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A guide to modern methods for poly(thio)ether synthesis using Earth-abundant metals

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Polyethers and polythioethers have a long and storied history dating back to the start of polymer science as a distinct field. As such, these materials have been utilized in a wide range of commercial applications and fundamental studies. The breadth of their material properties and the contexts in which they are applied is ultimately owed to their diverse monomer pre-cursors, epoxides and thiiranes, respectively. The facile polymerization of these monomers, both historically and contemporaneously, across academia and industry, has occurred through the use of Earth-abundant metals as catalysts and/or initiators. Despite this, polymerization methods for these monomers are underutilized compared to other monomer classes like cyclic olefins, vinyls, and (meth)acrylates. We feel a focused review that clearly outlines the benefits and shortcomings of extant synthetic methods for poly(thio)ethers along with their proposed mechanisms and quirks will help facilitate the utilization of these methods and by extension the unique polymer materials they create. Therefore, this Feature Article briefly describes the applications of poly(thio)ethers before discussing the feature-set of each poly(thio)ether synthetic method and qualitatively scoring them on relevant metrics (*e.g.*, ease-of-use, molecular weight control, *etc.*) to help would-be poly(thio)ether-makers find an appropriate synthetic approach. The article is concluded with a look ahead at the future of poly(thio)ether synthesis with Earth-abundant metals.

1. Introduction

Polyethers and polythioethers are important classes of polymers that share a significant portion of their recent synthetic history, properties, and applications. Polyethers, such as poly(ethylene oxide) (PEO), are characterized by their C–O–C backbone which

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Gouree Kumbhar

Gouree Kumbhar received her bachelors degree in Chemical Engineering from Institute of Chemical Technology (India) in 2018. She recently received her PhD in Chemical Engineering at Michigan State University working with Dr Robert C. Ferrier Jr. At MSU, her research was focused on design and engineering of charged polyethers for separation membranes and to study polyelectrolyte self-assembly. Her expertise lies in the synthesis of organoaluminium catalysts for epoxide polymerization, novel polymer chemistry synthesis, and materials design. She currently works for the Dow Chemical Company in Houston, TX.

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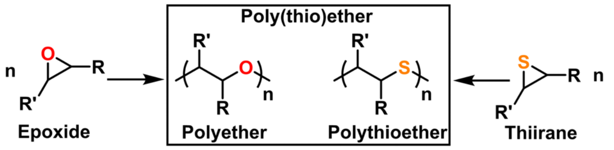

Fig. 1 Common monomers and polymer structures for poly(thio)ethers.

imparts flexibility (*i.e.*, low T_g), bio-compatibility, and ionic conductivity. Polythioethers, such as poly(propylene sulfide) (PPS), are characterized by their C–S–C backbone which imparts flexibility, bio-compatibility, and oxidative degradation resistance. Poly(thio)ethers are used in a wide variety of commercial and academic contexts ranging from cosmetics to drug delivery to energy storage. These polymers are most often produced from the ring opening polymerization (ROP) of multi-member oxygen or sulfur containing hetero-cycles. While 4-, 5-, and higher-member ring structures can be used as a monomer feed-stock for poly(thio)ethers, three-membered oxygen, (*i.e.*, epoxides or oxiranes), and sulfur (*i.e.*, episulfides or thiiranes) containing heterocycles are most often used owing to their polymerization efficiency and availability, as can be seen in Fig. 1. These monomers can be polymerized *via* a number of different mechanisms, which are unified by their incorporation of Earth-abundant metals such as aluminum, iron, and magnesium as a catalyst and/or initiator. As of this writing, there is no single method that can quickly and easily produce poly(thio)ethers with arbitrary composition, (micro)structure, molecular weight, and end group. As such, several different approaches are often used depending on the monomer, targeted molecular weight, and desired (micro)-structure for the given application. This Feature Article reviews the long and storied history of poly(thio)ether synthesis using Earth-abundant metals, discusses mechanistic aspects as well as features and quirks of contemporary synthetic methods, highlights the authors' specific contributions to the field, and expounds on the future of poly(thio)ether synthesis. We anticipate this article will help those who may want to synthesize a poly(thio)ether but do not know where to start as well as those who want an approachable look at the entire field.

2. How do we define an Earth-abundant metal?

We consider a broad definition of Earth-abundant metals consisting of a subset of the alkaline Earth metals (*e.g.*, Mg), alkali metals (*e.g.*, K, Na), first row transition metals (*e.g.*, Fe, Cr, Co, Zn), and post-transition metals (*e.g.*, Al, Sn). The metals covered here take various forms and each polymerization technique uses a different subset of metals, which is summarized in Table 1. We do not intend to give an exhaustive review of all Earth-abundant metals used in a particular synthetic scheme. Instead, we will provide an overview as well as recent notable examples. To assist readers who want to go more in depth, we will point out focused reviews where appropriate.

3. Application of poly(thio)ethers

3.1 Polyether applications

Polyethers and polythioethers share many of the same characteristics; they are low T_g polymers that are often biocompatible. Polyethers, especially PEO, have traditionally received more attention than polythioethers and so are in a slew of commercial applications. The most widespread use of polyethers is in the production of polyurethane foams through polyether polyols.[1–4] Since PEO is water soluble, it is often used as an emulsifier in the cosmetic[5] and food industries.[6,7] Owing to their interaction with ionic species as well as gases like CO_2, polyethers are employed in separations, such as polymer electrolytes for lithium ion batteries[8–10] or membranes for CO_2

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Shaylynn Crum-Dacon graduated from Tuskegee University with a Bachelor of Science in Chemical Engineering with a concentration in biochemical applications. After graduating, she worked at Los Alamos National Laboratory where she participated in research that primarily focused on additive manufacturing electrochemically active materials as well as investigated alternatives to nuclear waste containment materials. In 2018, she entered the Chemical Engineering doctoral program at Michigan State University where she, currently, researches polyether-based solid electrolytes for lithium batteries.

Nathaniel A. Lynd

Nathaniel A. Lynd is originally from Michigan and received a BS in Chemistry from Michigan State University, where he worked with the late Prof. Gregory L. Baker. Nate completed his PhD at the University of Minnesota under Marc A. Hillmyer. In 2007, Nate pursued postdoctoral studies at UC-Santa Barabara under Glenn H. Fredrickson, Craig J. Hawker, and the late Edward J. Kramer. Eventually, Nate took a position as staff scientist at Lawrence Berkeley National Laboratory in the Materials Sciences Division before joining the faculty of UT-Austin in the McKetta Department of Chemical in late 2015. Nate is currently the Laurence E. McMakin, Jr., Centennial Fellow in Chemical Engineering.

Table 1 Example metal structure associated with each polymerization method

Technique	Metal Form	Notes
AROP	K, Na, Cs cations	Counter-ions to oxyanions or thiolates
MAROP	AlR_3 and $[XAlR_3]^-$ $[NOct_4]^+$	AlR3 activates monomer, X = Cl or Br
CROP	Cationic Al, Zn, Mg complexes	Various bulky ligands (*e.g.*, salen, salpen, *etc.*)
Vandenberg	Bis-(μ-oxo) dialkyl aluminum (BOD)	Exact structure is unknown
DMC	MX_2 and $K_3M'(CN_6)$	M = Zn, Fe, Co, Ni; M = Co, Fe, Cr, Ir
Inoue	Zn- or Al-porphyrin complex	Substitutions on the metal possible (*e.g.*, –Cl, –OR, *etc.*)
Coates	Co- or Cr-salalen complex	Mono- or bi-metallic, substitutions on the metal possible
NAl adduct	$R_3N{:}AlR_3$ and BOD or mono-(μ-oxo)bisalkyl aluminum (MOB)	MOB acts as both a catalyst and initiator. BOD acts as initiator.

separation.[11,12] Due to their tunability and flexibility, polyethers are effective as anti-fouling coatings.[13] Finally, polyethers have been transformative to the biomedical field, with PEO enabling more stable medications through bioconjugation as well as novel methods for drug delivery.[14,15] For instance, the most recent mRNA vaccines to combat the COVID-19 pandemic used lipid bound PEO to help stabilize the mRNA for delivery.[16,17] Excellent reviews of polyethers by Wurm[18] and Frey[19] are recommended to learn more about their applications.

3.2 Polythioether applications

Polythioethers have been less commercially viable partially owing to synthetic challenges.[20] Traditionally, they were used in the vulcanization of rubber as well as in seals and sealants as commercial polymers like Thiokol,[21,22] although these ill-defined polymers are not strictly polythioethers.[23] More recently, they have found several academic applications and have been gaining traction in the biomedical space.[24,25] Owing to the backbone thioether groups propensity to oxidize, polythioethers are utilized to scavenge reactive oxygen species (ROS).[26] This ability has been used both in self-assembly schemes[27] as well as drug delivery schemes;[28] PPS in particular undergoes a hydrophobic to hydrophilic transition upon oxidation. As such, PPS is often combined with PEO to make micelles or vesicles for drug delivery as a sort of poloxamer (*i.e.*, Pluronic™) that can be oxidatively disassembled to deliver a payload to a target.[29–31] The backbone thioethers chelate a variety of metals and so can be used to incorporate metals into a polythioether matrix (*i.e.*, for antifouling applications),[32] to remove heavy metals like Hg[33] or detect the presence of metals.[34] Furthermore, due to the thioether backbone's interaction with Li-ions, polythioethers can be used as polymer electrolytes.[35,36] Excellent reviews of sulfur containing polymers especially polythioethers were written by Tirelli[24] and Plummer.[20]

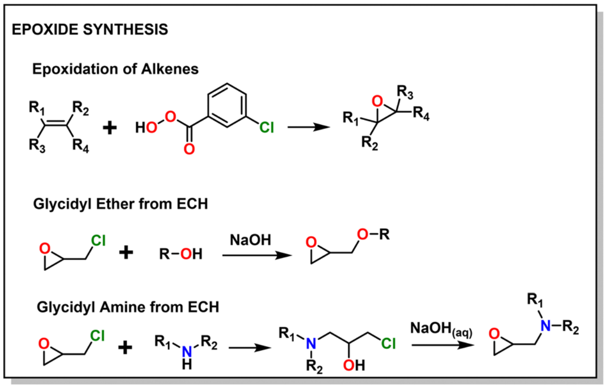


Fig. 2 Common epoxide synthesis methods.

4 Monomer synthesis

4.1 Epoxide synthesis

A major draw of polyether synthesis through epoxides is the diversity of their pendant groups coupled with their ease of synthesis and general availability. Epichlorohydrin (ECH), which is increasingly produced from renewable resources, is characterized by its pendant chloromethylene group which allows it to be used in a wide variety of reactions.[37] In the context of epoxide synthesis, it is extremely versatile; Glycidyl ethers can easily be made by reacting an alcohol with ECH in the presence of a base (*e.g.*, NaOH).[38] Glycidyl amines can easily be synthesized from reaction with a secondary amine and then subsequent ring closing reaction with NaOH.[39] Aside from ECH, epoxidation of alkenes is a common way to achieve epoxides with a variety of substituents.[40,41] Fig. 2 shows some general schemes involving the synthesis of epoxides.

4.2 Thiirane synthesis

Historically, thiiranes were difficult to stabilize and often resulted in the unintended formation of polymeric materials.[42,43] Staudinger first synthesized stable thiiranes in 1916.[44,45] Later, in 1921, Delépine provided a relatively straightforward synthetic scheme to prepare thiiranes from the reaction of chlorothioisocyanate and sodium sulfide.[46,47] A more modern take utilizes an epoxide reacted with thiourea or isothiocyanate, which produces episulfide in high yield.[42,43,48] Thiiranes can also be produced through thiocarbonyl ylide or aldazine N-oxide intermediates, which can preserve stereo-structure, but these are generally more difficult.[49] Fig. 3 shows an overview of these methods, with several other methods reported in the following ref. 45 and 48.

