosslinking membrane became apparently viscous, it was casted on a quartz plate to form a thin and uniform membrane. Scheme 5-1a depicts the concept for the crosslinked polyether membranes. The resulting membrane was free-standing, optically transparent, and flexible as can be seen in Scheme 5-1b. The membranes were post-modified with primary amines: methyl amine (MeA), n-butyl amine (nBuA), iso-butyl amine (isoBuA), and tert-butyl amine (tBuA). Since Cl groups of PECH can easily react with these amines, dipping method for membrane fabrication has been chosen.



Scheme 5-1 a) Synthesis of Amine Modified Cross-linked Polyether Membranes Using the MOB Initiator. b) Images of the representative cross-linked polyether membrane demonstrating optical transparency and flexibility.

5.3.1 Chemical properties

To investigate the polymerization of PO and ECH in the structure of membrane, ¹H NMR spectroscopy was utilized by taking the aliquot of PPO-PECH before the viscose solution casted on the quartz plate. ¹H NMR spectroscopy of the polymeric solution during reaction (**SI, Figure 5-7**) showed the Me group of PPO at 1.32 ppm, and protons corresponded to PPO and PECH

backbone are presented at 3.21-3.76 ppm. Residual peaks of monomers can be observed due to incomplete polymerization at this point. This is the only possible ¹H NMR spectroscopy as cross-linked membranes cannot dissolve in a solvent for NMR spectroscopy characterization. FT-IR spectroscopy was utilized to provide information about successful cross-linked PPO-PECH membrane preparation and amine attachment through post modification mechanism. As shown in **Figure 5-1**, the FT-IR spectrum of pristine membrane, PPO-PECH, has peaks around 1102, 903, and 611 cm⁻¹ suggesting the presence of C-O, C-C-O and C-Cl in the membrane structure. The amine modified membranes, PPO-PECH-MeA, PPO-PECH-nBuA, PPO-PECH-isoBuA, and PPO-PECH-tBuA presenting a characteristic peak of C-N at 1640 cm⁻¹, which is not visible in the PPO-PECH, suggesting the successful attachment of the amines into the polyether backbone membranes. Moreover, the broad peak around 3300-3451 cm⁻¹ for amine modified membranes

Entry	Sample ^a	T_{g}	G'e
		$(^{\circ}C)^{d}$	(MPa)
1	PPO-PECH ^b	-35	0.057
2	PPO-PECH-DMA ^c	-30	0.021
3	PPO-PECH-nBuA ^c	-29	0.025

Table 5-1 Characterization of Amine Modified Cross-linked Membranes.

PPO-PECH-iso-BuA^c

PPO-PECH-t-BuA^c

4

5

^a reaction condition: pristine membrane was prepared on using 14 mg of MOB initiator, propylene oxide (0.74 ml), epichlorohydrin (0.11 ml), and diglycidyl ether (0.1 ml) as a cross-linker. ^b pristine membrane. ^c the membrane was dipped in the amine solution (20 ml) at RT. ^d measured from second heating curve of DSC. ^e the plateau shear modulus was measured by rheometer.

-31

-34

0.037

0.043



Figure 5-1 FT-IR spectra of the copolymer membranes: pristine membrane PPO-PECH (red color) and amine modified membranes PPO-PECH-MeA (green color), PPO-PECH-nBuA (purple color), PPO-PECH-isoBuA (yellow line), and PPO-PECH-tBuA(wine color). Amine modified membranes are showing the characteristic peak of C-N at 1640 cm⁻¹ (dashed line).

