Green Chemistry

Construction and deconstruction: recent advances in degradable silicon-based polymers

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This review article presents recent advances in the design, synthesis, degradation, and recycling of degradable silicon-based polymers, with a focus on poly(silyl ether)s, and poly(silyl ester)s. These materials offer a promising route toward sustainable polymer technologies by integrating labile Si−O−C and Si−O−C(=O) linkages into polymer backbones, enabling controlled degradation without compromising performance. This article details synthetic strategies including step-growth and chain-growth polymerizations, explores degradation mechanisms under various chemical conditions, and highlights emerging catalytic systems, ranging from noble metals to earth-abundant and metal-free catalysts. Challenges and future directions for integrating degradability with high-performance properties are also discussed.

Green foundation

1. The development of degradable silicon-based polymers using bio-based monomers, earth-abundant or metal-free catalysts, and low-energy, catalyst-free processes is highlighted in this article. These innovations enable controlled degradation, chemical recycling, and closed-loop lifecycles, promoting sustainability and reducing environmental impact.

2. It addresses the urgent global challenge of plastic pollution by developing degradable and recyclable silicon-based polymers that maintain high performance while enabling environmentally responsible end-of-life options using both established/robust and cutting-edge chemical approaches.

3. These next generation silicon-based materials offer transformative potential across industries, from packaging to biomedical devices, by combining sustainability with advanced functionality, aligning with the growing demand for greener, circular materials.

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1. Introduction

Polymeric materials are essential to modern society and play a critical role in countless applications.[1] In particular, plastics

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and rubbers have revolutionized our daily lives with their affordability and versatility, being used in construction, household appliances, medical instruments, and packaging.[2] However, this surge in consumption has led to a significant increase in waste. More than 400 million tons of plastics are produced each year,[3] and about one-third of it ends up as waste.[4] Alarmingly, only 9% of this waste is recycled, while approximately 22% is improperly managed or is mismanaged at the end of its lifecycle. Synthetic polymers, known for their resistance to thermal, oxidative, and hydrolytic degradation, as well as biodegradation, persist in the environment for long periods of time, leading to accumulation and posing significant waste management challenges, especially in developing regions. To effectively address these issues, it is essential to focus on designing and synthesizing tailor-made polymers with degradable properties, while retaining the desirable features of their non-degradable counterparts.[5] Ideally, these materials should be designed to break down more readily after their intended use, minimizing environmental impact and promoting sustainable waste management practices.[6]

In this context, polymers containing silicon–oxygen bonds in their main chains have emerged as one of the most important classes of polymers.[7] For example, polysiloxanes, also known as silicones, are high-value polymers that exhibit unmatched properties due, in large part, to the unusual behavior of the Si–O bond.[8] In contrast, poly(silyl ether)s and poly(silyl ester)s incorporate carbon atoms into the backbone via Si–O–C linkages, introducing additional reactivity and diversity. The structural differences between polysiloxanes and poly(silyl ether)s/poly(silyl ester)s significantly influence their performance across various domains. Table 1 outlines some of the most noteworthy features of Si–O and Si–O–C (co)polymers. Polysiloxanes have a backbone composed solely of alternating silicon and oxygen atoms, which imparts exceptional thermal stability, chemical resistance, and flexibility. They also

Table 1 Typical features of Si–O and Si–O–C (co)polymers

Property	Si–O polymers	Si–O–C polymers
Thermal stability	Very high	Moderate to High
Chemical resistance	Excellent	Variable (depends on organic group)
Flexibility	High	Tunable (can be rigid or elastic)
Adhesion	Poor (needs treatment)	Good (better surface interaction)
Functionalization	Limited	Highly customizable

feature low glass transition temperature (T_g), very low surface energy and, consequently, high interfacial activity. These properties make them ideal for high-temperature and chemically harsh environments (e.g., marine, industrial). Depending on the organic component, poly(silyl ether)s and poly(silyl ester)s can be more rigid or brittle than polysiloxanes. While this structural modification can slightly reduce thermal and chemical stability, it greatly enhances the material's versatility. These polymers offer improved adhesion to organic and inorganic surfaces, greater potential for functionalization, and tunable mechanical properties. This makes them suitable for applications requiring specific interactions or degradability, such as biomedical devices or hybrid coatings.[9] Thus, poly(silyl ether)s and poly(silyl ester)s offer attractive solutions as customizable platforms for advanced, multifunctional materials.

The exploration of chemically labile bonds and their applications in polymer durability is of continued interest. In this respect, poly(silyl ether)s and poly(silyl ester)s are promising candidates, as they exhibit both generally high Si–O bond strengths (SiO ≈ 530 kJ mol^{-1})[10] and potential degradability with a variety of triggers. As these copolymers possess Si–O–C linkages in their repeating units, they are susceptible to hydrolysis or alcoholysis under acidic or basic (often containing fluoride anions) conditions, resulting in the degradation of their

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Carine Robert earned her Ph.D. in Paris in 2012, then joined Professor Kyoko Nozaki's group at the University of Tokyo as a JSPS postdoctoral fellow. In 2013, she became Assistant Professor at Chimie ParisTech-PSL, within the research group led by Professor Thomas. Her research focuses on the design of novel catalysts for the polymerization of cyclic polar monomers, with an emphasis on developing sustainable and efficient polymerization processes.

Régis M. Gauvin

Régis M. Gauvin completed his PhD under J. A. Osborn and J. Kress in Strasbourg University in 1999. After postdoctoral stays with D. Milstein in Rehovot (Israel) and with J.-M. Basset in Villeurbanne (France), he joined the CNRS as a researcher in 2002 in the Unit for Catalysis and Solid-State Chemistry, Lille University. Since 2019, he is a CNRS senior researcher in the Institut de Recherche de Chimie Paris, in Chimie ParisTech. His research interests revolve around organometallic chemistry applied to both homogeneous and supported catalysis, for small molecules and polymer synthesis with a flavour of bioresources upgrading.
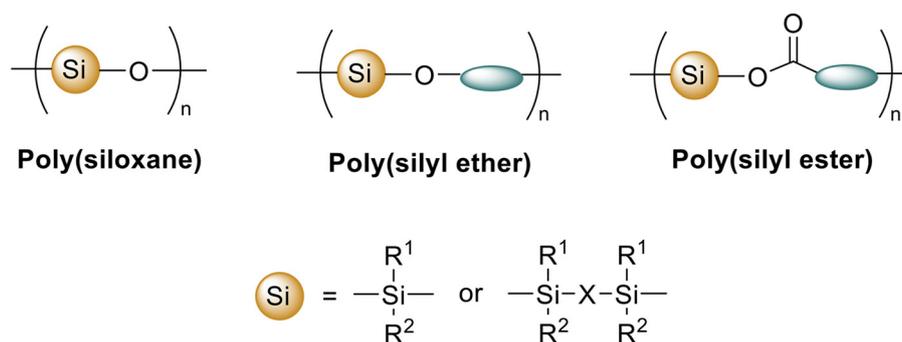
Fig. 1 Schematic representation of the chemical structure of poly(siloxane), poly(silyl ether), and poly(silyl ester).

backbone (Fig. 1).[11] In addition, incorporating chemically labile Si–O–C bonds into poorly degradable polymers can also be an efficient strategy to design degradable (co)polymers (Fig. 1).

The objective of the present review is therefore to provide an overview of degradable silicon-based polymers. In order to avoid redundancy with existing literature on polysiloxanes,[12–16] it will focus on two main classes: poly(silyl ether)s and poly (silyl ester)s. It begins by discussing the environmental need for degradable materials and introduces the unique properties of silicon-containing polymers. The review then delves into synthetic strategies and explores degradation mechanisms such as hydrolysis and alcoholysis. It highlights recent innovations in catalysis, including the use of earth-abundant metals and metal-free systems, and examines the recyclability and deconstruction of these materials. This article concludes with perspectives on future challenges and opportunities for integrating degradability with high-performance properties in sustainable polymer design.

Christophe M. Thomas received his Ph.D. in Switzerland under Professor Süss-Fink, followed by a postdoctoral fellowship in Professor Geoffrey Coates' group at Cornell University, supported by the Swiss National Science Foundation. He later joined Professor Ward's laboratories before being appointed Assistant Professor at the University of Rennes in 2004. In 2008, he became Full Professor at Chimie ParisTech (PSL University). His research focuses on homogeneous catalysis and polymer chemistry, emphasizing one-pot catalytic transformations, stereochemical control, and the development of biodegradable polymers from renewable resources, aiming to advance sustainable materials and environmentally responsible polymer technologies.

Christophe M. Thomas

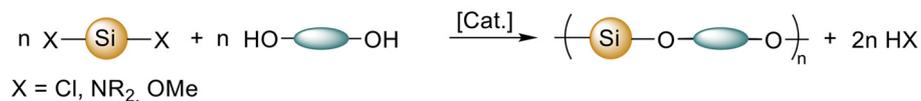## 2 Poly(silyl ether)s

2.1 Synthesis of poly(silyl ether)s by step-growth polymerization

The formation of poly(silyl ether)s is primarily based on step-growth polymerization using AA/BB comonomers, AA/BC comonomers, or AB monomers, to list the most classical approaches. Step-growth polymerization between two types of AA/BB comonomers can be divided into two forms based on the by-products released. In the first one, the reaction between dichlorosilanes, diaminosilanes, or bisalkoxysilanes (AA-type monomers) and diols (BB-type monomers) produces a potentially harmful by-product, namely hydrochloric acid, amine or alcohol, respectively. In the second form, polymerization between dihydrosilanes and diols or dimethyl ethers releases H_2 or methane as gaseous by-products (Fig. 2).

For example, Wei *et al.* synthesized poly(silyl ether)s by polycondensation of 4,4′-buta-1,3-diyne-1,4-diyldiphenol and dichlorodiphenylsilane, using triethylamine (TEA) as an acid scavenger (Fig. 3a).[17] Thermal analysis revealed no detectable glass transition temperature (T_g) over the test temperature range of 50–400 °C and showed exceptional thermal stability with a degradation temperature ($T_{d,-5\%}$) of 540 °C, exceeding other high temperature polymers. Rheological analysis indicated a 30-minute processing window at a lower curing temperature of 210 °C before the polymer transitioned to a vitrified thermoset. Although dichlorosilanes can be efficiently produced by the Müller–Rochow process, in which elemental silicon reacts with chloroalkanes, their moisture sensitivity poses significant challenges in handling, storage, and transportation.[18] This problem is driving the search for other monomers. For example, Tang synthesized a series of poly(silyl ether)s by the polycondensation between bis(diethylamino)dimethylsilane and various glycols (Fig. 3b).[19] While Tang's method represents a variation in synthetic approach, it still relies on chlorosilanes. This approach allows the CO_2-philicity of poly(silyl ether)s to be varied depending on the comonomers used. Increasing the silicon content can improve the solubility of poly(silyl ether)s in CO_2, mainly due to reduced polymer–polymer interactions. However, if the unwanted by-products HCl or diethylamine are not promptly removed

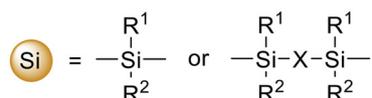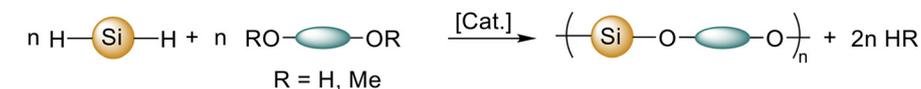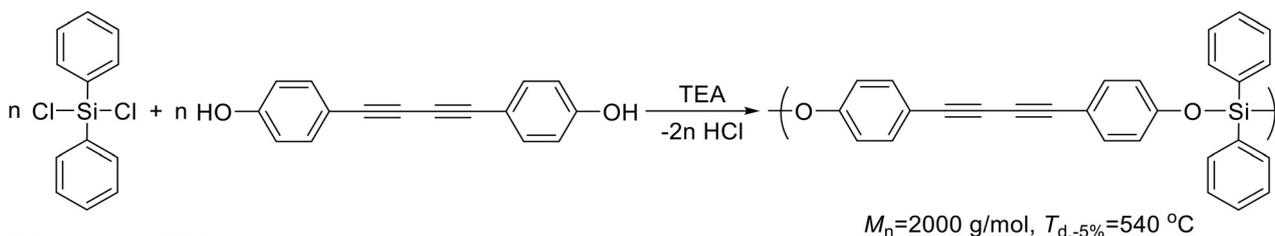## Polycondensation between AA/BB comonomers

(a) Type I

X = Cl, NR$_2$, OMe

(b) Type II

R = H, Me

Fig. 2 Representative synthetic approaches for poly(silyl ether)s: polycondensation between AA/BB comonomers.