5. Contemporary synthetic techniques for poly(thio)ethers

There are a multitude of methods to achieve poly(thio)ethers using Earth-abundant metals, each with their own pros and cons in terms of control over polymer properties. This section highlights the state-of-the-art. We opted to split this section

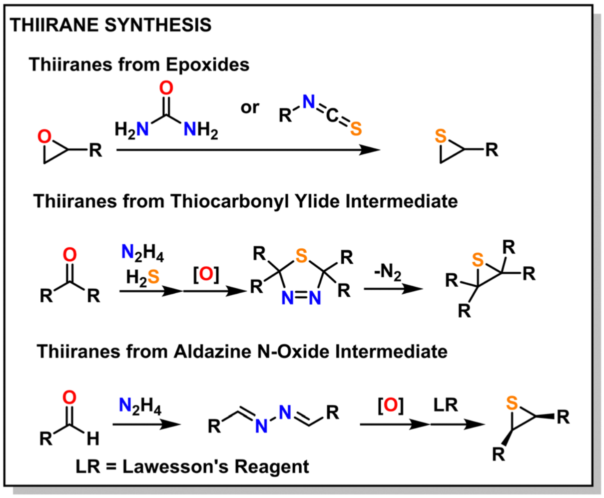


Fig. 3 Common thiirane synthesis methods.

into several sub-sections each devoted to a different class of synthetic method. To highlight the differences between methods and facilitate reader comprehension, we have provided qualitative "scores" for each of six different criteria for the polymerization method. These criteria are: molecular weight control, ease of use, monomer compatibility, (micro)structure control, kinetics, and end group control. The scores provided are based on our own assessments and are borne from each of the authors' unique backgrounds in physics, chemistry, and chemical engineering. The scores are subjective and are meant merely to guide the reader to find a suitable synthetic method for their needs. A table summarizing the relevant techniques in terms of some of these criteria can be seen below in Table 2.

5.1 A brief explanation of evaluation categories

Here we briefly explain the categories by which we have scored each polymerization technique. These are based on our opinion and are meant to help those less versed in poly(thio)ether synthesis to find the best method for their needs. For each category we assign four different criteria each worth one point.

Ease of use. Does the method require: (i) inert atmosphere? (ii) special reactors or glassware? (iii) complex catalyst/initiator synthesis? (iv) complex cleaning procedures?

Table 2 General attributes for synthetic methods of poly(thio)ethers

Technique	M_n (kg mol^{-1})	$Đ$	Monomers	Ease of use
AROP	<30	<1.2	GE, AT, GT	Hard
MAROP	<200	<1.2	AE, GE, AT, GT, O	Easy
CROP	<10	>1.5	O, R	Medium
Vandenberg	100–10 000	>2.0	AE, GE, AT, GT, O, R	Medium
DMC	<10	Varies	AE, GE, O	Easy
Inoue	<10	<1.2	AE, GE, AT, GT, O, R	Medium
Coates	<150	*ca.* 2.0	AE, GE, O	Medium
NAl Adduct	<100	<1.3	AE, GE, AT, O	Easy

AE = alkyl epoxide, GE = glycidyl ether, AT = alkyl thiirane, GT = glycidyl thioether, O = other, R = 4 or more member ring.

Molecular weight control. Does the method: (i) allow for synthesis of a target molecular weight? (ii) produce high molecular weight polymers (M_n > 100 kg mol^{-1})? (iii) produce low M_n polymers (M_n < 100 kg mol^{-1})? (iv) produce narrow $Đ$ polymers?

Polymer (micro)structural control. Can the method produce: (i) block and statistical copolymers? (ii) polymers with controlled tacticity? (iii) regio-regular polymers? (iv) polymers of different architectures (*e.g.*, star, branched, *etc.*)

Monomer compatibility. Can this method reliably polymerize (i) three membered hetero-cycles with alkyl substitutions? (ii) three membered hetero-cycle glycidyl (thio)ethers? (iii) four and higher membered heterocycles? (iv) other monomers (*e.g.*, epichlorohydrin)?

Kinetics. (i) Does the method have an induction period? (ii) Are the polymerizations "fast?" (iii) Can polymerization kinetics be enhanced (*e.g.*, through an additive)? (iv) Is the order in monomer and/or catalyst known and consistent?

End group control. Can the method produce polymers with end groups that are: (i) telechelic? (ii) functional/reactive? (iii) polymers (*e.g.*, macroinitiator)? (iv) uniform?

5.2 Anionic ring opening polymerization (AROP)

Why use it? If you are a seasoned chemist and want to make controlled, low to mid molecular weight poly(thio)ethers with decades of literature and theory support, then this may be the method for you Fig. 4.

Overview and development. AROP methods are some of the oldest synthetic routes for epoxide and thiirane polymerization and the most well-studied. In 1929 Staudinger demonstrated the controlled polymerization of EO[50] and Flory, in 1940, characterized the molecular weight distribution as a function of the initiator content.[51] Since thiiranes, especially ethylene sulfide (ES), are far less stable than their oxygen containing counterparts, polythioethers have been known for 200 years.[48] In 1954 Marvel and Weil demonstrated the polymerization of PS initiated by sodium ethoxide.[52] AROP of thiiranes was demonstrated by Sigwalt and Boileau in the 1960's.[53] Much of the more recent advances in AROP have involved reducing side reactions like chain transfer to monomer, as well as broadening the compatible monomer set. While the reach of AROP has significantly

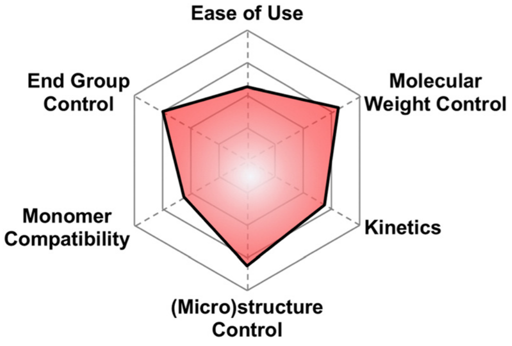


Fig. 4 Subjective scores for AROP with Earth-abundant metals visualized *via* radial plot. All parameters are scored from 0–4.

expanded since the early 1900s, the approach remains largely the same; an alcohol or thiol is de-protonated in solvent with an alkali metal salt (*e.g.*, potassium naphthalenide), which forms the initiator. Monomer is then added and the polymerization proceeds until the monomer is exhausted or the reaction is quenched. The process takes place under inert atmosphere, at mild to moderate temperatures, and in specialized glassware. Molecular weight ranges vary depending on the monomer, but $Đ$ are generally low. Recently, AROP methods without metals have been demonstrated using phosphazene[54–56] or organobases.[57]

Recent examples. AROP is still a very active technique especially for the polymerization of epoxides and thiiranes. As such, there are a number of notable recent examples. Meisner and co-workers generated a polymer electrolyte *in situ* in a lithium–sulfur battery cell by copolymerizing a thiirane with a PEG pendant and a di-thiirane.[58] The authors saw reasonably high ionic conductivities (*ca.* 7 mS cm^{-1}) in the presence of liquid electrolyte with high Coulombic efficiencies. Frey and co-workers copolymerized an epoxide with an acetal containing pendant with EO up to 10 kg mol^{-1} using potassium tertbutoxide as an initator.[59] The acetal group is a great leaving group and the authors demonstrated aldehyde, ester, and nitrile functional groups through post-polymerization modification. Kim and co-workers produced self-healable hydrogels by synthesizing PAGE-*b*-PEO-*b*-PAGE terpolymers from difunctional PEO macroinitiator deprotonated with potassium naphthalenide.[60] Post-polymerization modification of the AGE groups produced either pendant terminal thiols or pendant terminal ethyl groups which undergo reversible gelation triggered through redox of the thiol groups or temperature induced hydrophobic interactions of the alkyl tail.

Mechanism. In AROP of epoxides, an alcohol is deprotonated in solvent, with the oxyanion being balanced by a positive metal counterion, often K, Na, or Cs. Li is generally not suitable as a counter-ion due to the strong interaction with the oxyanion. Solvents are generally polar and aprotic like THF, dioxane, DMSO, *etc.* This compound forms the initiator, which, when epoxide is added, begins the ROP. Each monomer addition re-forms the anion, counterbalanced by the metal ion at the end of the polymer farthest away from the initiator. A similar approach is used for thiiranes, but usually begins with de-protonation of a thiol rather than an alcohol.[61] The polymerization is often terminated with acidic methanol. This process can be seen in the top scheme in Fig. 5. The addition of crown ethers (*e.g.*, 18-crown-6) and cryptands can significantly reduce side reactions as these increase the proportion of free ions.[62]

A number of side reactions can occur due to proton abstraction from substituted epoxides. Often this results in chain transfer to monomer, which limits molecular weight and bifurcates end group chemistry.[63] Certain solvents, like DMSO, can also cause chain transfer.[64] These side reactions can be suppressed with proper consideration of the metal complex used and identity of the counter-ion as well as the addition of compounds like crown ethers.[62] This can be seen in the middle scheme in Fig. 5.

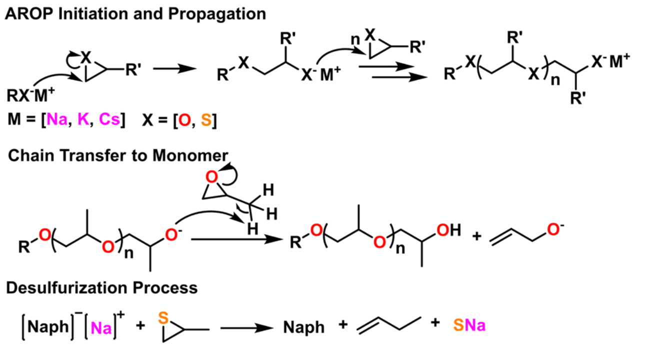


Fig. 5 (Top) General AROP initiation and propagation mechanism. (middle) Chain transfer to monomer, a common side reaction with epoxides. (Bottom) Desulfurization process endemic to thiirane AROP.

These side reactions are less problematic for substituted thiiranes as the thiolate ion is less basic than the alcoholate.[24] However, the presence of disulfides, perhaps due to the oxidation of the initiating thiol, can act as transfer agents during the polymerization, lowering and broadening molecular weight.[24,65] Therefore, protected thiols are sometimes used and de-protected right before the polymerization reaction. Certain Zn, Al, and Li initiators can cause "desulfurization" to occur during polymerization of substituted thiiranes, which results in the formation of disulfide bonds in the growing polymer chain and the formation of the relevant vinyl compound. This can be seen in the bottom scheme in Fig. 5.

Kinetics. AROP is a living polymerization method and the kinetics are first order in monomer. Polymerization rates depend on temperature and the identity of the metal ion. Larger ions (*e.g.*, Cs) result in faster kinetics and better suppression of side reactions, but K is often used because it provides a balance of celerity, control, and cost.[19,62] While kinetics vary depending on the above issues, polymerizations generally take hours to days to complete.