5.3.2 Thermal and Rheological Properties

Thermal and rheological properties of the membranes were characterized to further explore polymer composition – property relationships. Measured and derivative values from these experiments can be found in **Table 5-1**. For pristine membrane, one endotherm peak at -35 °C is evident, attributed to the glass transition of the membrane. The endothermic peak for the amine membranes shift to higher values after amine post-modification. These results suggest successful attachment of the amines. The DSC result and corresponding T_gs are depicted in the **Figure 5-2**, **a**. The thermal stability of the amine-modified membranes was measured by TGA under air atmosphere as shown in **Figure 5-2,b**. PPO-PECH shows only two stages of weight loss due to both water loss and backbone decomposition. According to TGA curves, amine modified membranes have a three-stage degradation profile; The first slight stage for weight loss below 100-200 °C is due to adsorbed humidity or residual solvent evaporation in the membranes. The second weight loss at 200–380 °C is associated with the degradation of amine attached to the backbone. The third weight loss above 400 °C is related to the decomposition of the polymer backbone (PPO-PECH-MeA, PPO-PECH-nBuA, PPO-PECH-iso-BuA, PPO-PECH-tBuA).



Figure 5-2 DSC measurements (a) and TGA characterization of (b) PPO-PECH (red color), and amine modified membranes PPO-PECH-MeA (green color), PPO-PECH-nBuA (purple color), PPO-PECH-isoBuA (yellow color), and PPO-PECH-tBuA(wine color).

All polymeric systems are known to encompass different physical, chemical, and mechanical properties. These depend mainly on (1) macromolecular makeup, (2) inter-chain bonding and packing, and (3) chemical and thermomechanical history. **Figure 5-3** shows the plateau shear modulus (Mpa) for pristine and all amine modified membranes. For the pristine membrane the shear modulus comes nearby 56 10⁻³ Mpa whereas for the amine modified

membranes the shear modulus decreases due to the presence of the amine in the membrane matrix. The enhancement of shear modulus for PPO-PECH-tBuA and PPO-PECH-isoBuA in comparison with PPO-PECH-nBuA and PPO-PECH-MeA membranes which is ascribed to the increased chain rigidity imparted due to steric hindrance of tBuA and isoBuA in comparison with isoBuA and MeA.



Figure 5-3 the plateau modulus (G') of the cross-linked membranes (PPO-PECH) and amine modified membranes PPO-PECH-MeA, PPO-PECH-nBuA, PPO-PECH-isoBuA, and PPO-PECH-tBuA.

In occlusion, we reported a cross linked polyether-based membrane using a MOB initiator for CO₂ transport. Post modification of the membranes by dipping method is easy and efficient resulting in the amine tethered membrane for primary amines attachment (PPO-PECH-MeA, PPO-PECH-nBuA, PPO-PECH-isoBuA, and PPO-PECH-tBuA). All the prepared membranes exhibited uniform structure and complete incorporation of comonomers into polymer films with thermal stability, optical transparency, and flexibility. The chemical composition of the membranes was investigated by FT-IR to determine successful amine attachments as well as membrane physical properties which characterized by DSC, TGA, and rheometer. These membranes are the candidate for permeation-separation of CO₂/N₂ due to favorable interaction of C-O with CO₂. Also, the effect of hindered amines as comparison with unhindered ones in the structure of the amine can be investigated for permeation-separation through CO₂.

5.4



Figure 5-4 ¹ H NMR and ¹³C NMR spectroscopy of MOB. ¹ H NMR (CDCl₃, 500 MHz) δ: -0.95 ([(CH₃)₂NCH₂CH₂(µ₂- O)Al(CH₃)₂·Al(CH₃)₃], -0.74 3.46 ([(CH₃)₂NCH₂CH₂(µ₂-O)Al(CH₃)₂·Al(CH₃)₃], 2.58 (s, CH₃-N-), 2.92 (t, -N-CH₂-CH₂-O-), 3.98 (t, -N-CH₂-CH₂-O-). ¹³C NMR (CDCl₃, 100 MHz) δ: 45.2 ([(CH₃)₂NCH₂CH₂(μ₂-O)Al(<u>C</u>H₃)₂·Al(<u>C</u>H₃)₃], 55.11 (CH₃-N-), 58.84 (-N-CH₂-CH₂-O-), 67.30 (-N-CH₂-CH₂-O-).



 $-\frac{2}{\text{ppm}}$ Figure 5-5 ¹H NMR spectroscopy of the polymeric solution with the ratio of PPO-PECH with ratio of PO:ECH (80:20).