(a) Wei, 2013

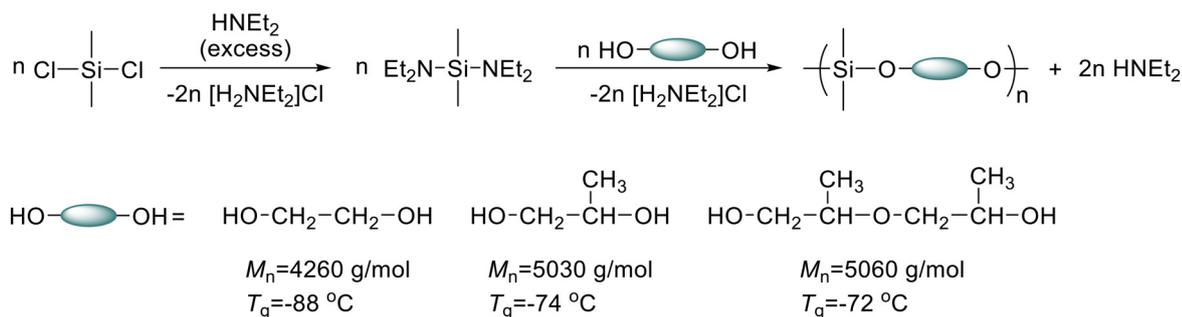M_n=2000 g/mol, $T_{d,-5\%}$=540 °C

(b) Tang, 2017

M_n=4260 g/mol
T_g=-88 °C

M_n=5030 g/mol
T_g=-74 °C

M_n=5060 g/mol
T_g=-72 °C

Fig. 3 Polycondensation of (a) dichlorodiphenylsilane and 4,4'-buta-1,3-diyne-1,4-diyldiphenol,[17] and of (b) bis(diethylamino)dimethylsilane and various diols[19] for poly(silyl ether)s synthesis.

during polymerization, the reaction can easily reach equilibrium, preventing further molecular weight increase and affecting polymer properties.

As an alternative approach, Miller *et al.* synthesized poly (silyl ether)s by using symmetrical silicon acetals as comonomers instead of moisture-sensitive dichlorosilanes (Fig. 4).[20] This innovative method allowed them to perform silicon acetal metathesis polymerization with various diols and SiMe$_2$(OMe)$_2$, catalyzed by strong Brønsted acids, such as methanesulfonic acid, *p*-toluenesulfonic acid (TsOH), and triflic acid (TfOH), which release alcohol by-products instead of hydrochloric acid. The authors proposed two mechanisms:

one involving the metathesis of two bis-silicon acetals, releasing SiMe$_2$(OMe)$_2$, and the other involving functional group exchange using a bifunctionalized premonomer containing both an alcohol and a silicon acetal group, with methanol elimination. Both routes yield the same poly(silyl ether)s. The timely removal of the methanol by-product is critical, as it significantly affects the molecular weight of the resulting polymer.

An alternative approach to the formation of Si–O bonds involves the use of readily available dihydrosilanes as comonomers, instead of moisture-sensitive dichlorosilanes or silicon acetals. Their condensation with diols into poly(silyl ether)s
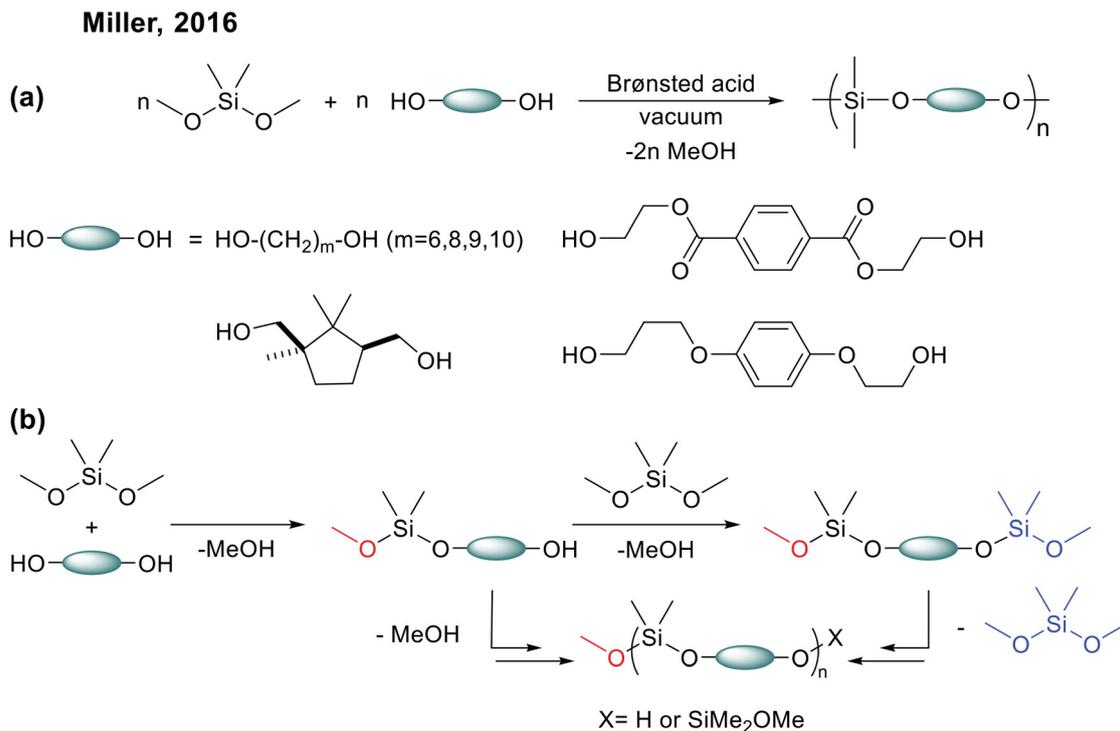
**Fig. 4** Polycondensation of dimethoxydimethylsilane with different diols (a), and the plausible mechanism (b).[20]
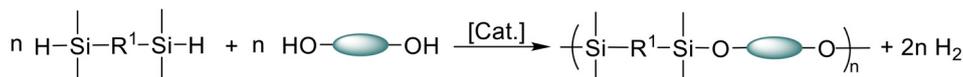
via dehydrocoupling polymerization has gained attractiveness due to the generation of H_2 as the only by-product. Early studies used catalytic systems containing noble metals such as palladium, platinum, rhodium, and iridium. For example, Kawakami *et al.* described the use of four bis(hydrosilane)s [1,4-bis(dimethylsilyl)benzene (BDMSB), 1,3-dihydro-1,1,3,3-tetramethyldisiloxane (DHTMDS), 1,5-dihydro-1,1,3,3,5,5-hexamethyltrisiloxane (DHHMTS), and 1, 2-bis(dimethylsilyl) ethane (BDMSE)] and two diols (ethylene glycol and 4,4′-bisphenol) to synthesize poly(silyl ether)s, in the presence of [Pd$_2$(dba)$_3$] (dba = dibenzylideneacetone), [10% Pd/C], [RhCl (PPh$_3$)$_3$] and [5% Rh/C] catalysts (Fig. 5).[21] Since the palladium complex was converted to Pd(0) metal particles with lower catalytic activity, and considering that the degree of metal aggregation was detrimental to the reaction efficiency, they adopted a method using palladium deposited on carbon (10% Pd/C), which has more dispersed metal centers less prone to aggregation. Poly(silyl ether)s were prepared with a higher number average molecular weight (M_n = 7400 g mol^{-1}) than those obtained with [Pd$_2$(dba)$_3$]. In comparison, [RhCl(PPh$_3$)$_3$] and Rh/C either failed to produce any polymeric product or yielded low molecular weight products. However, even when taking into account the above-mentioned interests of this approach, the high cost, low abundance, and high catalyst loading (up to 10 mol%) of noble metals are significant drawbacks in carrying out this reaction.

Wooley *et al.* incorporated labile silyl ether linkages along a poly(ε-caprolactone) (PCL) backbone (Fig. 6).[22] The silyl ether-based PCL was synthesized by cross-dehydrocoupling polymer-ization of BDMSB with PCL diol macromonomers, derived from the ring-opening polymerization (ROP) of ε-caprolactone. The PCL block serves as the relatively hydrolytically resistant block of the polymer backbone, while the more labile silyl ether linkages act as bridging functionalities. These selective hydrolytic cleavage conditions facilitated a stepwise degra-dation of the resulting silyl ether-based PCL. In a first stage, the silyl ether linkages in the backbone underwent rapid hydrolytic degradation under mild conditions, regenerating intermediate molecular weight PCL blocks. Further cleavage of the ester moieties within the more stable PCL blocks under harsher conditions resulted in a prolonged transition from polymers to small molecules, providing a stepwise degradation profile.

In order to develop more sustainable catalytic systems, earth-abundant metals, such as iron,[23–26] manganese,[27,28] cobalt[29] or copper[30] have been reported for the synthesis of poly(silyl ether)s by dehydrocoupling polymerization. For example, our group recently described a novel tandem catalytic system using a single iron complex to synthesize block PSE-PLA copolymers.[25] The iron catalyst enabled two distinct reactions: the formation of poly(silyl ether)s *via* dehydrocou-pling of dihydrosilanes with diols and the ROP of lactide to form polylactide (PLA) (Fig. 7). By combining these reactions, new copolymers with enhanced thermal stability and recycl-ability were obtained. The system operated under mild con-ditions with low catalyst loading (as low as 0.25 mol%). The resulting PSE-PLA block copolymers exhibited high degra-dation temperatures (up to 541 °C) and tunable thermal pro-
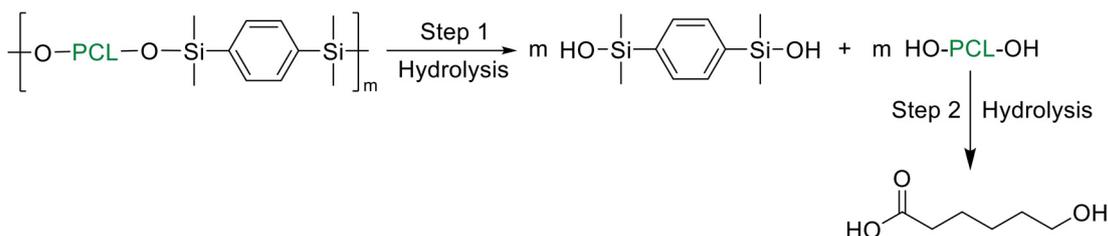
Kawakami, 1999
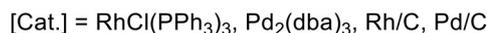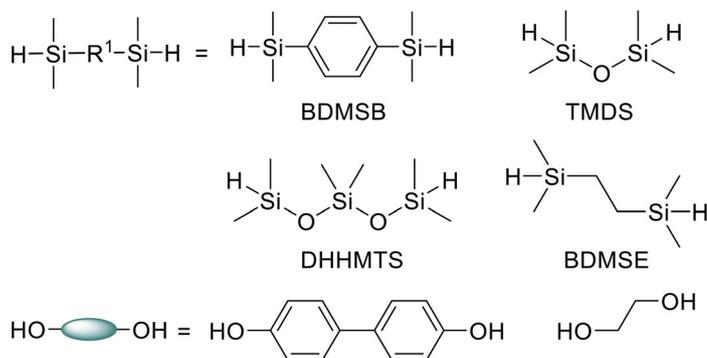
Fig. 5 Synthesis of poly(silyl ether)s *via* metal-catalyzed dehydrocoupling.[21]

Wooley, 2001

(a) Polymerization
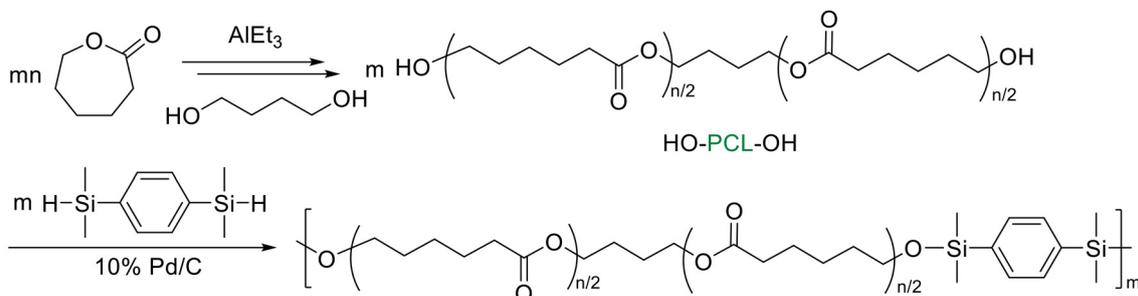
(b) Depolymerization

Fig. 6 Polymerization and depolymerization routes of silyl ether-based PCL.[22]

perties depending on the monomers used. Incorporating both bio-based (isosorbide) and non-bio-based (hydroquinone) diols allowed for further optimization of polymer performance. The copolymers can be chemically recycled through acid-catalyzed methanolysis (*e.g.* with methanesulfonic acid), recovering valuable monomers, such as isosorbide and methyl lactate.