Molecular weight control. AROP can achieve moderate M_n, which is tuned through monomer to initiator ratio. Molecular weight control depends on the particular monomer being used. For example, EO can be polymerized to > 100 kg mol^{-1} at low $Đ$ through AROP. However, PO can be polymerized only to *ca.* 4 kg mol^{-1}. Glycidyl ether monomers can be routinely polymerized to around 30 kg mol^{-1}, depending on the proclivity of the system to undergo chain transfer.[63] This limit can be breached under certain circumstances.[66] $Đ$ are generally low ($Đ < 1.1$) across the board. Since AROP of thiiranes produces less debilitating side reactions than epoxides, polymerization of substituted thiiranes can regularly achieve molecular weights *ca.* 100 kg mol^{-1} at narrow $Đ$. For instance, Boileau and Sigwalt demonstrated PPS up to 300 kg mol^{-1}.[53]

(Micro)structural control. Due to its living nature, statistical and block copolymers can readily be made by AROP. Branched polymers can be made through polymerization of epoxides with terminal alcohol pendants.[67] Star polymers can be synthesized through initiators with 3 or more alcohols/thiols, however for monosubstituted epoxides M_n are generally limited.[68,69] Polymers are atactic and regioregular. Isotactic polymers can be produced through the AROP of enantiopure monomers.[70]

Supported monomers. AROP handles EO polymerization extremely well, but struggles with substituted epoxides. Due to chain transfer issues, epoxides with alkyl tails like butylene

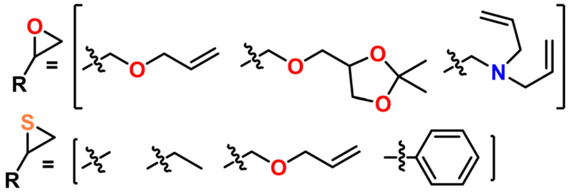


Fig. 6 Example monomers compatible with AROP.

oxide, cannot achieve appreciable molecular weights. Thiiranes significantly relax this condition. AROP is incompatible with polymerizations of four member and higher heterocycles. Generally, AROP is compatible with a wide variety of monosubstituted epoxides including glycidyl ethers,[19,71] glycidyl amines,[72,73] as well as a number of alkyl thiiranes[53,74–76] and thioglycidyl ethers.[77] Some examples can be seen in Fig. 6.

End group control. For uniprotic initiators, the generated poly(thio)ethers are heterobifunctional, with one end group determined by the initiator and the other an alcohol/thiol. Initiators with functional end groups (*e.g.*, ally alcohol) have been demonstrated to facilitate post-polymerization modification. A bromo- or chloro-containing terminating agent (*e.g.*, propargyl bromide) can be used to place a reactive functional group at the alcohol/thiol end.[19,24,61] Some example functional initiators and termination agents can be seen in Fig. 7. Telechelic polymers can be made through bi-functional initiators, but for mono-substituted epoxides are restricted to low M_n.[62] AROP is compatible with macroinitiators, like other polyethers,[19] but also those made from vinyl monomers like polystyrene[78] (PSt) and polyisoprene[79] (PI). Macroinitiators for thiirane polymerizations function in a similar way.[80,81]

Ease of use. AROP requires specialized glassware, clean monomers, and inert atmospheres for controlled polymerization. Working with new monomers can be challenging; the solvent, metal complex, initiator, and temperature all play a critical role in the activity of a polymerization.[19,62] That being said, AROP is very well studied and has been around since the beginning of polymers as a field and so there is plenty of literature to clarify the polymerization process for AROP neophytes.

5.3 Monomer activated ring opening polymerization (MAROP)

Why use it? If you want to polymerize a wide variety of epoxides up to high molecular weight with great control, but do not care too much about the end group, then this may be the technique for you Fig. 8.

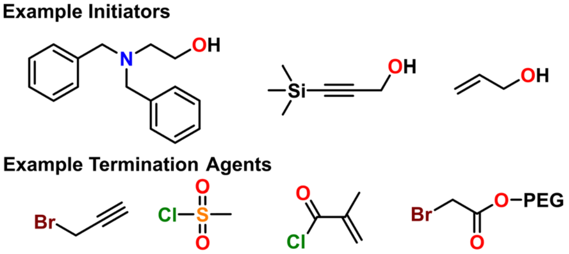


Fig. 7 Some example initiators and termination agents for AROP, which define polymer end groups.

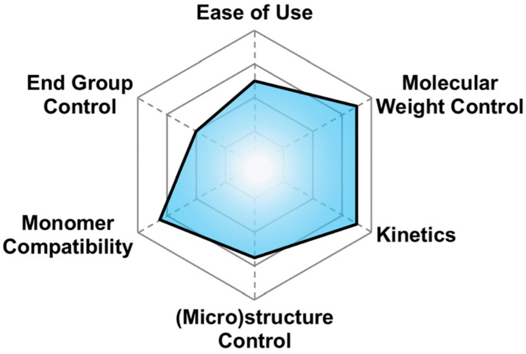


Fig. 8 Subjective scores for MAROP with Earth-abundant metals visualized *via* radial plot. All parameters are scored from 0–4, with 4 being the best.

Overview and development. MAROP is a beautiful extension of the AROP framework. Since its inception, there has been a concerted effort to improve AROP's handling of substituted epoxides. In the 2000s, Okuda demonstrated polymerization of monosubstituted epoxides using a system consisting of well-defined, bulky aluminoxane compounds which formed an aluminate (*i.e.*, "ate") complex in the presence of ammonium salts.[82] A few years later, Carlotti and Deffieux further improved this approach which resulted in what is now known as MAROP.[83] A Lewis acid, like trialkyl aluminum was combined with deprotonated alcohols counterbalanced by alkali metals (*e.g.*, sodium isopropoxide) or onium salts to form an initiator.[84] Excess Lewis acid in the system acts to activate the epoxide for polymerization. The beauty of this method is that it significantly suppresses chain transfer reactions so molecular weights >100 kg mol^{-1} can be achieved with substituted epoxides like PO, BO, and ECH, which would be impossible through classic AROP. Furthermore, these polymerizations are well controlled with typical $Đ<1.2$. Other activators including boron,[85] magnesium,[86,87] and alkali metal carboxylates[88] have been demonstrated.

Recent examples. There are a multitude of examples of MAROP in the literature as can be seen in the references from the supported monomers section. In one example, Lynd, Hawker and co-workers produced statistical co-polymers of EO and ECH. They transformed the ECH unit in the copolymers to methylene ethylene oxide (MEO) using potassium *tert*-butoxide.[89] The MEO unit could be easily cleaved with dilute solutions of trifluoroacetic acid, leading to degradable PEGs. The set of activators and initiators for the system has significantly expanded. For instance, Naumann and coworkers used N-heterocyclic olefins, which served to both initiate and stabilize the polymerization along with the Lewis acid magnesium bis(hexamethyldisilazide).[87] Similar to Carlotti and Deffieux's work, an excess of Lewis acid is needed. They were able to achieve extremely high M_n of PPO, up to 500 kg mol^{-1}, using this system.[86] Satoh and co-workers used an alkali metal (Cs or Na) carboxylate as an activator along with various alcohols as initiators.[88] This system allowed for the polymerization of epoxides and thiiranes, as well as a variety of copolymerizations with cyclic anhydrides.

Mechanism. The method utilizes Lewis acids (*e.g.*, trialkyl aluminum) and alkali metal alkoxides or onium salts. The

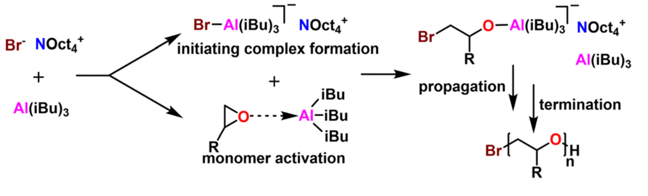


Fig. 9 MAROP mechanistic overview. The Lewis acid serves to both form the initiator complex as well as activate the epoxide for ring opening.

Lewis acid forms an "ate" complex with the alkoxide or onium salt, which acts as an initiator. The Lewis acid also serves to activate the epoxide monomer to facilitate ring opening. The original publications recounting MAROP use tri-isobutyl aluminum as the Lewis acid along with sodium isopropoxide.[83] However, this results in chain transfer to monomer. Later publications utilized onium salts (*e.g.*, $NOct_4Br$) with trialkyl aluminum Lewis acids, which suppressed side reactions. Because the Lewis acid acts to both activate the monomer and stabilize the polymerization, an excess is required. The amount of excess Lewis acid depends on the monomer and molecular weight targeted; For example, to polymerize ECH to 100 kg mol^{-1}, 5.4 times excess of Lewis acid compared with onium salt is needed.[84] Other initiating and Lewis acid species have been used and the mechanism remains largely similar, as can be seen in Fig. 9.

Kinetics. Kinetics are swift and depend on the monomer. When sodium isopropoxide is used as the initiator there is a noticeable induction time.[83] Increasing activator species relative to constant monomer and initiator concentrations significantly increases polymerization rate, but may broaden molecular weight.[62] Generally, polymerizations are completed in minutes to several hours.

Molecular weight control. Molecular weight with MAROP is controlled through the monomer to initiator (*e.g.*, onium salt) ratio. A variety of epoxides can be polymerized to M_n > 100 kg mol^{-1}. The $Đ$ is generally <1.2 for all monomers, although optimal activator concentrations, initiator identity, and temperature need to be determined for different monomers. Higher molecular weights require a higher ratio of activator to initiator. Side reactions are still present at higher T (T > RT), which broaden M_n.

(Micro)structural control. As this is a living polymerization system, block and statistical copolymers have been generated. Bi-functional initiators have been demonstrated using trialkyl aluminum and alkali carboxylates as the activator, while tri- and tetra-functional initiators have been demonstrated when using trialkyl boron as activator. Polymers are regio-regular with only head to tail linkages and are atactic. Stereo-regular polymers can be synthesized by using enantiopure monomer.[88]

Supported monomers. The most exciting aspect of this synthetic approach is that a great diversity of hetero-cycles can be polymerized, even ones thought to be "impossible".[90] Epoxides with saturated alkyl and unsaturated alkenyl pendants,[83,91–93] fluorine pendants,[94] glycidyl ethers,[95–99] as well as ECH,[100,101] epicyanohydrin,[102] thiiranes with alkyl pendants,[88] thioglycidyl ethers,[88] and oxetane.[103] Some examples can be seen in Fig. 10.

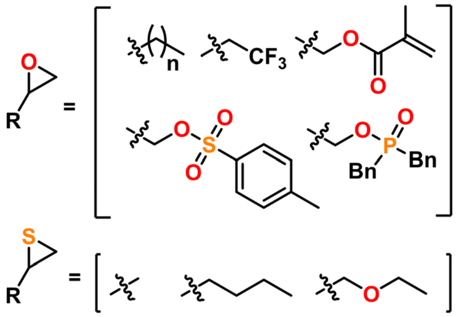


Fig. 10 Some example monomers compatible with MAROP.

End group control. End group control is probably the weakest aspect of MAROP. Unlike AROP or NAl adduct, which can choose from a variety of alcohols or thiols, MAROP is limited by the nucleophilicity of the initiating species. Generally, end groups consist of Br or Cl, but other examples like azide[104,105] and isopropyl have also been demonstrated.[83] When phosphazene bases are used in combination with trialkyl aluminum, protic initiators (*i.e.*, R-OH) could be used, thereby expanding the end group set and allowing for the polymerization of telechelic polyethers.[106] However, these result in chain transfer to monomer side reactions "in very low intensity" due to high basicity of the phosphazenes.[62] Macroinitiation of EO from anionically synthesized polystyrene (PSt) and polyisoprene (PI) has been demonstrated.[107]

Ease of use. MAROP is relatively easy to use. The polymerization requires an air and water free environment, but synthetic conditions are not nearly as strict as AROP. The specific monomer as well as targeted molecular weight affects the choice of initiator and concentration of activator and so some thought must go into polymer preparation. Specifically, the effective concentration of activator increases with the number of oxygens in the monomer. Aluminum species readily interact with polyethers which can make separation difficult. Polymerizations should be done at low temperatures (T < 0 °C) to control side reactions. Solvents generally consist of organic solvents like cyclohexane, toluene, or THF.

5.4 Cationic ring opening polymerization (CROP)

Why use it? If you need to polymerize something that is a 4 or more membered heterocycle, then this may be the method for you Fig. 11.