BILBIOGRAPHY

BIBLIOGRAPHY

(1) Han, Y.; Ho, W. S. W. Recent Advances in Polymeric Facilitated Transport Membranes for Carbon Dioxide Separation and Hydrogen Purification. *J. Polym. Sci. A* **2020**, 58 (18), 2435–2449.

(2) Ramasubramanian, K.; Zhao, Y.; Winston Ho, W. S. CO₂ Capture and H₂ Purification: Prospects for CO2-selective Membrane Processes. *AIChE J.* **2013**, 13 (1), 67-73.

(3) Xiao, L.; Zhang, H.; Scanlon, E.; Ramanathan, L. S.; Choe, E.-W.; Rogers, D.; Apple, T.; Benicewicz, B. C. High-Temperature Polybenzimidazole Fuel Cell Membranes via a Sol–Gel Process. *Chem. Mater.* **2005**, 17 (21), 5328–5333.

(4) Ogungbemi, E.; Ijaodola, O.; Khatib, F. N.; Wilberforce, T.; El Hassan, Z.; Thompson, J.; Ramadan, M.; Olabi, A. G. Fuel Cell Membranes--Pros and Cons. *Energy* **2019**, 172 (1), 155–172.

(5) Souzy, R.; Ameduri, B. Functional Fluoropolymers for Fuel Cell Membranes. *Prog. Polym. Sci.* **2005**, 30 (6), 644–687.

(6) Shukla, G.; Shahi, V. K. Poly(arylene Ether Ketone) Copolymer Grafted with Amine Groups Containing a Long Alkyl Chain by Chloroacetylation for Improved Alkaline Stability and Conductivity of Anion Exchange Membrane. *ACS Appl. Energy Mater.* **2018**, 1 (3), 1175–1182.

(7) Corry, B. Designing Carbon Nanotube Membranes for Efficient Water Desalination. *J. Phys. Chem. B* **2008**, 112 (5), 1427–1434.

(8) Cabassud, C.; Wirth, D. Membrane Distillation for Water Desalination: How to Choose an Appropriate Membrane? *Desalination* **2003**, 157 (1), 307–314.

(9) Cohen-Tanugi, D.; Lin, L.-C.; Grossman, J. C. Multilayer Nanoporous Graphene Membranes for Water Desalination. *Nano Lett.* **2016**, 16 (2), 1027–1033.

(10) Humplik, T.; Lee, J.; O'Hern, S. C.; Fellman, B. A.; Baig, M. A.; Hassan, S. F.; Atieh, M. A.; Rahman, F.; Laoui, T.; Karnik, R.; Wang, E. N. Nanostructured Materials for Water Desalination. *Nanotechnology* **2011**, 22 (29), 292001-202018.

(11) Shukla, G.; Shahi, V. K. Sulfonated Poly(ether Ether Ketone)/imidized Graphene Oxide Composite Cation Exchange Membrane with Improved Conductivity and Stability for

Electrodialytic Water Desalination. Desalination 2019, 451 (4), 200–208.

(12) Sizov, V. E.; Kondratenko, M. S.; Gallyamov, M. O.; Stevenson, K. J. Advanced Porous Polybenzimidazole Membranes for Vanadium Redox Batteries Synthesized via a Supercritical Phase-Inversion Method. *J. Supercrit. Fluids* **2018**, 137 (19), 111–117.

(13) Cao, L.; Kronander, A.; Tang, A.; Wang, D.-W.; Skyllas-Kazacos, M. Membrane Permeability Rates of Vanadium Ions and Their Effects on Temperature Variation in Vanadium Redox Batteries. *Energies* **2016**, 9 (12), 1058.

(14) Qiu, J.; Zhao, L.; Zhai, M.; Ni, J.; Zhou, H.; Peng, J.; Li, J.; Wei, G. Pre-Irradiation Grafting of Styrene and Maleic Anhydride onto PVDF Membrane and Subsequent Sulfonation for Application in Vanadium Redox Batteries. *J. Power Sources* **2008**, 177 (2), 617–623.