Notably, it was also demonstrated that blending different copolymers can further enhance thermal properties, offering a practical alternative to stereocomplex formation.

Dimethyl ethers can also be used in combination with dihydrosilanes. In this case, the by-product is methane instead of H_2. The reaction is catalyzed by strong Lewis acids such as tris
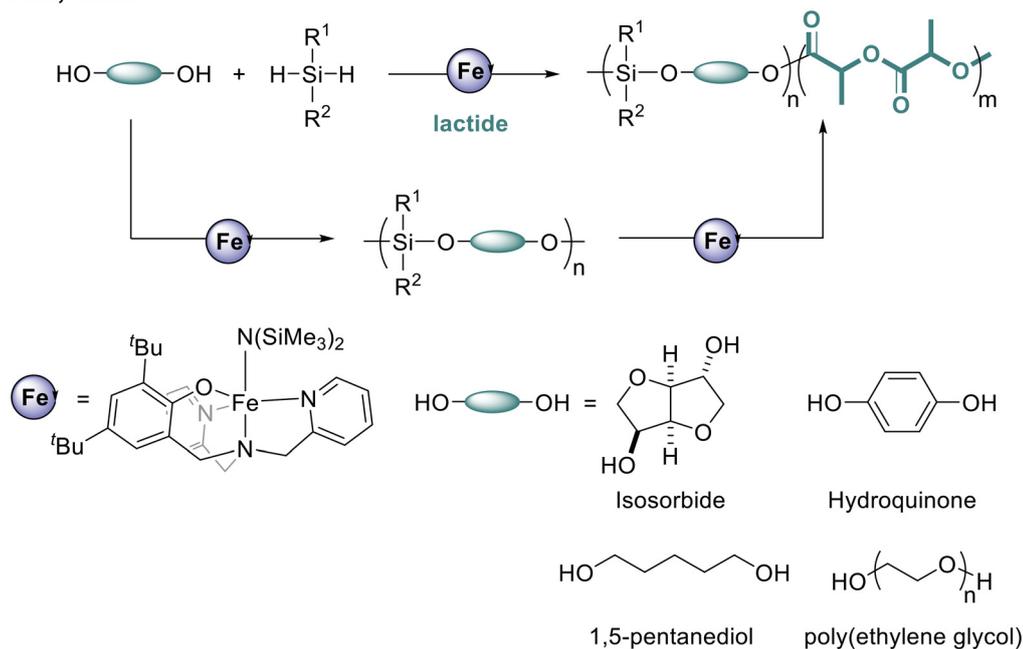
Thomas, 2025

Fig. 7   Tandem synthesis of PSE–PLA copolymers from dihydrosilanes/diols and lactide.[25]

(pentafluorophenyl)borane $B(C_6F_5)_3$.[31] This method is particularly advantageous when dealing with diols that have poor solubility in the reaction mixture. For example, while hydroquinone is poorly soluble in common solvents such as toluene or dichloromethane, its dimethyl ether dissolves readily, allowing for the production of high molecular weight polymers when reacted with either Ph_2SiH_2 or BDMSB in the presence of $B(C_6F_5)_3$ (Fig. 8).

Another approach to efficiently converting monomers without generating by-products is to use additional types of comonomers (other than diols) in the synthesis of poly(silyl ether)s (Fig. 9).[32]

Step-growth polymerization can typically be performed by reaction between dichlorosilanes, diphenoxysilanes or dihydro-

silanes (AA-type monomers) and diepoxides (BB-type monomers) (Fig. 9a). Early examples were developed by Nishikubo and coworkers (Fig. 10). They reported the preparation of poly(silyl ether)s with reactive pendant chloromethyl groups via the polyaddition of various bis(epoxide)s with dichlorosilanes or bis(chlorosilane)s (Fig. 10a).[33] These polymerizations proceeded regioselectively under mild reaction conditions, using quaternary onium salts or triphenylphosphine as catalysts. The quaternary onium halide salts exhibited higher catalytic activity, resulting in polymers with a higher M_n, compared to triphenylphosphine. This is attributed to their effective nucleophilicity towards epoxides and their superior ability as leaving groups within the intermediate species during the final reaction step. This polymerization strategy has also been extended
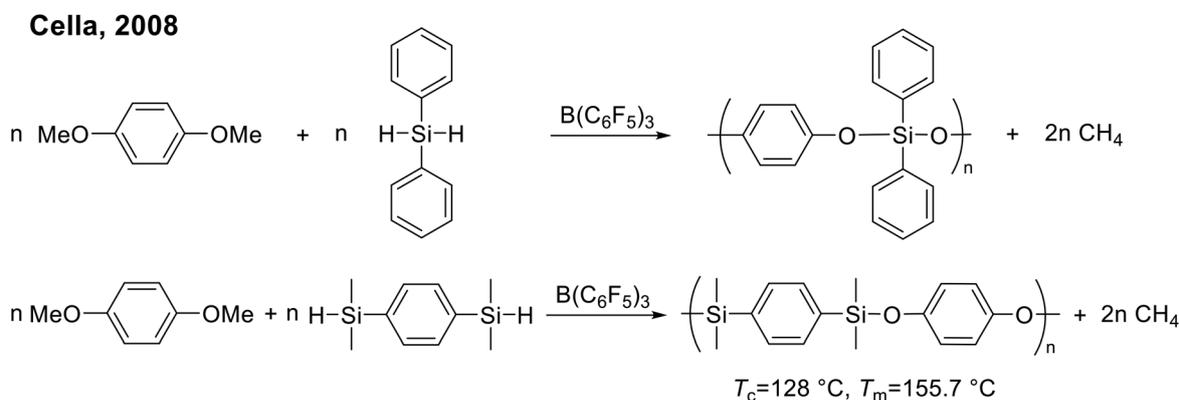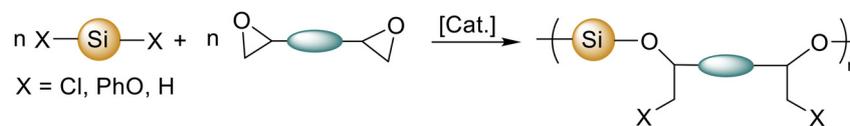
Cella, 2008

Fig. 8   Polycondensation of a bis(methyl ether) and Ph_2SiH_2 or BDMSB.[31]

Polyaddition between AA/BB comonomers
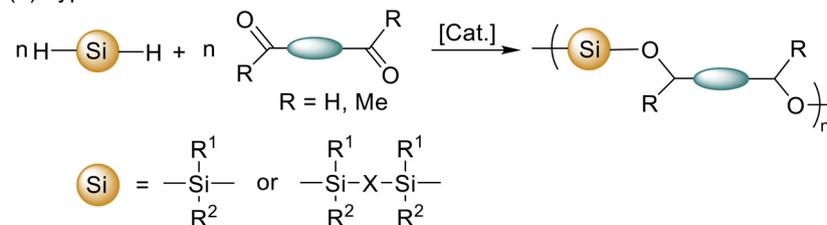
(a) Type I

(b) Type II

Fig. 9 Polyaddition between AA/BB comonomers into poly(silyl ether)s.

to the reaction of bis(oxetane)s with dichlorosilanes to yield poly(silyl ether)s with high molecular weights, up to 53 200 g mol^{-1} (Fig. 10b).[34] Nishikubo also reported a type of poly(silyl ether)s with phenoxy side groups, which were obtained by converting dichlorodimethylsilane to dimethyldiphenoxysilane through a substitution reaction and performing polyaddition with bisepoxides (Fig. 10c).[35] Notably, the resulting poly(silyl ether)s exhibited relatively high molecular weights (M_n > 10 000 g mol^{-1}) with yields ranging from 79% to 99%, even under mild reaction conditions, indicating the high efficiency of this polymerization.
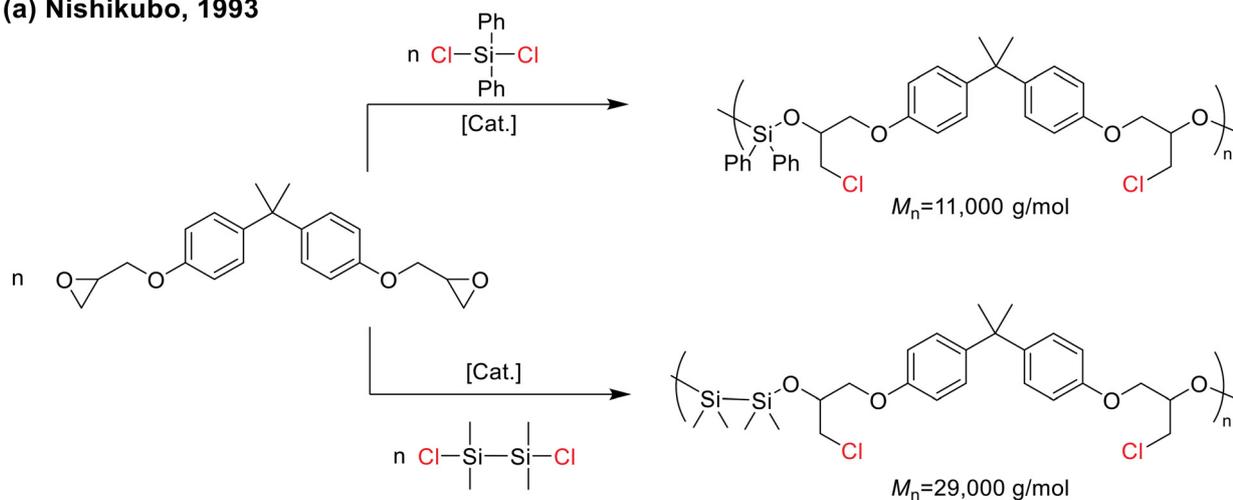
In order to avoid the use of chlorinated compounds, Laine *et al.* reported a similar method for the synthesis of poly(silyl ether)s by catalyzing the oxysilylation of four different diepoxides with 1,1,3,3-tetramethyldisiloxane (TMDS) *via* the Piers–Rubinsztain reaction, using B(C$_6$F$_5$)$_3$ as a catalyst (Fig. 11).[36] The reaction proceeds by ring-opening of the epoxy function, leading to the formation of new Si–O and C–H bonds, with two possible products depending on the regioselectivity. Considering the 0.1 mol% catalyst loading, these reactions are remarkably fast, reaching full conversion within five minutes. Non-sterically hindered epoxy groups can favor the formation of cyclic compounds, whereas more hindered epoxides lead to polymers with greater rigidity. This rigidity reduces the rate of cyclization and promotes the formation of linear polymers with longer chains and higher molecular weights. Interestingly, the resulting polymers remain stable for several hours in boiling water, thus demonstrating exceptional water resistance.

Polymerization can also occur by the reaction of dihydrosilanes (AA-type monomers) with dialdehydes or diketones (BB-type monomers), specifically by hydrosilylation of carbonyl groups, a classical reaction in homogeneous catalysis (Fig. 9b). Thus, poly(silyl ether)s can be synthesized by using transition metal (*e.g.*, ruthenium,[37,38] rhodium[39,40]) catalysts. For example, Fernández-Alvarez and Oro developed a Rh-based
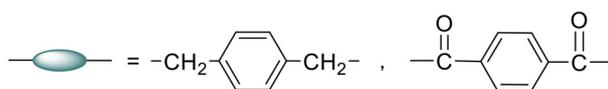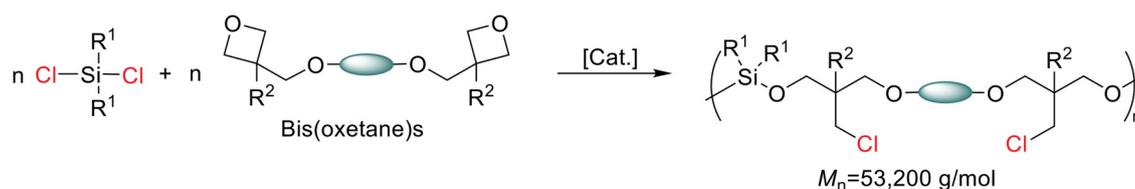
homogeneous catalytic system by incorporating a bulky *N*-heterocyclic carbene (NHC) as a ligand (Fig. 12).[40] They further immobilized this Rh(I)–NHC complex on a ordered mesoporous silicate material (MCM-41), to generate the corresponding heterogenized catalyst. The catalytic mechanism was studied using 1,1,1,3,5,5,5-heptamethyltrisiloxane (HeptMTS) and acetophenone as model substrates. ^{1}H NMR studies revealed the formation of unidentified Rh(I) hydride species, generated by the reaction of the Rh(I) NHC complex with the silane. Once the active catalyst is formed, oxidative addition of the silane to the Rh center produces an Rh(III) dihydride silyl species. Acetophenone then coordinates to the metal center and inserts into the Rh–Si bond, forming a Rh(III) alkyl hydride intermediate. This intermediate undergoes reductive elimination to yield the desired product and regenerate the Rh(I) hydride active species. These catalytic systems were then applied to the hydrosilylation polymerization of terephthalaldehyde with 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS), but yielded poly(silyl ether)s with a bimodal molecular weight distribution. This Rh-based heterogeneous catalyst showed excellent recyclability, maintaining high catalytic efficiency over four cycles.