Overview and development. CROP is another classic method for poly(thio)ether synthesis. CROP was originally the main method by which polymers of 4 and higher membered heterocycles were polymerized, such as dioxolane, oxetane, oxathialane, and THF.[108–111] Traditionally, strong protonic acids are used (*e.g.*, trifluoroacetic acid) to form the tertiary oxonium ion necessary to initiate the ROP. These proceed by the so-callled activated monomer mechanism (AMM). Several well-written and extensive papers by Penczek outline this method, although it is beyond the scope of this article.[112–114]

An alternative route is through a Lewis acid mediated ROP using cationic metal compounds. These proceed by the

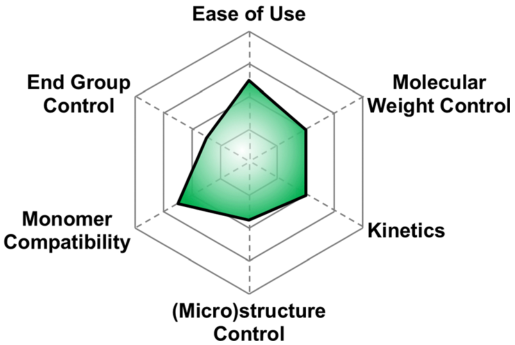


Fig. 11 Subjective scores for CROP with Earth-abundant metals visualized *via* radial plot. All parameters are scored from 0–4.

activated chain end (ACE) mechanism, meaning the metal remains at the end opposite of the propagating cation. The foundational catalysts involve poorly defined Zn, Mg, and Al-based compounds and polymerized both oxygen and sulfur-based heterocycles.[115,116] Defined metal complexes for CROP were first realized by Atwood and co-workers in the 1990's by using aluminum-salen complexes (*cf.* Fig. 12, left).[117] Since then, several other Al, Mg, and Zn compounds have been applied to epoxide polymerizations. Generally, this approach produces low molecular weight polymers (M_n < 10 kg mol^{-1}), at moderate to high $Đ$ ($Đ > 1.5$). Furthermore, the polymers are regio-irregular with many head to head and tail to tail defects present in the final polymer. The reader is encouraged to read the excellent review by Sarazin and Carpentier for an exhaustive list of structures related to epoxide polymerization with cationic metal compounds.[118]

Recent examples. A major recent avenue of investigation involving CROP has been the photo-induced and/or frontal polymerizations of epoxides, demonstrated by Crivello and others.[120–123] Although these types of polymerizations do not involve Earth-abundant metals, instead using photoactive diaryl iodinium compounds. However, some recent work has been published utilizing lithium salts as the initiating species. Miwa showed oxetane could be polymerized by Li salts in the early 2000s.[124] Cui applied this idea to epoxide polymerizations to synthesize polymer electrolytes.[125] More recently, Toyota used Lithium perchlorate to polymerize 3-glycidoxypropylmethyldimethoxysilane (GMDM) for use as a polymer electrolyte.[126] Molecular weights up to *ca.* 5 kg mol^{-1} were demonstrated with some cyclic products also formed. Nair and co-workers used a lithium salt as an initiator to synthesize polymer electrolyte gels from the polymerization of di-functional epoxide.[127] This is advantageous as a free-standing electrolyte membrane can be prepared in an hour with no additional modification necessary. A cobalt-based salen complex was recently developed by Lu and co-workers, which was able to polymerize cyclohexene oxide (CHO) up to mid-sized molecular weights (*ca.* 40 kg mol^{-1}) in minutes, however $Đ$ was *ca.* 2.[128]

Mechanism. Most cationic metal-mediated ring opening polymerizations are thought to proceed through an ACE mechanism. Here, a weakly coordinating anion (WCA) counters the cationic metal complex which serves to initiate the polymerization, adding a monomer at the oxygen, as can be seen in Fig. 13. This produces a carbenium ion at the opposite end which gets stabilized by the weak anion, resulting in a neutral metal center. The polymerization then proceeds through a typical cationic mechanism where subsequent monomer additions result in the formation of the oxonium ion at the propagating chain end.[114] Because the metal essentially becomes inactive after the first monomer addition, the composition of the cationic metal compound is largely irrelevant to the control of the polymerization reaction.[118]

Kinetics. Kinetics vary wildly, but are quite rapid for effective metal complexes. For instance, Dagorne and co-workers produced 9 kg mol^{-1} PPO in an hour at 0 °C with moderate polydispersity ($Đ$ = 1.7).[129] In another example, Bochmann and co-workers used a Zn complex (Fig. 12, right) to achieve M_n > 100 kg mol^{-1} for PPO and PCHO in minutes, but with high polydispersity ($Đ$ > 3.0).[130] Zn and Mg compounds are generally faster than their Al counterparts, but are less controlled.

Molecular weight control. Molecular weights are generally low (M_n < 10 kg mol^{-1}) and $Đ$ are generally high ($Đ$ > 1.5) with defined catalysts for epoxide polymerizations. Higher molecular weights have been demonstrated by classic poorly defined catalysts and certain defined metal complexes. For instance, certain salen and salpen complexes, as well as Zn and Mg complexes could achieve PPO with M_n > 100 kg mol^{-1}.[118] However, M_n could not be reliably controlled and the mechanisms were not understood in these instances.

(Micro)structural control. Polymers are generally atactic and regio-irregular. Statistical and block-copolymers have been

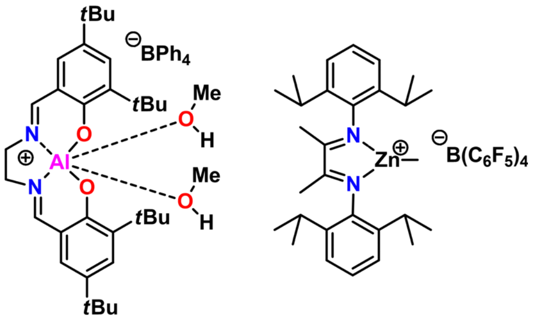


Fig. 12 Some example cationic structures for CROP. (left) Aluminum salen complex from Atwood.[117] (right) Zn-based structure from Bochmann.[119]

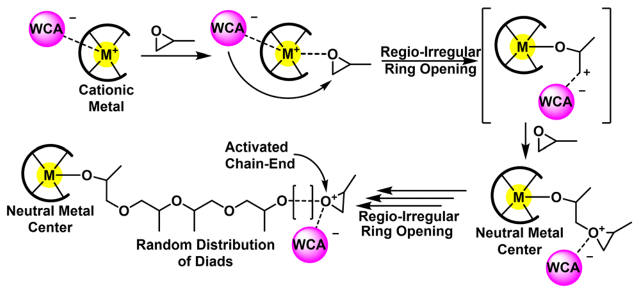


Fig. 13 Mechanistic overview for CROP. Adapted with permission from ref. 118. Copyright 2015 American Chemical Society.

synthesized.[131] For block-copolymers this is usually performed on four or higher member ring structures that proceed under a living polymerization.[131]

Supported monomers. Generally, three memember heterocylces (*i.e.*, epoxides, thiiranes) are best polymerized *via* other methods.[19] However, several epoxides and thiiranes have been polymerized; CROP is a classic method for the polymerization of ECH as well as its thiirane counterpart, chloromethylthiirane.[132] However, a useful draw of this polymerization method is that other cyclic ether species can also be polymerized like THF, trioxane, oxetane, and oxazoline, but these are more reliably produced using BF_3 or other non-Earth-abundant metals.[108–111,133,134]

End group control. As the polymerization proceeds by the ACE mechanism, the polymers are telechelic.[114] However, back-biting can occur, thus resulting in the formation of cyclic oligomers, reducing the number of end groups.

Ease of use. Many of the same considerations for AROP come into play with CROP; clean monomers/solvent need to be used with specialized glassware. Cationic metal complex initiated polymerizations are generally performed neat or in DCM or toluene. The defined cationic metal complexes are relatively straightforward to make and can be crystallized as pure products from the reaction media. Both well and poorly defined cationic metal complexes require handling of pyrophoric materials and so inert atmospheres are required. Low temperatures generally must be used for the polymerizations.

5.5 Coordinative methods

There are a number of Earth-abundant metal compounds that facilitate coordinative polymerizations of epoxides and/or thiiranes. Instead of listing every single Earth-abundant metal containing compound that polymerizes epoxides/thiiranes and proceeds by a coordinative mechanism, we opted instead to break these out into several general sub-categories. Specifically, we give examples of an undefined (Vandenberg's catalyst), a weakly defined (DMC Catalyst), a well-defined (Inoue's catalyst), and a well-defined, enantioselective (Coates' catalyst) catalyst, to give a general overview of the different types of catalysts one would encounter when synthesizing poly(thio)ethers from coordinative methods. These techniques were chosen based on their historical impact on poly(thio)ether synthesis, their use today, and their pedagogical utility for demonstrating disparate aspects of coordination polymerization. Excellent reviews by Coates on stereoselective coordination polymerization of epoxides[135] and by Kuran on coordinative polymerizations of heterocycles[136] can help the reader further explore this area.

5.5.1 Vandenberg's catalyst

Why use it? If you absolutely need to synthesize a poly(thio)ether to extremely high molecular weight and do not care too much about control, then this may be the technique for you Fig. 14.

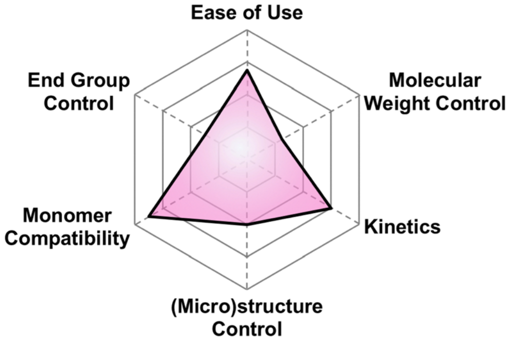


Fig. 14 Subjective scores for Vandenberg's catalyst visualized *via* radial plot. All parameters are scored from 0–4.

Overview and development. Vandenberg tells the story of the development of his eponymous catalyst in this ref. 137. We will summarize here. CC Price at the University of Pennsylvania developed a heterogeneous catalyst system, combining aluminum isopropoxide and zinc chloride enabling the polymerization of PO to high molecular weight.[138] EJ Vandenberg, an industrial chemist at Hercules Inc., began to see the similarities between his catalyst for vinyl ether polymerizations and Price's catalyst and sought to see if his catalyst would polymerize epichlorohydrin (ECH). Serendipitously, the monomer he used had a small amount of water present, which resulted in a small amount of semi-crystalline PECH. The adventitious water reacted with the alkyl aluminum in his catalyst, enabling the cationic polymerization of ECH. Simplifying his catalyst system to just include the alkyl aluminum and water resulted in controlled polymerization of ECH to high molecular weight. In furtherance of the mechanistic understanding of this catalyst system, Vandenberg attempted to block a reactive site with acetyl acetonate, which he hypothesized would decrease the effectiveness of his catalyst system.[139] On the contrary, he obtained high polyether quickly and in high yield. The likely active product of the reaction of two parts alkyl aluminum, one part acetylacetone, and one part water, seen in Fig. 15, is Vandenberg's catalyst, which is still used industrially today to produce a variety of commercial elastomers.

Recent examples. Despite its age, Vandenberg's catalyst is still used commercially today to produce Hydrin® elastomers.[137] Aside from commercial products, the catalyst is utilized in academia as well. For instance, Sanoja and Lynd employed Vandenberg's catalyst to produce crosslinked polymers and compared this with crosslinked materials made by a more controlled polymerization mechanism.[140] They found significantly different mechanical degradation profiles between these materials. Lynd and Chwatko discovered the catalyst could be used to homopolymerize lactones as well as copolymerize them with epoxides.[141] Statistical copolymerization between these two monomers allowed for degradable polyether materials. Finally, Beckingham, Sanoja, and Lynd used Vandenberg's catalyst to study the kinetics of epoxide copolymerizations.[142]

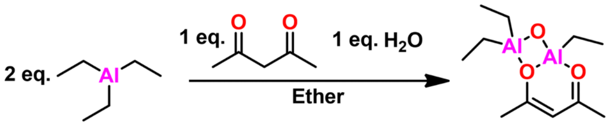


Fig. 15 Vandenberg's catalyst synthetic scheme.