(15) Zhang, Q.; Dong, Q.-F.; Zheng, M.-S.; Tian, Z.-W. The Preparation of a Novel Anion-Exchange Membrane and Its Application in All-Vanadium Redox Batteries. *J. Memb. Sci.* **2012**, 42 (18), 232–237.

(16) Prifti, H.; Parasuraman, A.; Winardi, S.; Lim, T. M.; Skyllas-Kazacos, M. Membranes for Redox Flow Battery Applications. *Membranes* **2012**, 2 (2), 275–306.

(17) Zhang, X.; Singh, B.; He, X.; Gundersen, T.; Deng, L.; Zhang, S. Post-Combustion Carbon Capture Technologies: Energetic Analysis and Life Cycle Assessment. *Int. J. Greenhouse Gas Control* **2014**, 27 (6), 289–298.

(18) Rezakazemi, M.; Ebadi Amooghin, A.; Montazer-Rahmati, M. M.; Ismail, A. F.;
Matsuura, T. State-of-the-Art Membrane Based CO2 Separation Using Mixed Matrix
Membranes (MMMs): An Overview on Current Status and Future Directions. *Prog. Polym. Sci.*2014, 39 (5), 817–861.

(19) Norahim, N.; Yaisanga, P. Recent Membrane Developments for CO2 Separation and Capture. J. Mol. Catal. A: Chem. 2018, 18 (3) 136-139.

(20) Dai, Z.; Noble, R. D.; Gin, D. L.; Zhang, X.; Deng, L. Combination of Ionic Liquids with Membrane Technology: A New Approach for CO2 Separation. *J. Memb. Sci.* **2016**, 497 (2), 1–20.

(21) Nik, O. G.; Chen, X. Y.; Kaliaguine, S. Functionalized Metal Organic Framework-Polyimide Mixed Matrix Membranes for CO2/CH4 Separation. *J. Memb. Sci.* **2012**, 413 (41), 48–61.

(22) Peydayesh, M.; Asarehpour, S.; Mohammadi, T.; Bakhtiari, O. Preparation and Characterization of SAPO-34--Matrimid® 5218 Mixed Matrix Membranes for CO2/CH4

Separation. Chem. Eng. Res. Des. 2013, 91 (7), 1335–1342.

(23) Iarikov, D. D.; Ted Oyama, S. Chapter 5 - Review of CO2/CH4 Separation Membranes. In *Membrane Science and Technology*; Oyama, S. T., Stagg-Williams, S. M., Eds.; *Elsevier* **2011** 14 (2), 91–115.

(24) Zhao, L.; Sang, P.; Guo, S.; Liu, X.; Li, J.; Zhu, H.; Guo, W. Promising Monolayer Membranes for CO2/N2/CH4 Separation: Graphdiynes Modified Respectively with Hydrogen, Fluorine, and Oxygen Atoms. *Appl. Surf. Sci.* **2017**, 405 (41), 455–464.

(25) Wang, Y.; Yang, Q.; Zhong, C.; Li, J. Theoretical Investigation of Gas Separation in Functionalized Nanoporous Graphene Membranes. *Appl. Surf. Sci.* **2017**, 407 (32), 532–539.

(26) Dai, Z.; Ansaloni, L.; Deng, L. Recent Advances in Multi-Layer Composite Polymeric Membranes for CO2 Separation: A Review. *Green Energy & Environment* **2016**, 1 (2), 102–128.

(27) Ho, W. S. W.; Sirkar, K. K. *Membrane Handbook*; Chapman & Hall: New York, U.S.A., 1992.

(28) Strathmann, H.; Winston, H. W. S.; Sirkar, K. K. Membrane Handbook. *Vam Nostrand Reinhold, New York* **1992**.

(29) Robeson, L. M. Correlation of Separation Factor versus Permeability for Polymeric Membranes. *J. Memb. Sci.* **1991**, 62 (2), 165–185.