To develop the application of poly(silyl ether)s in enantioseparation as chiral stationary phases, Zhou *et al.* synthesized highly optically active poly(silyl ether)s *via* copper-catalyzed asymmetric hydrosilylation polymerization. The authors first studied the hydrosilylation polymerization between TMDS and xenyldiketone (Fig. 13).[41] The resulting polymers exhibited a M_n of 11 800 g mol^{-1} and showed favorable reactivity with an 87% yield. Optimization studies revealed that *tert*-butyl methyl ether is the best solvent, and copper cyclohexanebutyrate with a chiral bisphosphine ligand provides the best performance. The reaction scope was then extended to five commercially available and inexpensive bis(hydrosilane)s in combination with sixteen different diketones. These polymerization reactions also showed high yields and produced high molecular

(a) Nishikubo, 1993

M_n=11,000 g/mol

M_n=29,000 g/mol

(b) Nishikubo, 2000

Bis(oxetane)s

M_n=53,200 g/mol

R^1= Ph, Me R^2= Me, Et

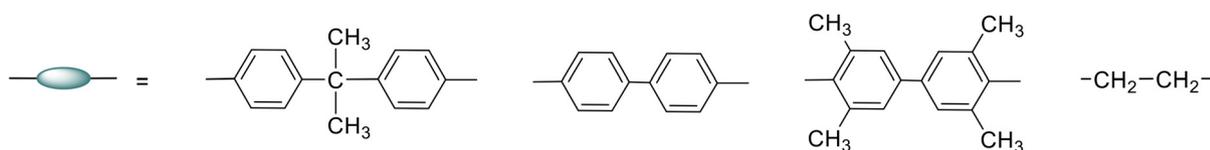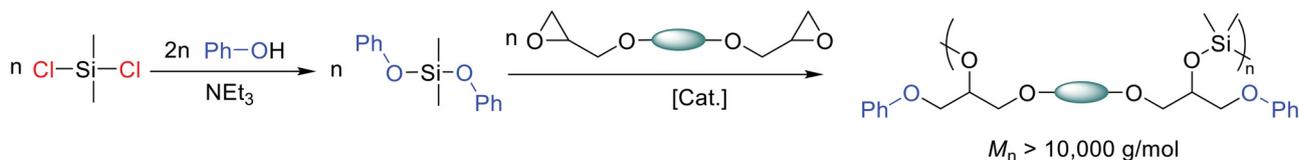**(c) Nishikubo, 1996**

M_n > 10,000 g/mol

Fig. 10 Synthesis of poly(silyl ether)s by polyaddition of (a) dichlorosilanes or bis(chlorosilane)s and bis(epoxide)s,[33] (b) dichlorosilanes and bis(oxetane)s,[34] (c) dimethyldiphenoxysilane and bisepoxides.[35]

weight materials (M_n up to 30 800 g mol^{-1}), demonstrating the versatility of this protocol. In addition, significant enantiomeric excess values (ranging from 81% to 99) were achieved through polymer hydrolysis, demonstrating the high stereoselectivity of the polymerization process. As a consequence, all investigated chiral poly(silyl ether)s exhibited interesting thermal stability, with decomposition temperatures ($T_{d,-5\%}$) ranging from 281 to 408 °C.
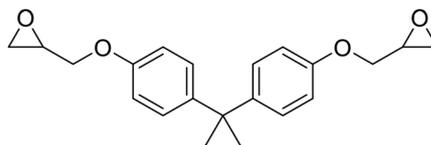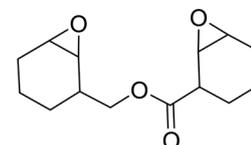
Interested in metal-free hydrosilylation polymerization methods,[11,42] Li and Hawker investigated the use of B(C_6F_5)$_3$, a proven catalyst for a range of hydrosilylation coupling reac-

tions involving the addition of silicon hydrides across unsaturated bonds.[43–45] This species proved highly efficient for the hydrosilylation polymerization of BDMSB and 1,2-diphenylethanedione as model substrates at room temperature (Fig. 14).[46] Unlike transition-metal catalysts that trigger the reaction by an oxidative insertion into the Si–H bond, B(C_6F_5)$_3$ activates the Si–H bond to form a Lewis acid/base adduct, which is then susceptible to attack at the silicon by the Lewis basic substrate.[43b] The driving force of the reaction is the formation of the Si–O–C bond, with regeneration of B(C_6F_5)$_3$. The same mechanistic pathway promoted by B(C_6F_5)$_3$ is also

Laine, 2020
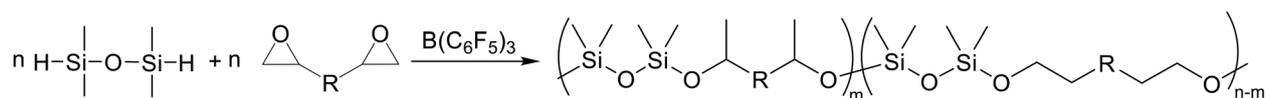
Diepoxides used:
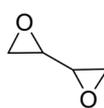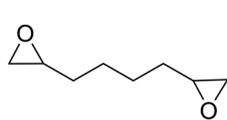
M_n=1700 g/mol M_n=2400 g/mol M_n=6800 g/mol M_n=1200 g/mol

Fig. 11 Polycondensation of diepoxides and hydrosilanes catalyzed by B(C6F5)3.[36]

Fernández-Alvarez and Oro, 2014

HeptMTS

HexMTS

M_w=34,000 g/mol, T_g=-89.4 °C, T_d=456 °C

[Rh]-X   (X=Br, Cl)

+R2MeSiH
(R=Me3SiO)   -R2MeSiCl

R2MeSiH

[Rh]-X (X=Br, Cl)
Homogeneous Catalyst

[Rh]-Cl on MCM-41
Heterogeneous Catalyst
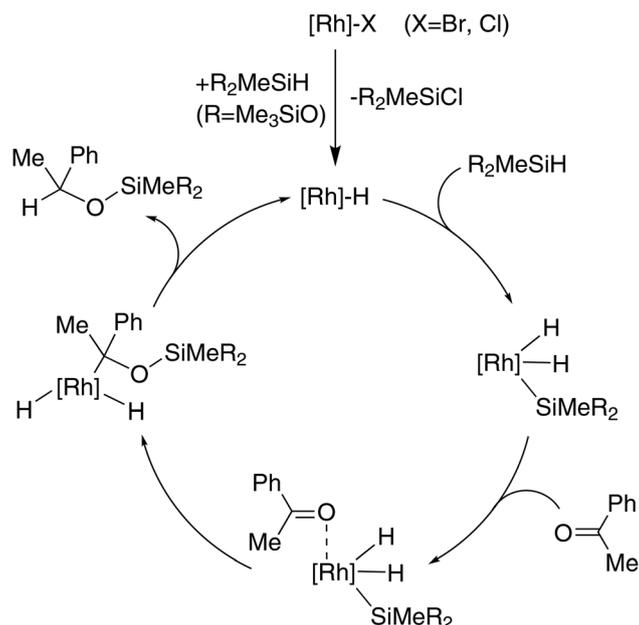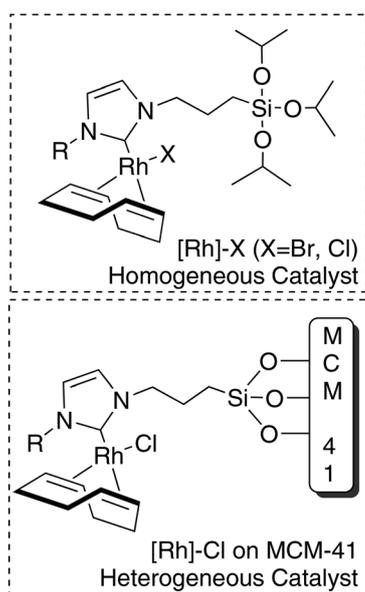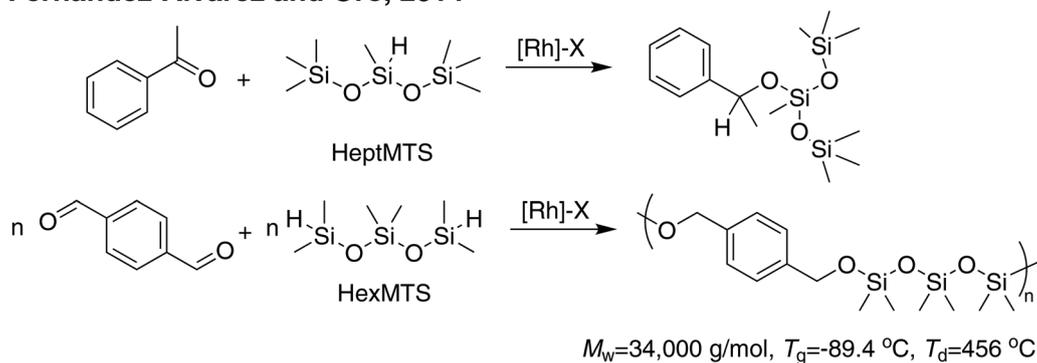
Fig. 12 Hydrosilylation polymerization of terephthalaldehyde and HexMTS catalyzed by Rh-based catalysts, along with the plausible mechanism.[40]

responsible for the cleavage of O–CH3 fragments (Fig. 8) and C–O bonds in epoxides (Fig. 11), indicating a consistent mechanism across these transformations. Thus, a low loading of the borane catalyst (0.5 mol%) and a short reaction time (30 min) in equimolar conditions resulted in the formation of the poly(silyl ether)s with high molecular weights (M_n =

Zhou, 2020
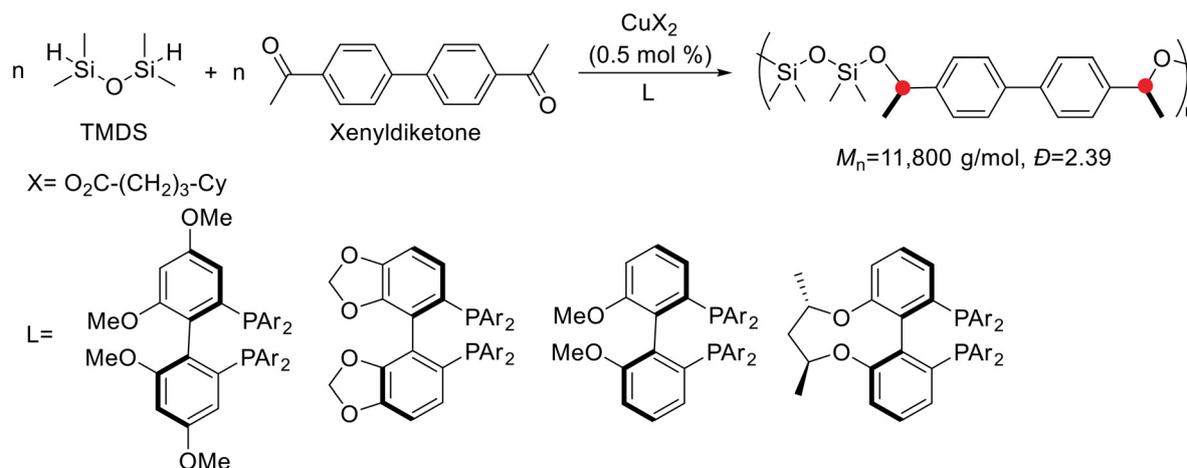
Fig. 13 Hydrosilylation polymerization of diketones and hydrosilanes catalyzed by Cu-based catalysts.[41]