Mechanism. The reaction of water, acetyl acetonate, and trialkyl aluminum produces a whole host of side reactions, the product of any of which, or a combination, could be the active catalyst. Vandenberg and Price hypothesized a bimetallic polymerization pathway.[143,144] Okuda experimentally determined this was the case for related compounds.[145] We have previously investigated the mechanism for the catalyst and determined the most likely catalytic structure is a bis-(μ-oxo) di-aluminum species,[146] which is consistent with the suspected structure. The epoxide is recruited through the oxygen opposite the acetyl acetonate, which causes a break in the four-membered bis-(μ-oxo) ring allowing for the epoxide to be ring opened and added. The bis-(μ-oxo) ring then recloses and a subsequent monomer can be added. We have previously mapped out the mechanism through DFT studies, the results of which are shown below in Fig. 16.

Kinetics. The polymerization kinetics of this catalyst are generally swift, with polymerizations often taking minutes to hours. Kinetics are first order in monomer based on our kinetic studies.[142,146] Since the active catalytic species cannot be separated from the reaction, the order of reaction involving the catalyst is unknown.

Molecular weight control. Molecular weights typically range from 100 kg mol^{-1} to 10 000 kg mol^{-1}.[139] However, $Đ$ are high, often greater than 2. Owing to the ill-defined nature of the catalyst, little control is possible. Further complicating control is that the activity of the catalyst varies batch to batch and so meaningful concentration/control relationships are difficult to obtain.

(Micro)structural control. Block and statistical copolymers of a variety of monomers have been demonstrated. Polymers produced with this method are isotactically enriched to about 30% and mostly regio-regular with a small amount of regio-defects.

Supported monomers. A variety of monomers are compatible with the Vandenberg catalyst. It was one of the few catalysts of its time that could polymerize ECH, a sometimes difficult to polymerize monomer, up to high molecular weight.[137] Aside from ECH, a variety of glycidyl ethers,[139,147] epoxides with alkyl pendants,[139] epihalohydrins,[148] thiiranes,[115] di-substituted epoxides,[149] cyclic ketals,[150] oxetane,[151–153] and lactones[141] can be polymerized.

End group control. Owing to the ill-defined nature of the catalyst system, end group control is not possible. Polymers are very large which makes end group characterization difficult. As such, there is probably a mix of end groups.

Ease of use. The catalyst system is easy to synthesize, but does require careful monitoring and some experience with handling pyrophorics. However, polymerizations are facile and high molecular weight polymers are produced with ease at mild to moderate temperatures in bulk or in solvent. The solvents used are typically diethyl ether, heptane, benzene, or toluene. As stated above, catalyst effectiveness is batch to batch. Residual aluminum can interact with the polyether, making removal difficult.

5.5.2 Double metal cyanide (DMC) heterogeneous catalyst system

Why use it? If you do not want to deal with pyrophorics, but still want to polymerize a broad set of epoxide substrates to 10 kg mol^{-1}, then this may be the technique for you Fig. 17.

Overview and development. DMC catalysts are classic industrial catalyst systems that have received renewed attention in the last few decades. Originally, these catalysts were developed in the 1960's by General Tire, Inc. to produce polyether polyols for the production of polyurethane.[154] The catalysts are formed from the precipitation of a metal salt of formula MX_2 like $ZnCl_2$ and a metal cyanide salt of formula $K_3M'(CN_6)$ like K_3FeCN_6 in the presence of a complexing agent (CA), often *tert*-butyl alcohol, but aldehydes, ketones, ethers, amides, ureas, nitriles, and sulfides have also been identified and a co-complexing agent or initiator in the form of a multivalent alcohol.[155] The metals generally consist of M = Zn^{II}, Fe^{II}, Co^{II}, or Ni^{II} and M′ = Co^{III}, Fe^{III}, Cr^{III}, and Ir^{III}. An example catalyst structure is shown in Fig. 18. The resultant catalyst is often nanosized and heterogeneous in nature with its structure affected by the CA chemistry as well as the synthesis temperature.[155]

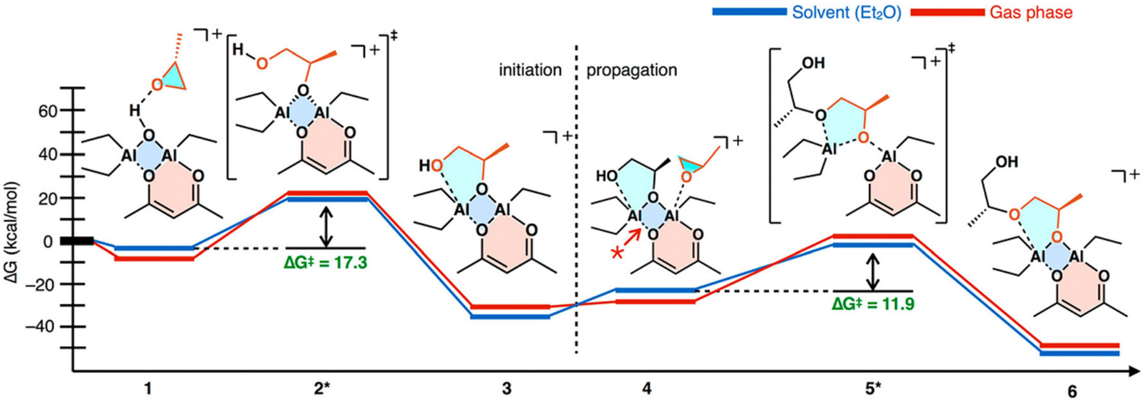


Fig. 16 Polymerization mechanism of Vandenberg's catalyst as determined from DFT studies. Reproduced with permission from ref. 146. Copyright 2018 American Chemical Society.

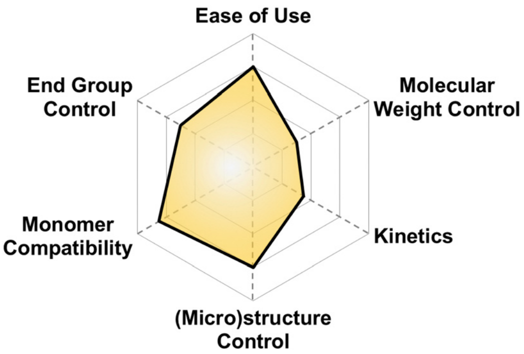


Fig. 17 Subjective scores for DMC catalysts with Earth-abundant metals visualized *via* radial plot. All parameters are scored from 0–4.

Epoxide polymerizations with DMC catalysts are done at around 100 °C, in an air free environment, under pressure, and in the absence of solvent. The resultant polyethers are often less than 10 kg mol^{-1} in size and can be narrow *Đ*, although this varies broadly. The DMC catalysts are also effective for the alternating polymerization of CO_2 and epoxides.

Recent examples. There has been a recent resurgence of work on DMC catalysts. Lopez and co-workers[157] as well as Kim and co-workers[155] clarified some of the mechanistic aspects of the DMC catalysts as well as structure–activity relationships for the polymerization of epoxides. Frey and co-workers highlighted a unique aspect of the DMC catalyst, which is their proclivity to polymerize a broad set of monomer classes.[158] Here, they copolymerized hexamethylcyclotrisiloxane (D3) and PO using a DMC catalyst up to 3 kg mol^{-1} at low *Đ*. The resulting copolymer exhibited a composition gradient microstructure, but incorporation of PO and D3 was apparent from the single T_g which decreased with higher incorporation of D3. This same group also prepared a statistical copolymer of PO and glycidyl methyl ether (GME) using DMC catalysts up to 4.5 kg mol^{-1} at low *Đ*. Marquez and co-workers prepared a layered DMC catalyst which crystallized.[159] This catalyst showed enhanced capability over traditional catalysts to polymerize epoxyhexane. Kim and co-workers demonstrated the polymerization of glycidol with controlled branching.[160]

Mechanism. Owing to the heterogeneous nature of the catalyst as well as solubility issues, the polymerization mechanism is not fully known. However, DMC catalysts are thought to have a dual polymerization mechanism; an ACE-type CROP mechanism and a coordination-insertion mechanism.[155] This dual mechanism is a result of the heterogeneity of the catalyst, with surface sites providing the coordination route *via* bound initiator and internal metal (*e.g.*, Zn^{2+}) sites providing the CROP due to the relative absence of bound initiator. The coordinative pathway provides regioregular polyether while the CROP pathway is regio-irregular. A scheme of both pathways can be seen in Fig. 19.

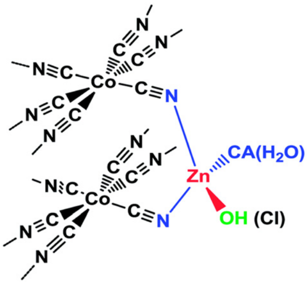


Fig. 18 Example DMC catalyst structure. Reproduced with permission from ref. 156. Copyright 2014 Royal Society of Chemistry.

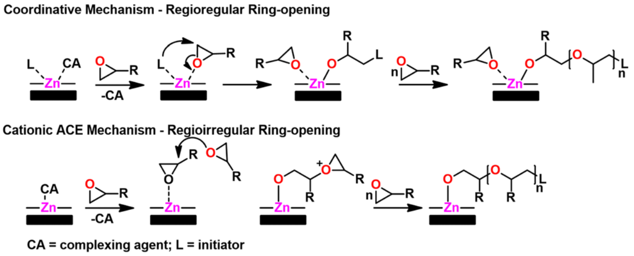


Fig. 19 DMC catalyst mechanism. Adapted with permission from ref. 155. Copyright 2019 Elsevier.

Kinetics. The kinetics of DMC catalyst mediated polymerizations of epoxides are quite fascinating.[161,162] Induction times of minutes to hours are often noted; the induction time depends on the strength of the interaction between the CA and the catalyst surface with weaker interactions leading to lower induction times.[155,162,163] A bell curve-like polymerization rate profile is observed; once the catalysts become active the polymerization rate increases rapidly until the acme, after which rapid catalyst deactivation occurs. The breadth, skewness, and peak height of the kinetics profile are affected by polymerization temperature, catalyst composition, and CA chemistry. To ball park the polymerization time, it takes minutes to a couple hours to produce polyethers using this method, with PO polymerizations being on the faster side and ECH on the slower side. The upside is that the system scales well and so 100s of grams of polymer can be produced in less than a couple hours.

Molecular weight control. Reported molecular weights typically cap out at around 10 kg mol^{-1} for all monomers studied. However, there is often residual, high molecular weight polymer owing to the suspected dual mechanism, which is mitigated through the addition of a co-CA.[157,163] *Đ* vary wildly and depend on the specific monomer, polymerization temperature, catalyst composition, CA(s), and catalyst preparation temperature. The preparation of low *Đ* ($Đ < 1.1$) PPO is well demonstrated, but other monomer substrates are less well explored and control may not be achievable.

(Micro)structural control. A wide variety of alcohols have traditionally been utilized with DMC catalysts in the polymerization of epoxides. Linear,[155] star,[164] and branched[160] polymers have been demonstrated. These disparate architectures are achieved *via* the number of the alcohols of the initiator; multi-alcohol initiators generate branched structures, while

one and two alcohol-containing initiators generate linear polyethers. Statistical and block copolymers have also been demonstrated. Polymers produced this way are atactic and mostly regio-regular with some regio-defects owing to the hybrid polymerization mechanism. Isotactically enriched polymer can be synthesized by using enantiopure monomer.[156]

Supported monomers. PO is by far the most common monomer polymerized with DMC catalysts owing to the commercial roots of this technique, however other monomers like glycidyl ethers,[155,165] epoxy alkanes,[155] and ECH[156] have also been polymerized with this method. The catalyst composition plays a significant role in monomer compatibility and so catalysts are best tailored to the specific monomer of interest. Furthermore, this method also facilitates the copolymerization of epoxides with a variety of disparate monomers such as CO_2,[166,167] anhydrides,[168,169] and siloxanes,[158] enabling the synthesis of unique polymers.

End group control. The end group is dictated by the initiating ligand that is used.[155] Several mono- and multi-functional alcohols have been demonstrated and so end group control is robust. The polymer grows from the metal center on the catalyst and once the polymerization is terminated, a terminal OH is present. This facilitates production of both heterobifunctional and telechelic polyethers. Alcohol containing CAs are initiative, which affects uniformity of end groups.