(30) Robeson, L. M. The Upper Bound Revisited. J. Memb. Sci. 2008, 320 (1), 390-400.

(31) Wang, Z.; Zhang, L.; Zhang, Y.; Wang, S. Facilitated Transport Membranes for CO_2 Separation [J]. *Membrane Science and Technology* **2003**, 4 (1), 221-227.

(32) Han, Y.; Ho, W. S. W. Polymeric Membranes for CO2 Separation and Capture. *J. Memb. Sci.* **2021**, 628 (45), 119244-119249.

(33) Tontiwachwuthikul, P.; Meisen, A.; Lim, C. J. CO2 Absorption by NaOH, Monoethanolamine and 2-Amino-2-Methyl-1-Propanol Solutions in a Packed Column. *Chem. Eng. Sci.* **1992**, 47 (2), 381–390.

(34) Lee, J. J.; Yoo, C.-J.; Chen, C.-H.; Hayes, S. E.; Sievers, C.; Jones, C. W. Silica-Supported Sterically Hindered Amines for CO2 Capture. *Langmuir* **2018**, 34 (41), 12279–12292.

(35) Amooghin, A. E.; Sanaeepur, H.; Pedram, M. Z.; Omidkhah, M.; Kargari, A. New Advances in Polymeric Membranes for CO2 Separation. *Polymer science: research advances, practical applications and educational aspects* **2016**, 7 (1), 354–368.

(36) Gottschlich, D. E.; Roberts, D. L.; Way, J. D. A Theoretical Comparison of Facilitated Transport and Solution-Diffusion Membrane Modules for Gas Separation. *Gas Sep. Purif.* **1988**, 2 (2), 65–71.

(37) Zou, J.; Ho, W. S. W. CO2-Selective Polymeric Membranes Containing Amines in Crosslinked Poly(vinyl Alcohol). *J. Memb. Sci.* **2006**, 286 (1), 310–321.

(38) Tong, Z.; Vakharia, V. K.; Gasda, M.; Ho, W. S. W. Water Vapor and CO2 Transport through Amine-Containing Facilitated Transport Membranes. *React. Funct. Polym.* **2015**, 86 (3), 111–116.

(39) Chakraborty, A. K.; Astarita, G.; Bischoff, K. B. CO2 Absorption in Aqueous Solutions of Hindered Amines. *Chem. Eng. Sci.* **1986**, 41 (4), 997–1003.

(40) Sartori, G.; Ho, W. S.; Savage, D. W.; Chludzinski, G. R.; Wlechert, S. Sterically-Hindered Amines for Acid-Gas Absorption. *Sep. Purif. Methods* **1987**, 16 (2), 171–200.

(41) Sartori, G.; Savage, D. W. Sterically Hindered Amines for Carbon Dioxide Removal from Gases. *Ind. Eng. Chem. Fundam.* **1983**, 22 (2), 239–249.

(42) Sartori, G.; Leder, F. Process for Removing Carbon Dioxide Containing Acidic Gases from Gaseous Mixtures Using Aqueous Amine Scrubbing Solutions, *Synthesis* **1978** 4 (7) 142–148.

(43) Zhao, Y.; Winston Ho, W. S. Steric Hindrance Effect on Amine Demonstrated in Solid Polymer Membranes for CO2 Transport. *J. Memb. Sci.* **2012**, 4 (6) 132–138.

(44) Bevan, A. PEUCKER-EHRENBRINK, B. & SCHMITZ, B. (eds) 2001. Accretion of Extraterrestrial Matter Throughout Earth's History. Xxvi 466 Pp. New York, Boston, Dordrecht, London, Moscow: Kluwer Academic/Plenum Publishers. Price Euros 126.50, US \$110.00, £77.00 (hard Covers). ISBN 0 306 46689 9. *Geological Magazine*. **2003**, 4 (2) 494–494.