Li and Hawker, 2019
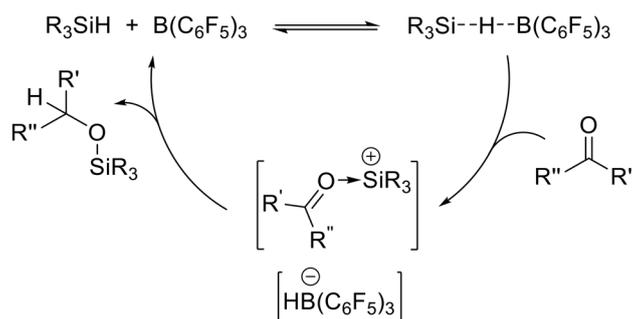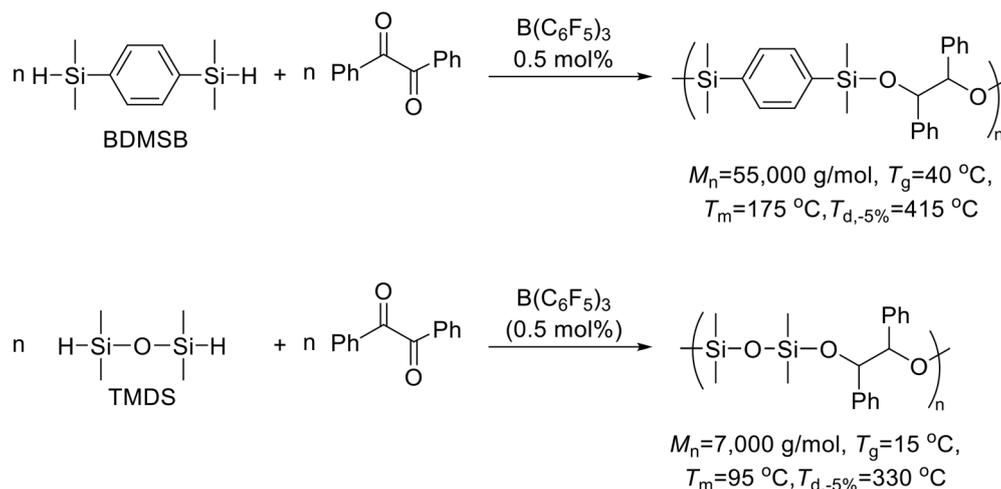
Fig. 14 B(C$_6$F$_5$)$_3$-catalyzed hydrosilylation polymerization of bis(hydrosilane)s and 1,2-diphenylethanedione, along with the postulated mechanism.[46]

55 000 g mol^{-1}) and narrow dispersity ($Đ$ = 1.8), achieving a yield of over 80%. This methodology has been applied to a variety of commercially available aryl-substituted α-diketones and bis(hydrosilane)s, such as TMDS and 1,2-diphenylethanedione, yielding polymers with M_n = 7000 g mol^{-1}, T_g = 15 °C, T_m = 95 °C, $T_{d,-5\%}$ = 330 °C.

To further extend the range of substrates, poly(silyl ether)s have also been prepared by polycondensation and polyaddition of dihydrosilanes (AA-type monomers) with difunctional hydroxyketones (BC-type monomers). For example, Thomas and Conejero synthesized bio-based poly(silyl ether)s by copolymerizing dihydrosilanes with renewable derivatives, such as 5-hydroxymethylfurfural (HMF), vanillin and syringaldehyde (Fig. 15).[47] This polymerization process was catalyzed by a low catalyst loading (as low as 500 ppm) of industrially relevant Pt^{II} complexes in the environmentally benign solvent 2-methyl-tetrahydrofuran (MeTHF) and was carried out under mild conditions. The poly(silyl ether)s obtained showed good thermal stability ($T_{5\%}$ up to 301 °C for HMF-based PSEs), and tunable glass transition temperatures (from −60 °C to 29 °C) depending on monomer combinations. Aromatic silanes (e.g. Ph_2SiH_2) increased T_g due to added rigidity, and aliphatic silanes (e.g. Et_2SiH_2) resulted in lower T_g. Therefore, mixed silanes allowed fine-tuning of T_g values. The regioselectivity of the polymerization was determined by ^{29}Si NMR and $^1H–^{29}Si$ HMBC NMR spectroscopy. In the vanillin-based poly(silyl ether)s, approximately 50% of the silyl ether linkages were "head-to-tail" linkages, as expected from a statistical distribution where the phenol and aldehyde moieties have similar reactivities. Importantly, the resulting (statistical or alternating) copolymers were degradable via acid-catalyzed hydrolysis or methanolysis (Fig. 15). HMF-based PSEs showed nearly complete degradation under acid hydrolysis, yielding original bio-based monomers, whereas vanillin-based PSEs were more resistant, especially when bulky silanes were used.

Recently, Zhu and Mitsuishi reported a metal-free synthesis of alternating silyl ether-carbosilane copolymers via $B(C_6F_5)_3$-catalyzed hydrosilylation polymerization (Fig. 16).[48] In this process, dihydrosilanes were used as AA-type monomers, while commercially available unsaturated ketones containing both vinyl and carbonyl reactive groups were used as BC-type monomers. The reaction between 2-cyclopenten-1-one and BDMSB

was first studied as a model step-growth polymerization system. Two main chain structures resulting from 1,2-addition and 1,4-addition were produced in the resulting copolymers. A reaction mechanism was proposed in which the Si–H bond, activated by the borane catalyst, reacts with the carbonyl group of the substrate to form silyl enol ether cations along with the hydridoborane couteranion. In nonpolar solvents, the reaction tends to favor the formation of 1,2-adducts, while polar solvents stabilize cationic intermediates, resulting in a higher ratio of 1,4-adducts. The C=C bond in the resulting silyl enol ethers then undergoes further hydrosilylation with another Si–H bond to form a copolymer with alternating Si–O–C and Si–C bonds. In addition, the reactivity of several commercially available α,β-unsaturated ketones in combination with BDMSB was investigated. Only α,β-unsaturated ketones underwent efficient hydrosilylation, as the 1,4-conjugation in these ketone monomers is critical for successful polymerization at both the C=O and C=C functional groups. This underscores the importance of selecting appropriate BC-type monomers in the design of efficient tandem catalytic systems.

Kanazawa and Aoshima reported the synthesis of high molecular weight terpolymers with ABC-type, pseudo-periodic sequences by the cationic terpolymerization of 1,3-dioxa-2-sila-cycloalkanes, vinyl ethers, and aldehydes using $B(C_6F_5)_3$ as a catalyst (Fig. 17).[49] The key reaction mechanism in the terpolymerization process involves the reaction between an aldehyde and the oxonium ion derived from the silyl monomer, forming a carbocation that can then react with a vinyl ether. Notably, the vinyl ether itself does not react directly with the oxonium ion derived from the silyl monomer. Due to the presence of labile acetal and silyl ether linkages in the main chain, different degradation products are formed depending on the specific degradation conditions. Hydrochloric acid degradation of the terpolymers yields products resulting from the cleavage of both acetal and silyl ether groups. In contrast, degradation with bases or fluoride ions selectively cleaves the

Thomas and Conejero, 2022

R= Me, Ph   Vanillin M_n=32,000 g/mol, T_g=29 °C, $T_{d,-5\%}$=208 °C

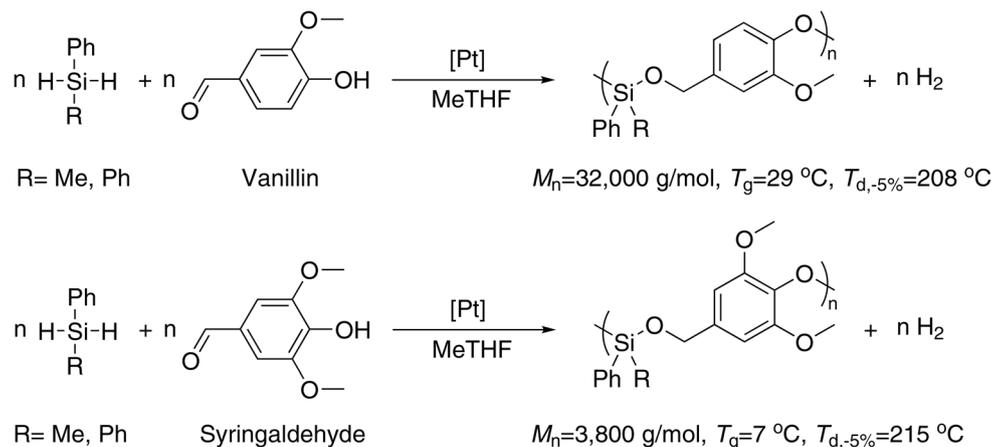R= Me, Ph   Syringaldehyde M_n=3,800 g/mol, T_g=7 °C, $T_{d,-5\%}$=215 °C

Fig. 15 Synthesis of bio-based poly(silyl ether)s from hydrosilanes and two lignin-based derivatives.[47]
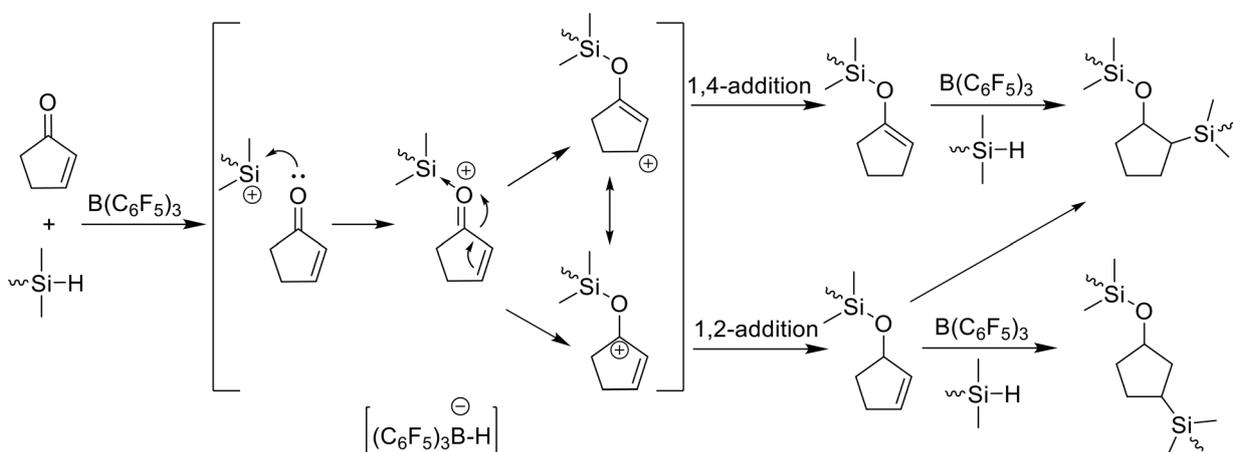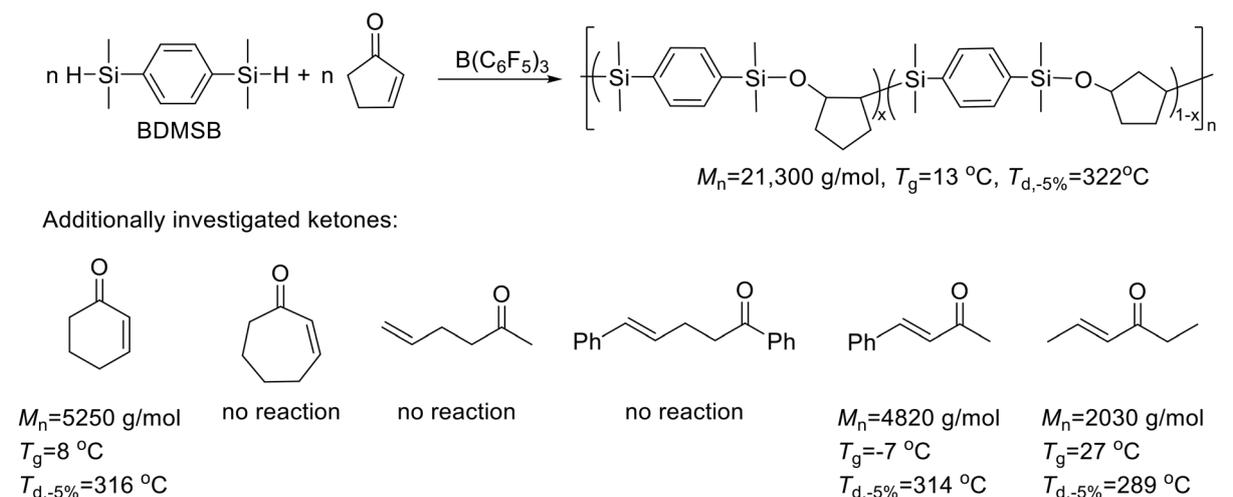
Zhu and Mitsuishi, 2024

Fig. 16 Hydrosilylation polymerization for alternating silyl ether–carbosilane copolymers using unsaturated ketones, along with the plausible reaction mechanism for two types of products by 1,2- or 1,4-addition.[48]

silyl ether groups while preserving the acetal moieties. This dual labile linkage structure provides a unique opportunity for tailored degradation profiles that could be exploited for applications requiring specific degradation characteristics.