Ease of use. The preparation of the catalyst is relatively straightforward and proceeds through a mixture of the metal cyanide salt with the second metal salt in the presence of CA(s) at moderate temperatures. However catalyst structure–polymerization activity is not fully understood and so applying this method to understudied systems could be tricky.[155] Pressure-resistant reactors and air free environments are required for polymerization reactions. Polymerizations proceed at mild to moderate temperatures and can be performed in bulk. The catalyst becomes inactive when exposed to air and does not remain with the polymer. Furthermore, because of the size of the inhomogeneous catalysts, separation is largely straightforward to obtain a pure polymer product.

5.5.3 Inoue's metal porphyrin catalyst

Why use it? If you want to polymerize basically anything to 10 kg mol^{-1} with good control, then this may be the technique for you Fig. 20.

Overview and development. The reader may find it interesting to read the story of the development of this striking class of catalysts in Inoue's own words found in this citation in English[170] and this in Japanese.[171] We will summarize here. In 1978, Inoue and co-workers first demonstrated a chloroaluminum tetraphenyl porphyrin (AlCl-TPP) catalyst that allowed for the facile polymerization of epoxides[172,173] to controlled molecular weight *via* a coordination-insertion type polymerization.[174] Chemical structures of these catalysts can be seen in Fig. 21. Inoue followed this work up with several other catalysts with different substitutions in place of the Cl (*e.g.*, –OR, –SR, *etc.*) as well as Zn in place of Al. The Zn based catalysts were found to be effective for polymerization of thiiranes.[175]

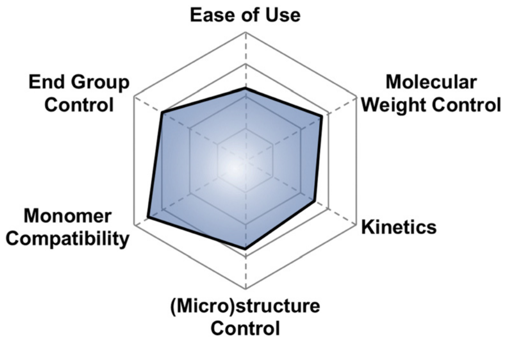
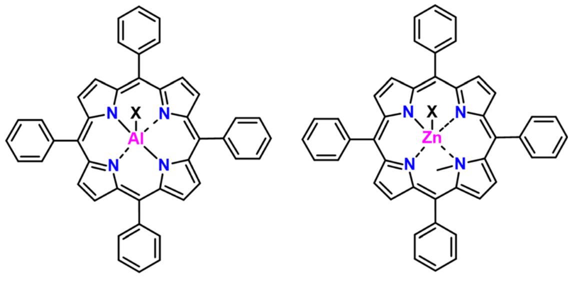


Fig. 20 Subjective scores for Inoue's metal porphyrin catalyst visualized *via* radial plot. All parameters are scored from 0–4.

Inoue tested the polymerization of epoxides in the presence of several alcohols, anticipating that these would lead to a broadening of the M_n. Instead, Inoue found that these alcohols, in the presence of the TPP catalyst, underwent rapid reversible chain transfer with the growing polymer chain resulting in a narrow $Đ$ and a single peak on the GPC. He termed these polymerizations "immortal" since they could not be killed.[176] Aside from Zn and Al, other metals have recently been used in the polymerization of epoxides, like Cr, Mn, and Co.[177–179]

Recent examples. Due to the diversity of compatible monomer classes, this catalyst is currently heavily utilized for ring opening copolymerization (ROCOP) of epoxides with other species, rather than in pure poly(thio)ether synthesis. Honda and co-workers investigated the alternating polymerization of oxetane and CO_2 with a variety of metalloporphyrins and organo-cocatalysts.[180] They were able to selectively synthesize poly(trimethylene carbonate) with near 100% carbonate linkages using the AlCl-TPP catalyst along with tetra-*n*-butyl ammonium bromide. Wang and co-workers exploited the robustness of the metallo-porphyrin system along with clever choice of chain transfer agent for the one pot synthesis of block copolymers of poly(methyl methacrylate) (PMMA) and poly(propylene carbonate) (PPC).[181] Here, the metalloporphyrin served dual roles; to initiate the alternating polymerization of propylene oxide and CO_2 as well as a photoredox catalyst for



X = [Me, Et, Cl, OR, OAr, O_2CR, SR]

Fig. 21 TPP catalyst structures with Al (left) and Zn (right).

photoinduced electron/energy transfer-reversible addition–fragmentation chain transfer (PET-RAFT) polymerization of vinyl monomers. The RAFT agent contained a carboxylic acid moiety that served as a chain transfer agent (CTA) for PO/CO_2 polymerization, which resulted in the block copolymer. A similar approach with cyclic anhydrides as opposed to CO_2 was demonstrated by the same group a few years later.[182] Some excellent recent reviews have highlighted metalloporphyrins as switchable catalysts[183] as well as their role in sustainable polymerization[184] and we encourage the reader to check those out if interested.

Mechanism. The polymerization mechanism for the metal porphyrin catalysts is coordination-insertion, where the monomer adds at the metal center, as shown in Fig. 22a. The species bound to the metal center (*e.g.*, Cl, –OR, –SR) initiates the polymerization. Inoue found that by adding a Lewis acidic aluminum species a rapid increase in kinetics for both epoxides[185] and thiiranes[170,171] was achieved. Here, the Lewis acid species activates the monomer, facilitating enchainment and ring opening while simultaneously suppressing side reactions, evoking MAROP, as seen in Fig. 22b. Adding alcohols or thiols as CTAs, results in the rapid exchange between the protic species and the propagating polymer chain, as seen in Fig. 22c. This occurs far faster than a single monomer addition, leading to immortal-type polymerizations.[176] For the polymerization of thiiranes, adding thiols as a CTA resulted in this immortal character, while alcohols did not.[175] Furthermore, adding chemicals that are traditionally catastrophic for epoxide polymerizations like HCl had no effect on the polymerization, further demonstrating how robust this approach is.[186]

Kinetics. The polymerizations are living in nature and first order in monomer. There is a significant increase in kinetics with the addition of bulky Lewis acids that work to activate the monomer. The presence of CTA significantly slows the polymerization kinetics down. Generally, depending on monomer, CTA/TPP ratio, targeted M_n, and presence of Lewis acid, polymerizations take hours to several days.

Molecular weight control. Molecular weights are very well controlled regardless of the presence of Lewis acid and/or CTA and depends on the monomer to (initiator + CTA) ratio. For most polymerizations involving CTAs, M_n < 10 kg mol^{-1}. However, the original report of this system demonstrated M_n > 80 kg mol^{-1}. $Đ$ are typically <1.2 for polymers M_n < 10 kg mol^{-1}. Higher molecular weight may have higher $Đ$. Addition of CTA does not broaden the molecular weight distribution, but leads to lower overall M_n.

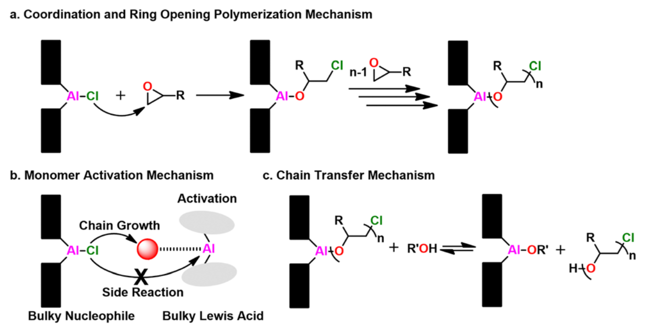


Fig. 22 Al-porphyrin catalyst mechanism overview. (a) Coordination and ring opening, (b) Monomer activation, (c) Chain transfer.

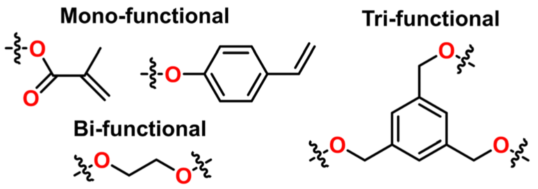


Fig. 23 Example (multi-)functional end groups through choice of CTA.

(Micro)structural control. Block and statistical copolymers have been demonstrated. Alternating copolymers have been demonstrated with epoxides and CO_2 or anhydrides. The functionality of the protic CTA dictates branching architectures; for instance a dihydroxyl containing CTA enables the formation of telechelic polymers or facile polymerization of triblock copolymers. Similarly, compounds with 3 or 4 protic groups result in three and four arm star polymers. Some example multi-functional groups can be seen in Fig. 23. The polymers formed with TPP catalyst are strictly regioregular and isotactically enriched, reminiscent of other coordinative systems.

Supported monomers. Perhaps the strongest aspect of this approach is the scope of monomer substrates that can be used. A wide variety of substituted epoxides and thiiranes have been polymerized. Additionally, oxetanes, lactones, lactides, siloxanes,[187] (meth)acrylates, and other monomers can be polymerized. Each class of monomers requires a slightly different catalyst.[170] For instance, thiiranes polymerize from the Zn–porphyrin catalyst, while epoxides proceed from the Al-porphyrin catalsyt.

End group control. The end group is dictated by both the substitution on the metal and the identity of the CTA used. In the case of the AlCl-TPP catalyst, a completed polyether will be heterobifunctional with a chloro group on one end and a hydroxyl on the other. Al-TPP catalysts with substitutions other than Cl are a bit trickier to prepare making end group control less than facile. CTA can be added to diversify the end groups; Polymerization occurs from both the CTA as well as the aluminum porphyrin catalyst itself so a mixture of polymers with both end groups will be obtained in this way. The ratio of protic species to TPP catalyst can be increased to ensure the vast majority of polymers are capped with the targeted end group. However, this comes at the cost of M_n or kinetics. Some example functional end groups can be seen in Fig. 23.

Ease of use. Synthesis of the AlCl-TPP catalyst involves the room temperature reaction of tetraphenylporphyrin with ClEt$_2$Al under nitrogen, while the Zn-TPP catalyst uses diethyl zinc and *N*-methyl tetraphenylporphyrin. The metal compounds are pyrophoric and so require caution when handling. Separation of the prepared catalyst is made by simply removing the volatile compounds under reduced pressure. Other catalysts (*i.e.*, those with groups different than Cl) are more difficult to synthesize, and involve multi-step reactions. Polymerizations are generally performed at mild temperatures (RT - 50 °C) in bulk or solvent (often DCM). Unlike MAROP or other coordinative methods, the catalyst is generally easy to remove through extraction owing to its size.

5.5.4 Coates' enantioselective bimetallic Co- or Cr-catalyst

Why use it? If you want to make fully isotactic polyethers from a broad set of racemic epoxide substrates, then this may be the technique for you Fig. 24.

Overview and development. An account in Coates' own words of the development of this catalyst system can be found in this reference which doubles as an excellent review of stereo-selective polymerizations of epoxides.[135] While exploring a cobalt catalyst for copolymerizations of PO/CO_2, Coates and coworkers found one catalyst system resulted in a mixture of polyether and polycarbonate chains with the polyethers being nearly 100% isotactic in nature. This catalyst was a cobalt(III) complex oxidized by acetic acid and it polymerized PO to high M_n (> 100 kg mol^{-1}) at moderate $Đ$ (< 1.5) at 0 °C in bulk or select solvents with extremely high isotacticity from a racemic mixture of PO.[188]

The authors explored various substitutions at the metal center and periphery and saw significant effect on activity. As a result of these factors, they proposed a bimetallic polymerization mechanism and synthesized a bimetallic version of the catalyst.[189,190] This bimetallic catalyst, when combined with an ionic salt, polymerizes a wide variety of mono-substituted epoxides to moderate to high M_n with moderate $Đ$ and a high degree of isotacticity. Later, similar chromium-based catalysts were synthesized, which facilitated architectural control through chain shuttling agents (CSAs).[191] In the case of the chromium catalysts with CSA, it is an immortal polymerization.[192]

Recent examples. Often, these catalysts are used to copolymerize epoxides with CO_2 to form polycarbonates.[193] In another example, Coates and co-workers explored the mechanical properties of a suite of isotactic poly(propylene oxide) (iPPO) of different structures. They found enantioenriched iPPO had similar mechanical performance to Nylon-6,6. They also observed photodegradation of the polymer under UV light and suggested this could be selectively stabilized to program in a degradation profile.[194]

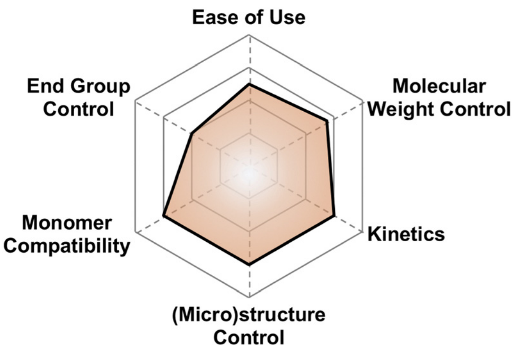


Fig. 24 Subjective scores for Coates' bimetallic catalyst visualized *via* radial plot. All parameters are scored from 0–4.