(45) Zhao, Y.; Wan, Z.; Feng, Z.; Yang, D.; Zhang, Y.; Qu, F. Triaxial Compression System for Rock Testing under High Temperature and High Pressure. *Int. J. Rock Mech. Min. Sci.* **2012**, 52 (3), 132–138.

(46) Liu, S. L.; Shao, L.; Chua, M. L.; Lau, C. H.; Wang, H.; Quan, S. Recent Progress in the Design of Advanced PEO-Containing Membranes for CO2 Removal. *Prog. Polym. Sci.* **2013**, 38 (7), 1089–1120.

(47) Lin, H.; Freeman, B. D. Materials Selection Guidelines for Membranes That Remove CO2 from Gas Mixtures. *J. Mol. Struct.* **2005**, 739 (1), 57–74.

(48) Khan, M. M.; Halder, K.; Shishatskiy, S.; Filiz, V. Synthesis and Crosslinking of

Polyether-Based Main Chain Benzoxazine Polymers and Their Gas Separation Performance. *Polymers* **2018**, 10 (2) 2021-2028.

(49) Rodriguez, C. G.; Chwatko, M.; Park, J.; Bentley, C. L. Compositionally Controlled Polyether Membranes via Mono (μ-Alkoxo) Bis (alkylaluminum)-Initiated Chain-Growth Network Epoxide Polymerization: *Synthesis*. **2020**, 6 (7), 321-329.

(50) Rodriguez, C. G.; Ferrier, R. C.; Helenic, A.; Lynd, N. A. Ring-Opening Polymerization of Epoxides: Facile Pathway to Functional Polyethers via a Versatile Organoaluminum Initiator. *Macromolecules* **2017**, 50 (8), 3121–3130.

(51) Ferrier, R. C.; Imbrogno, J.; Rodriguez, C. G.; Chwatko, M.; Meyer, P. W.; Lynd, N. A. Four-Fold Increase in Epoxide Polymerization Rate with Change of Alkyl-Substitution on Mono-μ-Oxo-Dialuminum Initiators. *Polym. Chem.* **2017**, 8 (31), 4503–4511.

Chapter 6. Conclusion and Future Work

The first part of this thesis concludes a series of studies on development of a new methodology for polymerization and copolymerization of epoxides and episulfides, with the synthesis of aluminum-based initiators (SAl). We further expanded upon the architecture of SAl initiator by only changing the ligand to control the shape of homopolymers and copolymers. Then, we utilized the SAl star shape initiator to design novel amin tethered membrane for CO_2 separation. In the last chapter, we developed a new membrane grafted with primary hindered and unhindered amines to investigate the efficacy of this membrane for CO_2 capture.

In the first step, we presented a new platform for synthesis of aluminum-based initiator for polymerization of different epoxides. We investigated the synthesis of four different thioaluminum compounds (SAIs) and evaluated the efficacy as initiators for epoxide polymerization. These initiators showed living polymerizations with controlled molecular weight, low dispersity, and were tolerant to the epoxide functional group. We used electrospray ionization mass spectrometry (EIS-MS) and ¹H NMR spectroscopy to confirm the end group. We studied the kinetic behavior of this platform which showed the dependence on catalyst concentration and SAI end group. Next, we used SAI initiator for copolymerization (statistical and block copolymers) of different epoxides with targeted 30 kg/mol molecular weight and we used DOSY NMR to further investigate the presence of only one diffusion coefficient in the polymer matrix. We also combined the traditional RAFT polymerization technique with our SAI initiators, allowing for facile synthesis of vinyl-*b*-epoxide copolymers to easily and readily synthesis of poly(methyl methacrylate-*b*-epichlorohydrin) (P(MMA-*b*-ECH)). This technique will allow us to further tune polyether chemistry by giving us access to the vast array of thiol compounds that can act as end groups as well as facilitates the synthesis of block copolymers from disparate monomer classes.