Achieving equimolar stoichiometry of homo-functionalized monomers is particularly challenging when dealing with highly reactive and moisture-sensitive reagents, especially when proper reaction conditions cannot be controlled. In contrast to the use of AA/BB comonomers for polymerization, the use of an AB monomer is a practical solution because the incorporation of reactive functional groups within a single molecule avoids these difficulties.[50] However, this introduces a new criterion: the functional groups within the AB monomer must be stable and unreactive towards each other to allow purification and characterization. These functional groups must also maintain an appropriate level of reactivity during the polymerization process to ensure the successful formation of high molecular weight polymers. Currently, there are a limited number of reports on the synthesis of poly(silyl ether)s

from AB-type monomers, mainly involving self-polycondensation of AB monomers and self-polyaddition of AB monomers. In the case of self-polycondensation reactions, Zhou et al. synthesized a family of AB monomers containing Si–H and –OH functionalities, and successfully prepared various poly(silyl ether)s by Ir-catalyzed dehydrocoupling of the neat monomers (Fig. 18a).[51] By optimizing the reaction conditions, the resulting poly(silyl ether)s with aliphatic and aromatic backbones were obtained in moderate to high yields, with high M_n (up to 92 700 g mol^{-1} with Đ = 3.70), good thermal stability and tunable glass transition temperatures (from −42 °C to −83 °C). Notably, the T_g of poly(silyl ether)s with an aromatic backbone was higher than that of those with an aliphatic backbone. As an example of the self-polyaddition approach, Weber's group reported the synthesis and polymerization of aliphatic ω-dimethylsilyloxyketone AB-type monomers, 5-dimethyl-silyloxy-2-pentanone and 4-dimethylsilyloxy-2-butanone, by Ru-catalyzed hydrosilylation reaction between Si–H and C=O groups (Fig. 18b).[52] However, these poly(silyl ether)s exhibited

Kanazawa and Aoshima, 2022
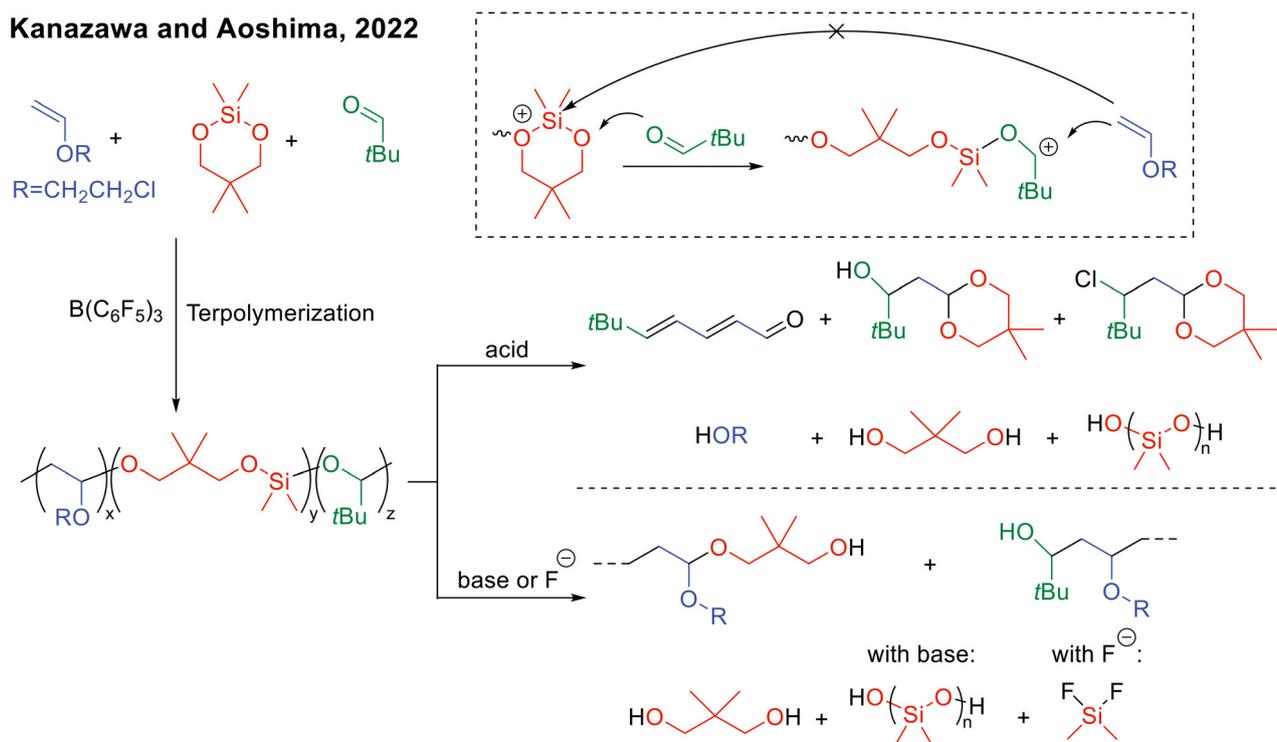
Fig. 17 Cationic polymerization of silyl ether-based poly(vinyl ether) and degradation of acetal and silyl ether groups in the backbone by acids, bases, or fluoride ions.[49]

(a) Zhou, 2018

= (CH$_2$)$_5$, M_n=30,500 g/mol
(CH$_2$)$_7$, M_n=92,700 g/mol, T_g=-76 °C
(CH$_2$)$_8$, M_n=25,500 g/mol
(CH$_2$)$_9$, M_n=46,900 g/mol, T_g=-83 °C
CH$_2$O-Ph-CH$_2$, M_n=20,800 g/mol, T_g=-42 °C

[Ir]= [Ir(COD)Cl] / Ph$_2$P(CH$_2$)$_3$PPh$_2$

(b) Weber, 2002

m=1,2

m=1: M_n=4400 g/mol, T_g=-88 °C
m=2: M_n=5900 g/mol, T_g=-81 °C

[Ru]= [RuH$_2$(CO)(PPh$_3$)$_3$]
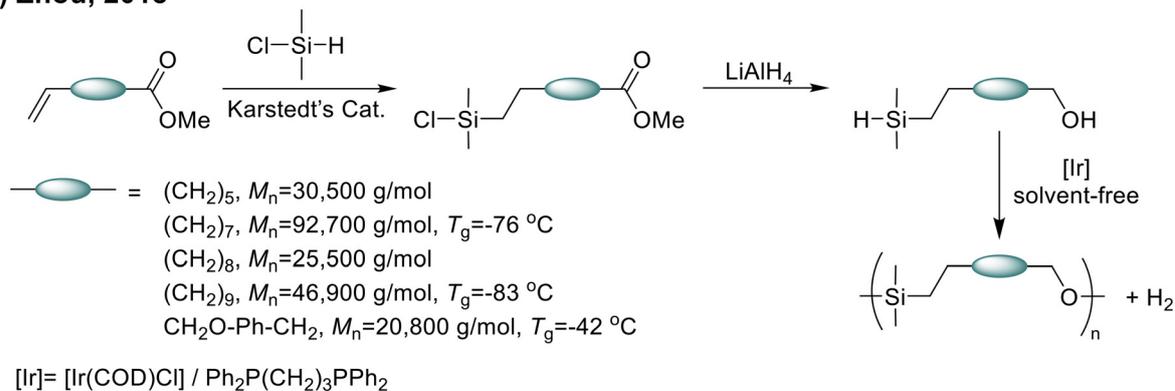
Fig. 18 Examples of polymerization of AB monomers by (a) self-polycondensation[51] and (b) self-polyaddition.[52]

low thermal stability, with degradation starting below 150 °C. This can be attributed to their relatively low molecular weights (4400 g mol^{-1} and 5900 g mol^{-1}, respectively).

2.2 Degradation behavior of poly(silyl ether)s obtained by step-growth polymerization

Although some specific polymers, such as aliphatic polyesters, can undergo both biodegradation and chemical degradation, only chemical degradation of poly(silyl ether)s has been reported because only few enzymes have the ability to efficiently cleave silyl ether (Si–O–C) bonds.[47,53] After chemical d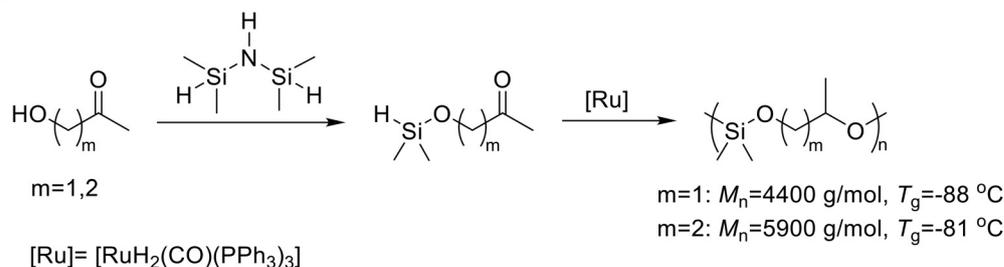egradation by acid- or base-catalyzed hydrolysis or alcoholysis, AA/BB-type poly(silyl ether)s typically yield disilanol or bis(alkoxysilane) compounds and the diol monomer, while AB-type poly(silyl ether)s yield a derivative of the monomer with silanol or alkoxysilane and hydroxy terminal groups (Fig. 19). These degradation products have the potential for reuse after further isolation from the degradation mixture.

Most of the reported work on the degradation of poly(silyl ether)s has focused primarily on investigating the effect of operating conditions.[28,30,54] For example, Du et al. reported bio-based poly(silyl ether)s synthesized by dehydrogenative cross-coupling between isohexide and commercially available hydrosilanes catalyzed by a Mn complex (1.0 mol%) (Fig. 20).[28] The hydrolytic degradation of these bio-based poly(silyl ether)s in a THF solution under different conditions was further investigated by monitoring the molecular weight change over time. As expected, hydrolysis can be accelerated by the introduction of a catalytic amount of inorganic acids or bases. Under acidic or basic conditions (2 vol%) in THF at room temperature, the polymers underwent partial degradation, with an initial molecular weight decrease within 5 h, followed by limited molecular weight loss over a longer period of time. Thus, the degraded polymeric products obtained under acidic conditions (2 vol% HCl/H$_2$O, pH = 2) showed an M_n of 6900 g mol^{-1} lower than that obtained under basic conditions (2 vol% KOH/H$_2$O, pH = 11), namely 8200 g mol^{-1}. Moreover, increasing the con-
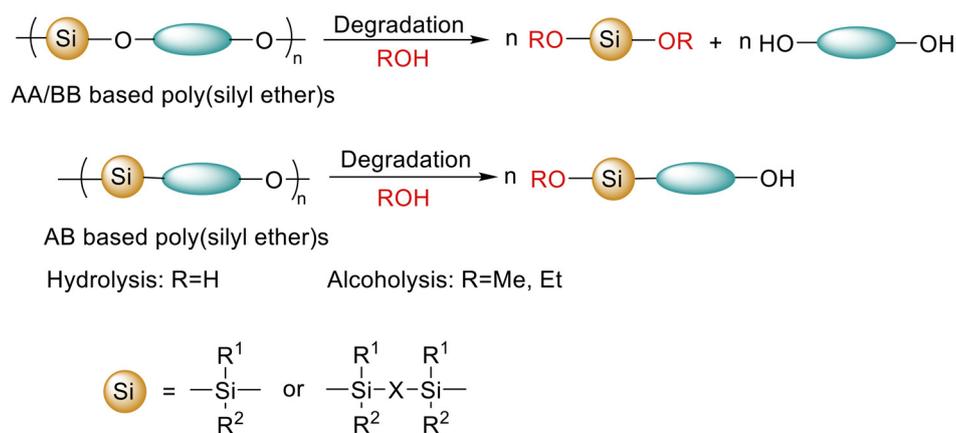

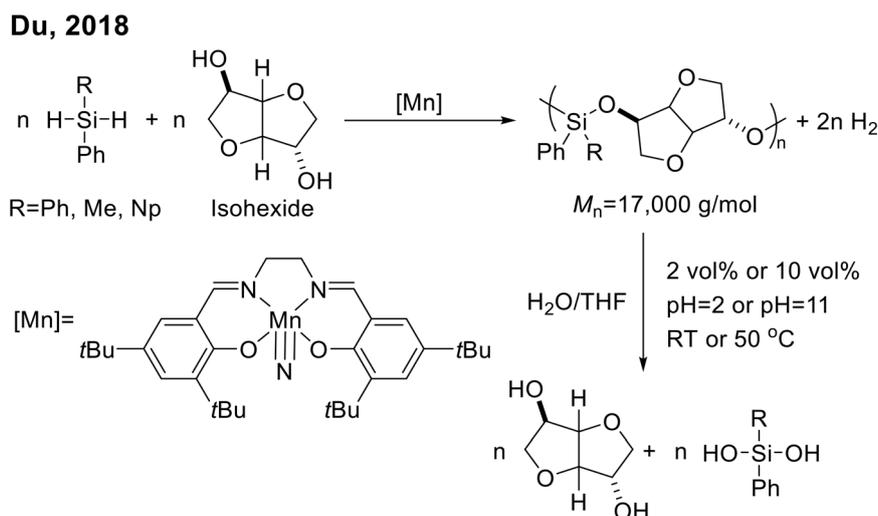**Fig. 19** Representative degradation routes of poly(silyl ether)s.