Mechanism. The mechanism was elucidated using DFT studies and can be seen in Fig. 26.[195] Briefly, they found that the stereochemistry of the binapthol linker determines the enantionmer preference during polymerization. The polymerization proceeds *via* coordination-insertion by a bimetallic pathway. The Cr catalyst displays an induction time which is a result of trace water.[192]

Kinetics. The catalysts are characterized by high turn over numbers and, as such, polymerizations are swift. As an example, PO can be polymerized to 30 kg mol^{-1} in 15 minutes. Kinetics are affected by the specific catalyst used, the ionic salt co-catalyst, solvent, and the monomer. Most polymerizations take place in the minutes to hours range. The Cr catalyst undergoes a noticeable induction time of *ca.* 20% the total polymerization time depending on CSA used and substitution on the metal center.[192] Polymerizations are living and, when combined with a CSA, are immortal.[192]

Molecular weight control. M_n are controlled through monomer to (bimetallic catalyst + CSA) ratio. Moderate to high M_n (M_n up to 150 kg mol^{-1}) can be achieved for a broad swath of epoxide substrates. There is a significant exotherm using this system so low molecular weight polymers may require additional considerations. $Đ$ are generally moderate between 1.5 and 2 depending on the catalyst, ionic salt co-catalyst, and monomer. Lower $Đ$ can be achieved with alkyl linked bimetallic Cr catalysts.[196]

(Micro)structural control. The major advantage of this method is the synthesis of polyethers with high degrees of regio- and stereo-regularity, as well as enantioselectivity of the monomer. As such, most of the polymerizations explored with this system are homopolymerizations of racemic epoxides and so limited data on statistical copolymers is extant. Stereoblock copolymers were demonstrated by polymerization of racemic PO with a racemic catalyst.[194] Block coplymers were demonstrated using a telechelic polymer as a CSA. In this way, PPO-PCL-PPO terblockcopolymers were synthesized. Similarly, tri-functional CSAs resulted in 3-arm polymers.[191]

Supported monomers. A broad array of epoxide monomers are supported like those with alkyl, aryl, unsaturated, and

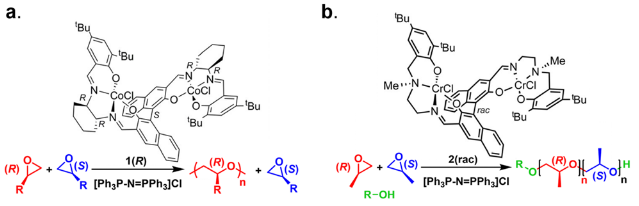


Fig. 25 (a) Example structure of an enantioselective bimetallic cobalt catalyst and (b) racemic bimetallic chromium catalyst and their associated polymerizations. Adapted with permission from ref. 189 and 191. Copyright 2010 and 2017 American Chemical Society.

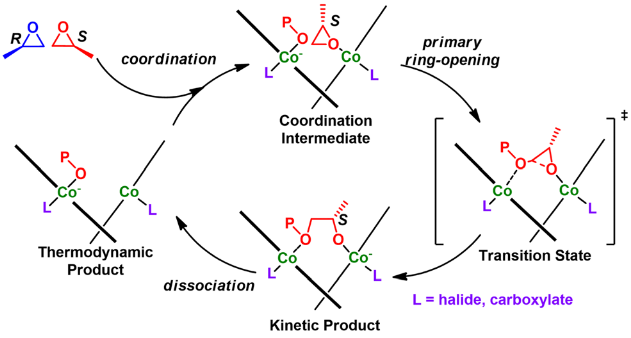


Fig. 26 Enantioselective polymerization with double cobalt catalyst.

fluorinated groups as well as glycidyl ethers, as can be seen in Fig. 27. Compatible epoxide substrates depend on the chemistry of the catalyst, but the catalyst shown in Fig. 25 seems to be the most general. While thiiranes have not been explored with the bimetallic version of this catalyst, a related monometallic chromium based catalyst by Nozaki has shown capability to copolymerize thiirane and CO_2.[197,198] As such, these catalysts may also be amenable to thiirane polymerizations.

End group control. In the absence of CSA, the substitution on the metal center determines one end group, and so polymers are heterobifunctional. In the presence of CSA, one end group is determined by the CSA.[191] While this provides additional end group control it comes at the cost of molecular weight and end group uniformity in a similar way to Inoue's catalyst.

Ease of use. Polymerizations are performed in air-free environments at low to moderate temperatures. Bulk polymerization is possible, but solvents (toluene or dimethoxyethane) are generally employed to mitigate the exotherm. Because the enantioselectivity is dictated by the catalyst stereostructure, only 50% of a racemic mixture of monomer can be polymerized by one catalyst. A racemic mixture of catalysts of opposite stereochemistry can mitigate this effect, but they must be synthesized separately and combined. Catalyst ligands are synthesized through a multi-step process in low-medium yields. Catalyst is often made in high yields and can be crystallized out of the reaction mixture.

5.5.5 Other coordinative methods. Several other coordination catalysts exist for epoxide and thiirane polymerizations. Here, we will briefly highlight some additional catalysts systems that are interesting. These will be unscored owing to limited scope or body of work associated with these methods.

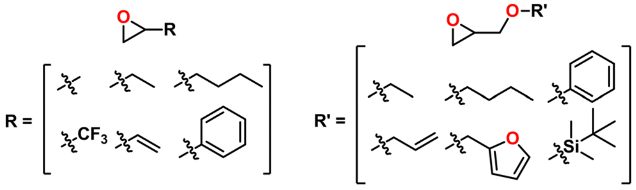


Fig. 27 Monomers synthesized with Coates' enantioselective cobalt catalyst.

Fig. 28 Isospecific polymerization of racemic PO with magnesium catalyst.

5.5.5.1 Di-alkyl magnesium. Di-alkyl magnesium species were explored in the 1950s and 1960s for the polymerization of epoxides.[199,200] Since then, this system has received very little attention. Recently Mejia and co-workers resurrected and modified this system and found that isotactic polymers could be synthesized from a racemic mixture of monomers, as can be seen in Fig. 28.[201] They used di-*n*-butyl magnesium to polymerize, in the bulk, PO up to 65 kg mol^{-1} with $Đ$ increasing to 2.3 with increasing M_n. Based on their kinetics studies, the polymerizations appear to be living. The end group was characterized by ESI-MS and determined to be a butyl group, suggesting two chains growing simultaneously from one Mg. Later they used this system to copolymerize CHO and CO_2 which resulted in isotatically enriched polymer with a high percentage of carbonate linkages.[202]

5.5.5.2 Alkyl aluminum/phosphonic acid/Lewis base catalyst. Vandenberg's work spawned several other catalytic systems. In the 1960s and 1970s Vandenberg as well as others[203] investigated a catalyst system consisting of tri-isobutyl aluminum, phosphonic acid, and trimethyl phosphine, which was found to effectively polymerize epoxides like PO, ECH, and AGE and resulted in amorphous polymers. Structurally defined catalysts based on this system were developed by Mason and co-workers in 2000.[204] These catalysts consisted of methyl phosphonic acid and trialkyl aluminum and polymerized ECH to high molecular weight but with high $Đ$ ($Đ > 1.9$), while PO could only be polymerized to *ca.* 4 kg mol^{-1} but at low $Đ = 1.2$. Later work added water or organic Lewis bases and these ill-defined catalysts achieved similar activity with high molecular weights and moderate to high $Đ$.[205]

5.5.5.3 Tin phosphate catalyst. In the 1960's and on, a few groups investigated the condensation product of organotin halides with trialkyl phosphates for the polymerization of epoxides.[206,207] The product of this condensation was found to polymerize epoxides, like PO and ECH, to high molecular weight with high stereospecificity and, unlike many other examples presented in this article, they can be handled in air. Kragl and co-workers recently began to further characterize this system to better understand the factors that influence the polymerization of epoxides.[208] They prepared the catalyst from butyl tin chloride and tributyl phosphate in a 1 : 2 ratio. They found that they could polymerize PO up to *ca.* 40 kg mol^{-1} with 85% isotacticity. They could control the molecular weight through addition of propylene glycol. This system was further explored by Iwasa and co-workers to polymerize several other substituted epoxides up to 100 kg mol^{-1} but with high $Đ > 2.0$.[209]

5.6 Amine-aluminum (NAl) adduct catalyst

Why use it? If you want to synthesize poly(thio)ethers from a broad set of monomer substrates up to 100 kg mol^{-1} with a diverse set of end group options with no need for special glassware, then this may be the technique for you Fig. 29.

Overview and development. In 2017, Rodriguez, Ferrier, and Lynd developed a new method to synthesize polyethers through the ROP of epoxides.[210] We sought to create a well-defined, aluminum-based catalyst with the feature set (monomer functional group tolerance, ease of use, *etc.*) of Vandenberg's catalyst, but with more control over M_n. The first attempts at a viable catalyst produced bis-(μ-alkoxo) dialkylaluminum (BOD) species from the reaction of ether alcohol and trialkyl aluminum. These catalysts were well-defined and did polymerize epoxides, but did so extremely slowly.[146] However, features reminiscent of the Vandenberg catalyst like epoxide compatbility and enriched-isotacticity were present. Replacing the ligand with dibenzyl amino ethanol, as seen in Fig. 30, combined with a serendipitous miscalculation of reaction stoichiometry resulted in a very effective epoxide polymerization platform. The resulting mono-(μ-alkoxo)bis-alkylaluminum (MOB) compound quickly polymerized a wide variety of epoxide substrates up to molecular weights of 100 kg mol^{-1}. Interestingly, these polymers were characteristically atactic.[210]

Kinetics were enhanced four times by replacing the triethyl aluminum species with a triisobutyl aluminum species.[211] Further kinetic enhancement of nearly 100× was achieved by changing the ligand from di-benzyl amino ethanol to di-methyl amino ethanol.[212] The startling increase in polymerization kinetics with the change in amine substitution suggested an important interaction between the trialkyl aluminum species and the amine. We hypothesized that a rearrangement occurred; the trialkyl aluminum species datively bound to the oxygen could associate with the amine, facilitating dimerization of two MOB species, a common occurrence for aluminum species.[213] To test this, we prepared an amine aluminum (NAl) adduct from the reaction of triethyl amine and trimethyl aluminum, which we anticipated would act like a catalyst. We combined this with the BOD species that we anticipated would act like an initiator. The resulting polymerization kinetics matched the kinetics of the MOB species, lending credence to our hypothesis. We found this separate catalyst and initiator system was quite convenient; By increasing the relative concentration of the catalyst to the initiator we found a commensurate increase in kinetics. Furthermore, this allowed for the decoupling of kinetics from initiator structure, facilitating end group control. A scheme showing both approaches to epoxide polymerization can be seen in Fig. 31.