In the second step, we showed that SAI initiators also can polymerize episulfides with a excellent control over molecular weights, relatively low polydispersity, and in short reaction time. Taken together, we copolymerized epoxides and episulfide to present a novel method for synthesis of statistical epoxide-stat-episulfide for the first time with control over molecular weight. We also synthesized a block copolymer of the same monomer to show the versatility of this method. We demonstrated statistical copolymerization of PS and epoxides to obtain unique, compositionally controlled copolymers. Polymer structure was characterized by various means such as ¹H and ¹³C NMR spectroscopy, DOSY, SEC, DSC, and SAXS. In the next step, we synthesized a new class of SAI initiators to show chemical flexibility of our method to tune the initiator structure enabling us to impart architectures on the PS containing (co)polymers in the form of ABA copolymers and star (co)polymers. Finally, we synthesized a PEG-*b*-PPS from a PEG macroinitiator and characterized it by ¹H and ¹³C NMR spectroscopy, DOSY, DSC, and SEC. This facile and tunable aluminum initiator system opens the door for a more robust and controlled synthesis of PS-epoxide copolymers that can be applied in biomedical and other contexts.

In the third step, we investigated the use of t-H initiator to present a one-pot and solvent free platform for synthesis of architecturally controlled star shape polyether-based membrane. To design a membrane suitable for CO₂ transport, we tuned the monomer feed ratio of propylene oxide (PO) and epichlorohydrin (ECH) for synthesis of poly(propylene oxide-statepichlorohydrin (PPO-PECH) in the presence of poly(ethylene oxide)-diglycidyl ether as a cross linker evolute a 3-D structure of membrane. The produced films were optically clear and flexible films in all cases with different PO:ECH ratios. We used the optimized PPO-PECH with ratio of 90:10 to further modify the film with a range of amines like trimethylamine (TEA), dimethylamine (DMA), triethylamine (TEA), and diethylamine (DEA) by membrane dipping method. We characterized chemical, physical, and mechanical properties of resultant secondary amine grafted and qaurtenized membranes. PPO-PECH-TMA showed higher conductivity, higher water uptake, swelling ratio, and alkaline stability in compare with pristine and the other modified membranes due to higher basicity of TMA in the structure of the membrane.

In the last step, we used previously reported MOB initiator to synthesis a (propylene oxide-*stat*-epichlorohydrin) (PPO-PECH) membranes utilizing bifunctional, poly(ethylene glycol) diglycidyl ether as a cross linking agent. We used of previously modified PO:ECH ratio (80:20) to be able to compare the capability of multi-armed membrane with the linear one for CO₂ separation. We also modified the prepared membrane with the range of unhindered to hindered primary amines *via* dipping method. We investigated the chemical structure and physical properties of the membranes were characterized by FT-IR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and rheometer. These membrane as facilitated transport membranes are designed specifically for CO2 transport and will be studied for CO₂/CH₄ separation. We will investigate the permeability and selectivity of the amine tethered membranes and compare the effect of hindered and unhindered amines for the mentioned application.

This conclusion suggests that the innovative and easy to synthesis SAl initiator is a versatile platform for polymerization of epoxides and episulfide and it may be used as a general

method for polymerization of other heterocycle monomers like lactides and lactones. This might be single and simple system to controllably polymerize all of these monomers like epoxide, episulfide, lactide, and lactone either individually or simultaneously. Our investigations into an aluminum-based catalyst and initiator system demonstrate a single system *can* also copolymerize these monomers to prepare new and novel materials that will have different applications. Also, as we should that using SAI we can polymerize off of another polymer chain or combine it with traditional methods like RAFT, may be further used ti design new methodologies for polymerization

Moreover, The SAl initiator can be modified to target different architecture of polymer as different thiols are commercially available as we synthesized ABA triblock copolymers and star shape copolymers. The only need to control the architecture is utilizing new thiol ligands that can be readily react with AlMe₃ to yield in specific shape of initiator and eventually (co)polymer.

Furthermore, by addition of a cross linker we could expand the use of the SAl initiators to synthesis membranes and design the membrane matrix to be utilized for important applications like CO₂ separation. In future, combining different heterocycle monomers will result new copolymeric material and with using the same approach, different membrane with diverse applications can be synthesized.

183