Fig. 20 Synthesis of bio-based poly(silyl ether)s from hydrosilanes and isohexide.[28]

centration of HCl/H$_2$O (10 vol%) or raising the temperature to 50 °C further accelerated the degradation rate, and finally almost complete degradation was achieved.

When considering a (nucleophilic) degradation mechanism, the degradation rate of poly(silyl ether)s can be influenced by others parameters, such as the steric hindrance and electronic properties of the substituents on the silicon and carbon atoms within the silyl ether bonds.[55] For example, Li and Hawker showed that the degradation of poly(silyl ether)s can be performed in CHCl$_3$/HCl (1 mM) solution (Fig. 14).[46] As a result, both silylphenylene-based and siloxane-based poly (silyl ether)s were found to be susceptible to acid-catalyzed hydrolysis. Interestingly, the siloxane-derived poly(silyl ether) exhibited a faster degradation rate than the former, which can be attributed to a decrease in steric hindrance and electronic effects within the Si–O bond relative to the phenylene group.

Our group also showed that bio-based (statistical or alternating) PSEs were degradable *via* acid-catalyzed hydrolysis or methanolysis (Fig. 15).[47] The degradation properties of these PSEs were dependent on both the hydroxyaldehyde and the dihydrosilane precursors used, with a higher stability conferred by bulky comonomers (Table 2). In particular, HMF-based PSEs showed nearly complete degradation under acid hydrolysis, yielding original biobased monomers, whereas vanillin-based PSEs were more resistant, especially when bulky silanes were used.

As our understanding continues to deepen at the molecular level, we can expect further development to achieve more precise control over degradation and product utilization.

2.3 Synthesis of poly(silyl ether)s by chain-growth polymerization

In the step growth polymerization methods described previously, silyl ether bonds are formed during the polymerization process. Alternatively, poly(silyl ether)s can also be synthesized *via* ring-opening metathesis polymerization (ROMP), if silyl ether bonds are already present in the cyclic monomers. Following this approach, Johnson synthesized poly(silyl ether)s by ROMP of cyclic bifunctional silyl ether-based olefins using a Ru-based Grubbs 3rd generation catalyst (Fig. 21).[56] Seven- and eight-membered cyclic monomers (*i*PrSi$_7$ and *i*PrSi$_8$) were prepared and subsequently studied for polymerization, using ethylvinyl ether as terminator. ROMP of *i*PrSi$_7$ did not lead to homopolymerization but resulted in the formation of isomerized *i*PrSi$_7$ and dimerized *i*PrSi$_7$. In contrast, ROMP of *i*PrSi$_8$ at 3 °C resulted in high molecular weight species (M_n = 47 700 g mol^{-1}). This difference is due to the different enthalpic driving forces of these two cyclic monomers. As a result, poly(*i*PrSi$_8$) is an ultra-low T_g polymer (−88 °C) with a strong resistance to crystallization, making it potentially suitable for low temperature applications. In addition, its maximum mass loss rate during thermal decomposition occurred at 486 °C, which is consistent with the typical behavior of polymers containing both siloxane and olefin groups. The authors also used *i*PrSi$_8$ in subsequent research on copolymerization with ROMP-active olefins, resulting in the formation of silyl ether-based polymers.

Johnson also used the reactivity of these eight-membered silyl ether olefins in combination with a variety of ROMP-active cyclic olefins (*e.g.* dicyclopentadiene,[57] cyclooctene, norbornene derivatives) to produce statistical copolymers that exploit the inherent degradability of silyl ether bonds. For example, new silyl ether-based polynorbornene copolymers were obtained from norbornene-terminated PEG and eight-membered cyclic bifunctional silyl ether olefins by ring-opening metathesis polymerization using a 3rd generation Grubbs catalyst (Fig. 22).[58] Under mild acidic conditions, the obtained

Table 2 Selected thermal properties and degradation performance of poly(silyl ether)s obtained by Pt-catalyzed polymerization[47]

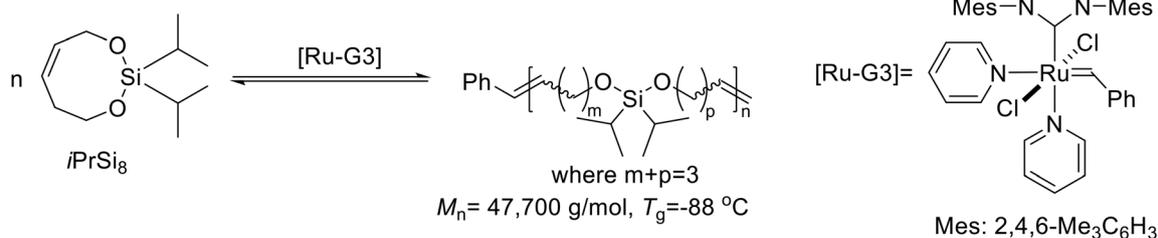| Copolymer	T_g (°C)	$T_{5\%}$ (°C)	M_w loss (acid hydrolysis)	M_w loss (methanolysis)
Poly(HMF-*co*-Ph$_2$SiH$_2$)	7	301	Nearly 100%	15–30%
Poly(HMF-*co*-Et$_2$SiH$_2$)	−60	280	Nearly 100%	15–30%
Poly(HMF-*co*-MePhSiH$_2$)	−15	270	Nearly 100%	15–30%
Poly(vanillin-*co*-MePhSiH$_2$)	7	245	25%	70%
Poly(vanillin-*co*-Ph$_2$SiH$_2$)	29	208	25%	7%
Poly(vanillin-*alt*-HMF-*co*-MePhSiH$_2$)	21	237	Nearly 100%	N/A

Fig. 21 Ring-opening metathesis polymerization of cyclic silyl ether-based olefins.[56]
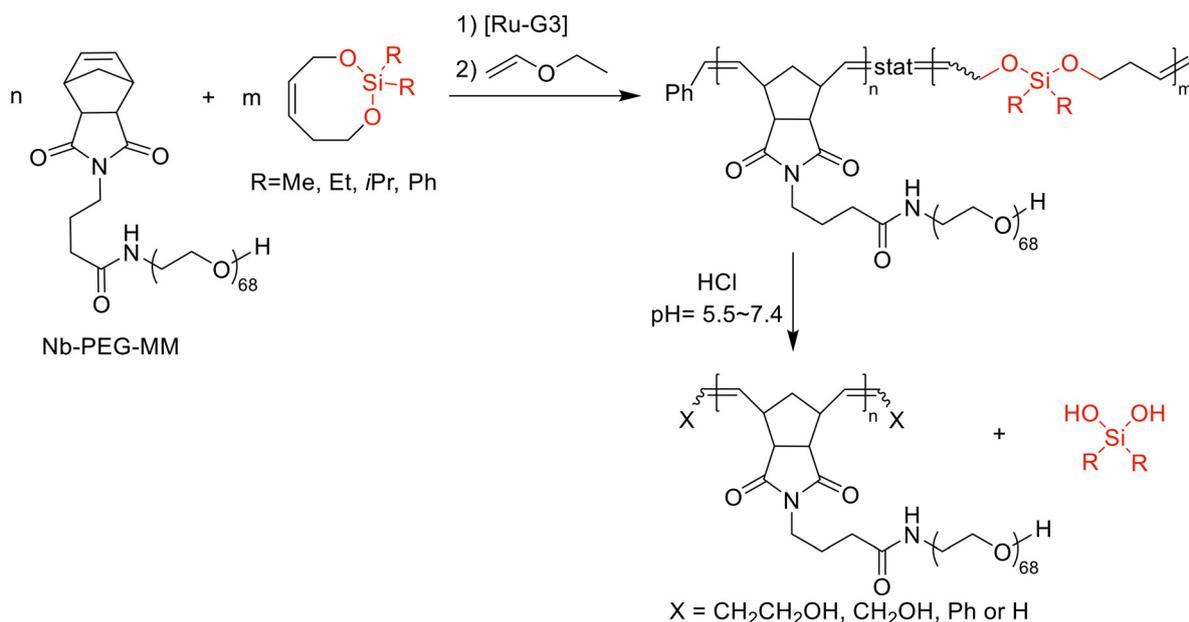
Johnson, 2019

Fig. 22 ROMP of a norbornene-terminated PEG macromonomer and cyclic silyl ether olefins, and the degradation behavior of the resulting copolymer under mildly acidic aqueous conditions.[58]

copolymers were able to degrade to the corresponding macromolecular degradation products and silanol. By adjusting the silyl ether substituents (methyl, ethyl, isopropyl, and phenyl groups), the degradation rate over time can be modified by several orders of magnitude with minimal impact on copolymerization control.

Although silyl ether-based polymers are generally degraded by chemical triggers such as acids, bases, and fluoride, they often resist degradation by milder agents such as biological nucleophiles. This resistance can limit their end-of-life management and reduce their potential for environmental degradation. Johnson and coworkers also performed the deconstruction of polynorbornenes using a nucleophilic aromatic substitution (S_NAr)-triggered cascade approach.[59] The terpolymers were synthesized from the iPrSi$_8$, norbornene-containing pentafluorophenyl (Nb-PFP) substituent and norbornene-terminated PEG (Nb-PEG-MM) in the presence of a 3rd generation Grubbs catalyst (Fig. 23). Deconstruction of the terpolymer was achieved by exposure to thiols (1-dodecanethiol and 2-mercaptoethanol) under basic conditions. The mechanistic studies showed that 1-dodecanethiol attacks the *para* position of the electrophilic PFP ring by a S_NAr mechanism in the presence of a base. The thus released fluoride ion then cleaves the Si–O bond of the silyl ether, resulting in the formation of the corresponding deconstruction product. This approach expands the deconstruction methods for silyl ether-based polymers, enabling the creation of innovative functionalities and new end-of-life solutions.

To develop a strategy to achieve deconstructable "PE mimics" with potential routes for chemical recycling and/or environmental deconstructability, Johnson *et al.* incorporated

chemically cleavable silyl ether bonds into the backbone of PE-like materials (Fig. 24).[60] These silyl ether-based copolymers were synthesized by a one-pot catalytic sequence, involving the copolymerization of cyclooctene and iPrSi$_8$, followed by hydrogenation of the C–C double bonds. The chemical recycling of silyl ether-based polyethylene was then investigated under relatively mild conditions. The cleavage of the silyl ether bond was successfully achieved using either 0.5 M acetic acid in toluene at 80 °C or 0.2 M tetrabutylammonium fluoride (TBAF) in THF at 60 °C (blue cycle in Fig. 24). However, using dichlorosilanes for repolymerization does not create a fully "closed loop" process because new silane monomers are required in each cycle. To explore an alternative chemical recycling route for these systems, deconstruction *via* an octanoic-acid catalyzed bond-exchange between *n*-propanol and the copolymer backbone was performed in toluene at 80 °C (red cycle in Fig. 24). To complete the cycle, repolymerization was achieved by removal of *n*-propanol at 100 °C, resulting in a polymer with the same molecular weight as the original polymer.

Notably, both the original and recycled silyl ether-based polyethylene exhibited mechanical properties comparable to those of non-functionalized high-density polyethylene, indicating significant potential for practical applications.