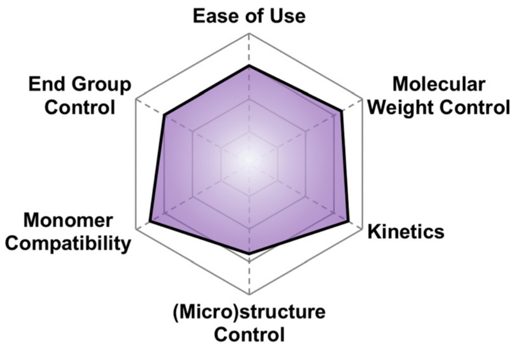


Fig. 29 Subjective scores for the NAl Adduct Catalyst visualized *via* radial plot. All parameters are scored from 0–4.

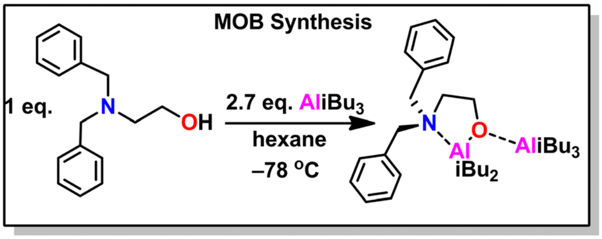


Fig. 30 Synthesis of the MOB catalyst/initiator for epoxide polymerizations.

Safaie, Ohno, and Ferrier later expanded this system by preparing initiators from thiol containing ligands.[214] End group control was verified through ESI-MS, unequivocally demonstrating this method produces hetero-bifunctional polyethers. Furthermore, macroinitiators were prepared from polymers with thiol or alcohol end groups *via* reaction of trimethyl aluminum. In this way, chain extension from PEO as well as polymers prepared *via* RAFT like polystyrene and poly(methyl methacrylate) (PMMA) with epoxides was demonstrated.[214,215] Additionally, bi-functional initiators were demonstrated through disulfide ligands, which enable the facile synthesis of telechelic polyethers and triblock copolymers. Finally, this polymerization method is compatible with episulfides as well; PS can be controllably homopolymerized up to 100 kg mol^{-1} and statistical and block copolymers of epoxides and PS can be prepared.[215]

Recent examples. Since the inception of the NAl adduct catalyst in 2017, there has been some utilization in the literature. Freeman and Lynd synthesized cross-linked polyether membranes from a variety of hydrophilic and hydrophobic epoxides in order to better understand how this affects CO_2 transport and selectivity.[216] They found good CO_2 permeabilities and selectivity against N_2. Lynd, Sanoja, and Ganesan explored the relationships between dielectric contrast, phase behavior, and ionic conductivity using statistical copolymers of cyanoethyl glycidyl ether (CEGE) and AGE or BGE.[217] PCEGE has a significantly higher dielectric constant than AGE and

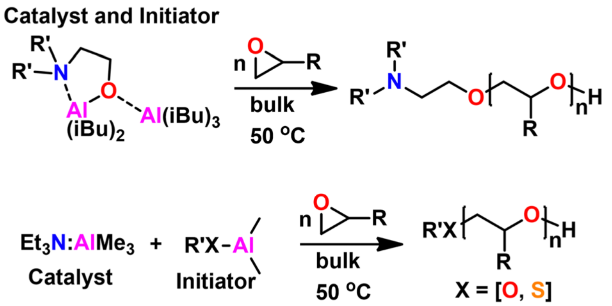


Fig. 31 (Top) Epoxide polymerization with MOB catalyst/initiator. (Bottom) Epoxide polymerization with separate NAl adduct catalyst and initiator.

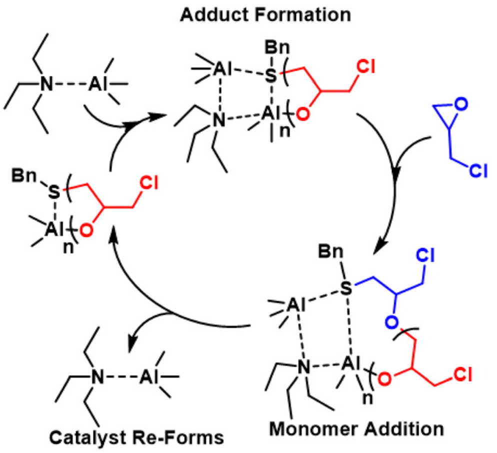


Fig. 32 Proposed polymerization mechanism with the NAl adduct catalsyt. Reproduced with permission from ref. 219. Copyright 2023 Royal Society of Chemistry.

BGE, which resulted in interesting phase behavior as well as surprising deviations of the ionic conductivity from predicted behavior. In a final example, Lynd and co-workers investigated how polyethers with a DMSO pendant affected cryopreservation compared with traditional cryoprotectants.[218] Here, they polymerized PECH up to 90 kg mol^{-1} and modified it with a DMSO unit by replacing the Cl with sodium methane thiolate and oxidizing it. These recent examples highlight the flexibility of this method for polymerizing a broad swath of poly(thio)ethers.

Mechanism. The mechanism has been elucidated through DFT studies in a recently accepted publication and can be seen in Fig. 32.[219] Based on experimental observations, the polymerization proceeds through a coordination-insertion polymerization of activated monomers with anionic character. The initiator and NAl catalyst form a four-membered ring, reminiscent of the proposed Vandenberg catalyst structure, which serves to coordinate, activate, and ring open epoxides. Each successive addition of monomer results in the reformation of separate NAl adduct catalyst. The polymer grows cyclically with both ends bridged by the dialkyl aluminum. Upon termination, the aluminum is cleaved and a linear polymer results.

Kinetics. The polymerization kinetics are first order in monomer for all studied initiators for this system. The kinetics are 0th order in catalyst,[214] similar to Grubb's catalyst for ROMP.[220] The propagation rate is affected by initiator, catalyst, and monomer chemistry, as well as catalyst to initiator ratio.[212,214,219] Polymerizations take between minutes and days depending on these factors. Generally, the rates are faster than those of AROP and can be enhanced by increasing the catalyst to initiator ratio.[212] The Et_3NAlMe_3 catalyst so far offers the best control and kinetics.

Molecular weight control. Molecular weights up to 100 kg mol^{-1} for several monomers, like ECH, PO, BO, and PS, have been demonstrated.[214,215] $Đ$ depends on the monomer chemistry but are generally low ($Đ < 1.3$). The catalyst chemistry also impacts $Đ$.[219] The original Et_3NAlMe_3 catalyst provides the best control, but certain substitutions on the amine and/or Al can result in the broadening of molecular weight, with little impact on kinetics. Therefore, this system would be appropriate to study $Đ$ effects of polyethers.

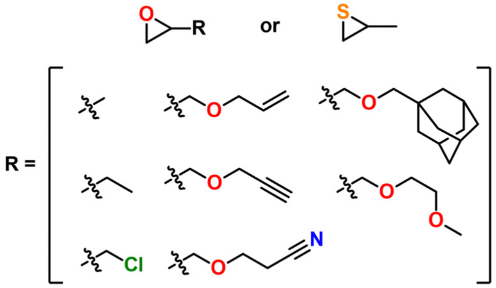


Fig. 33 Select monomers polymerized with the NAl system so far.

(Micro)structural control. Statistical copolymers can be produced through simultaneous polymerization of two monomers. The reactivity ratios vary depending on the monomer pair,[221] but polymerizations are typically random.[211] Block copolymers can be achieved through sequential addition of monomers. Bifunctional initiators have been demonstrated to easily prepare tri-block copolymers.[215] Polymers are regio-regular and atactic. Polymerization of enantiopure monomers to produce isotactic polymers has not been tested, but should be viable.

Supported monomers. A wide range of epoxide monomer substrates have been effectively polymerized both as homopolymers and copolymers. The method is compatible with alkyl epoxides, glycidyl ethers, epichlorohydrin, and propylene sulfide. Some highlights of monomer substrates that have been polymerized with this method can be found in Fig. 33.

End group control. End group control is facilitated through the use of the separate initiator and catalyst system and tuned through the choice of initiator ligand. So far, mono-functional alcohols, mono-functional thiols, and bi-functional thiols can be used to prepare initiators. Both aryl and alkyl groups have shown to be compatible, as well as a variety of macromolecules like PSt, PMMA, and PEO. Macroinitiated polymerizations are done in solvent, usually benzene. Choice of initiator does effect polymerization kinetics, but does not impact polymerization control (*i.e.*, $Đ$).[212,214]

Ease of use. The polymerization method requires no special glassware, no solvent, and mild temperatures (T = RT – 80 °C). In fact, the Ferrier group often does polymerizations in glass scintillation vials. Monomer can be used straight from the bottle without any additional purification. The initiator and catalyst are easy to synthesize and crystallize directly from the reaction medium, only requiring drying for purification. Polymerizations and catalyst/initiator synthesis must be done in an air-free environment as alkyl aluminum is air-sensitive. The MOB serves as both a catalyst and initiator and has been shown to be broadly compatible with a number of functional epoxide substrates. As such, this would be the easiest starting point for a polymerization with this system.

6 Conclusions and future directions

As the reader may have noticed, there are a multitude of polymerization techniques to synthesize poly(thio)ethers using

Earth-abundant metals. All of the techniques mentioned here have seen recent developments in terms of monomer scope, (micro)structural consideration, molecular weight improvements, *etc.* As such, this is still a highly active field and is increasing in activity as facile techniques like MAROP and the NAl adduct catalyst have improved accessibility to these wonderful polymers. Furthermore, with the increasing importance of energy storage, CO_2 sequestration, and mRNA delivery, polyethers and polythioethers have received renewed interest. The monomers remain ripe for utilization as a feedstock for a tunable polymeric materials platform. Furthermore, epoxide-based polyethers and by extension episulfide-based polythioethers have the potential to be made completely from biorenewable resources.[222–224]

Significant challenges remain, however, in the area of accessibility. As this article demonstrated, there are several techniques to synthesize poly(thio)ethers, but none of them are as facile, broadly applicable, and accessible as techniques like RAFT polymerization for vinyl-based monomers.[225] RAFT agents can be purchased from chemical storefronts and monomers require limited or no preparation to successfully perform a RAFT polymerization. As it stands, regardless of the method used to synthesize poly(thio)ethers, several chemical steps need to take place, whether it is the synthesis of the initiator, catalyst, or purification of the monomer. Simplifying synthetic processes to make them more approachable would broaden the user base for these techniques/materials. As an extension of this, efforts need to be made to make these heterocycle polymerizations more robust to air; all of the techniques described above require an air-free environment and most also require the handling of pyrophoric materials. This necessitates additional equipment that a lab that is not dedicated to polymer synthesis may not have, limiting potential utilization.

Another major concern is sustainability. As mentioned above, epoxides can be sourced from fully biorenewable resources.[222–224] However, poly(thio)ether degradability is lacking; there is significant difficulty to place even some degradable units within a poly(thio)ether backbone,[89] let alone fully de-polymerize it. This is a problem not only from a plastic waste point of view, but also in the biomedical applications poly(thio)ethers are generally used in.[226,227] Combining epoxide/thiirane monomers with "waste" monomers like CO_2 is a major area of interest and has seen rapid advancement. However, issues remain applying renewably sourced epoxides and thiiranes as well as in engineering the properties of the final materials and their degradability.[228] Therefore, sustainability in the form of degradability and depolymerization should be improved.

In conclusion, there are many ways to synthesize poly(thio)ethers, which are excellent materials, applicable in several technological contexts. However, they are often overlooked for vinyl-based polymers. This is, at least partially, due to the ease and diversity of vinyl polymerization methods along with the accessibility of clear-cut tutorials that accompany them.[225,229–232] With this article, we hope to have provided an informative and approachable overview of the different techniques for poly(thio)ether synthesis to garner interest from a broader scientific base. We hope this will be a positive step towards increased adoption of poly(thio)ethers, approaching that of vinyl-based polymers. We anticipate this will lead to the development of new methods and spark new ideas to help solve challenges in the field especially in the context of accessibility and sustainability.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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