3 Poly(silyl ester)s

3.1 Synthesis of poly(silyl ester)s by step-growth polymerization

Silyl esters are functional groups formed by attaching a silyl moiety to the oxygen atom of a carboxylic acid. In addition to being commonly used as protecting groups for carboxylic acids
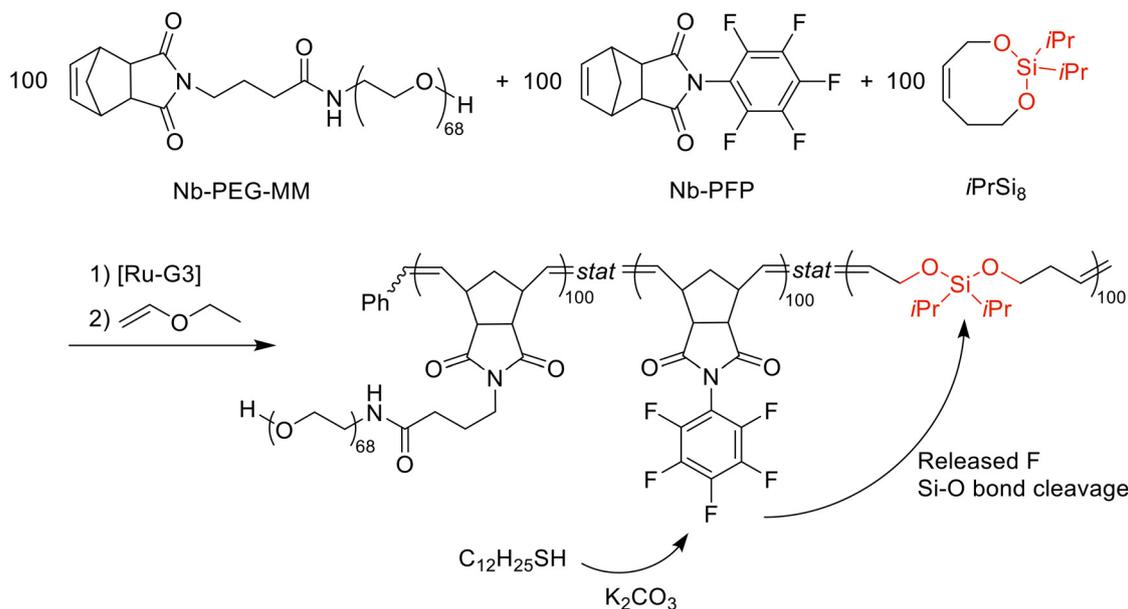
Johnson 2023

Fig. 23 Synthesis of a polynorbornene graft terpolymer containing PFP substituent, and its deconstruction by a S_NAr-triggered cascade.[59]

Johnson, 2023
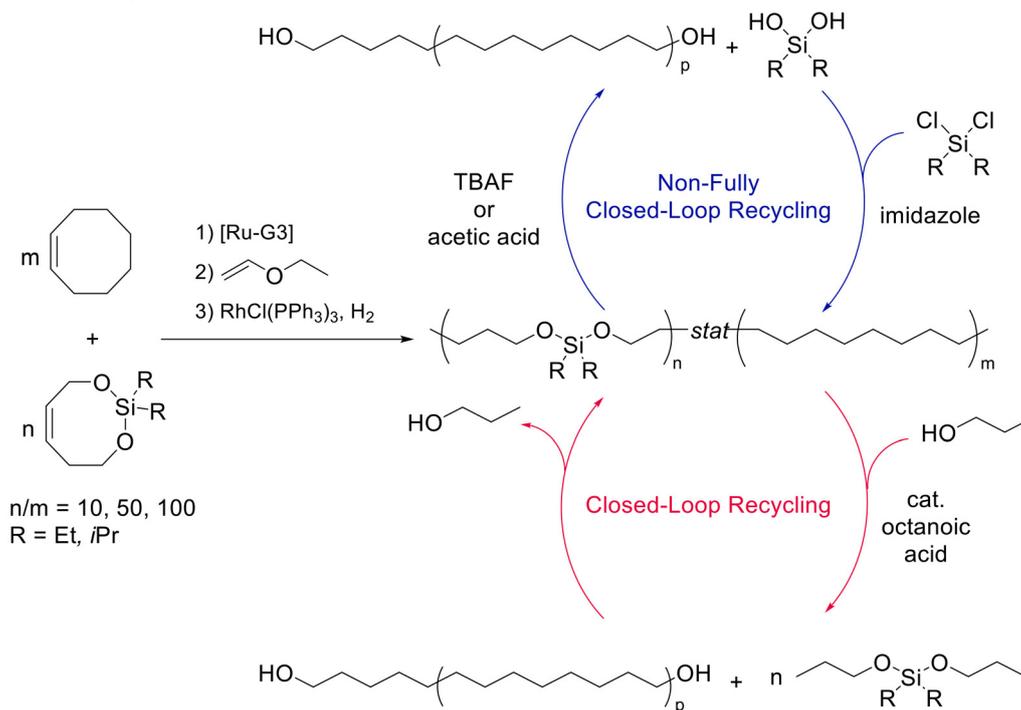
Fig. 24 One-pot synthesis of silyl ether-based polyethylenes, and their recycling routes.[60]

in organic synthesis, silyl ester groups can be incorporated into polymer structures as repeating units to form poly(silyl ester)s.[61,62] Similar to poly(silyl ether)s, the polymer chains of poly(silyl ester)s can be formed by step-growth polymerization

under specific conditions, although examples are relatively rare. Several synthetic strategies have been developed to prepare poly(silyl ester)s, starting from AA/BB comonomers, or AB monomers.

Several types of AA/BB comonomers can undergo step-growth polymerization to produce corresponding poly(silyl ester) chains, accompanied by the generation of different by-products. First, the poly(silyl ester)s can be synthesized by the condensation reaction between disilanols and diacyl chlorides.[63,64] Cazacu et al. synthesized new poly(silyl ester) structures containing ferrocenyl moieties within the backbone, obtained from 1,10-di(chlorocarbonyl)ferrocene and two siloxane derivatives (i.e., diphenylsilanediol and 1,3-bis(hydroxy)tetramethyldisiloxane) using pyridine to scavenge the released hydrochloric acid (Fig. 25a).[63] Consequently, the M_n of the siloxane-containing poly(silyl ester) (10 660 g mol^{-1}) is higher than that of the diphenyl counterpart (6920 g mol^{-1}), while the thermostability of the former is lower than that of the latter.

As an alternative method, the polycondensation can be carried out by the dehydrocoupling reaction between dihydrosilanes and dicarboxylic acids, resulting in the production of hydrogen gas. For example, Kawakami et al. synthesized poly(silyl ester)s by Pd-catalyzed dehydrocoupling polymerization between BDMSB and two different dicarboxylic acids, namely adipic acid and terephthalic acid (Fig. 25b).[65] Structural analysis showed that there were minimal side reactions during the polymerization process, allowing the production of polymers with well-defined structures. Specifically, the adipic acid-derived poly(silyl ester) exhibited an M_n of 4400 g mol^{-1}, while the terephthalic acid-derived poly(silyl ester) showed poor solubility in common solvents due to its rigid structure.

Meanwhile, the poly(silyl ester) derived from adipic acid had a T_g of −14.2 °C and a T_m at 93.3 °C, along with high thermal stability ($T_{d(onset)}$ = 326 °C). In contrast, the poly(silyl ester) derived from terephthalic acid showed a crystalline texture upon cooling from the melt, as observed by polarizing microscopy. However, its DSC curve reveals no clear melting or crystallization temperatures, suggesting an atypical crystalline behavior.

Due to the high cost and the challenge of catalyst removal after polymerization, catalyst-free polymerization approaches have attracted considerable attention. Two types of catalyst-free reactions have been developed to synthesize poly(silyl ester)s based on the AA/BB monomers. The polymerization can be carried out by the transsilylation reaction between trimethylsilyl ester and chlorosilane functional groups, with the elimination of trimethylsilyl chloride as the driving force, as explored by Wooley's group.[66–69] For example, the authors synthesized poly(silyl ester)s using bis(trimethylsilyl) adipate along with three examples of dichlorosiloxanes: 1,3-dichlorotetramethyldisiloxane, 1,3-dichlorotetraisopropyldisiloxane, and 1,3-dichlorotetraphenyldisiloxane (Fig. 26a).[69] These reactions took up to 2 weeks to reach full conversion. The poly(silyl ester) featuring the higher degree of polymerization was obtained from 1,3-dichlorotetramethyldisiloxane due to its lower steric hindrance and suitable viscosity in the polymerization reaction medium compared to the isopropyl- and phenyl-substituted counterparts. When 1,6-bis(chlorodimethylsilyl)hexane is used as the dichlorosilane, reaction with the bistri-

(a) Cazacu, 2006

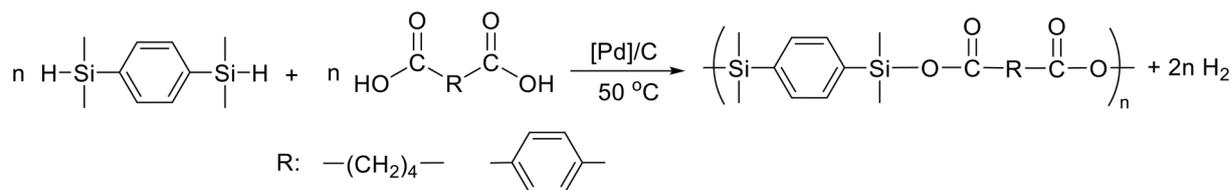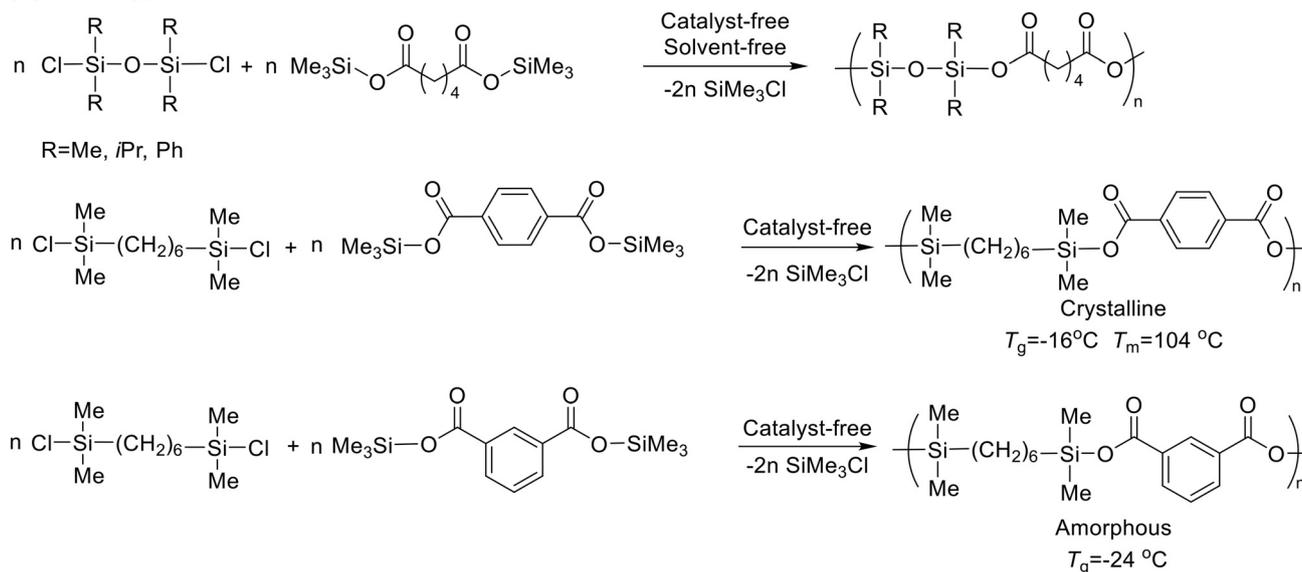M_n=6,920 g/mol

M_n=10,660 g/mol
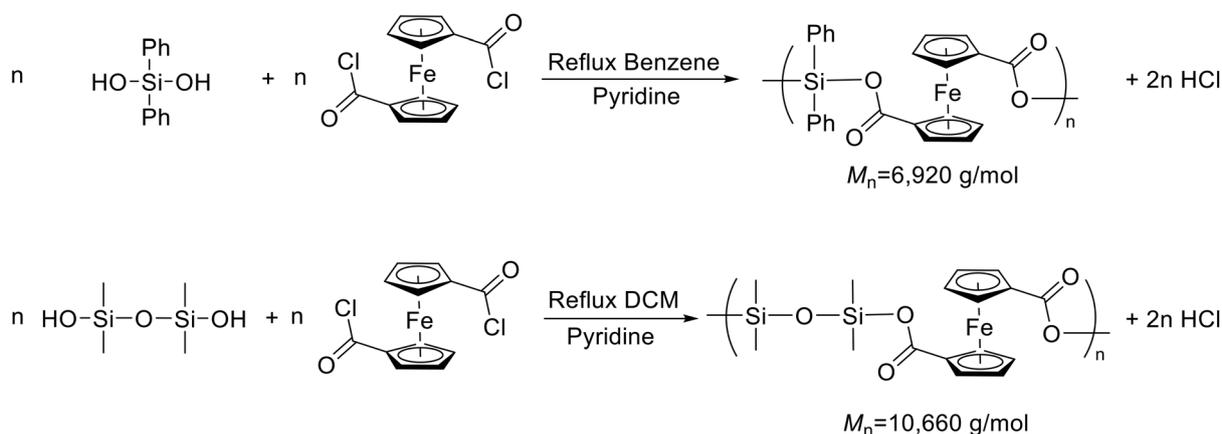
(b) Kawakami, 1999

Fig. 25 Synthesis of poly(silyl ester)s by polycondensation between AA/BB comonomers: (a) 1,10-di(chlorocarbonyl)ferrocene with 1,3-bis(hydroxy)tetramethyldisiloxane and diphenylsilanediol,[63] (b) BDMSB with adipic acid and terephthalic acid.[65]
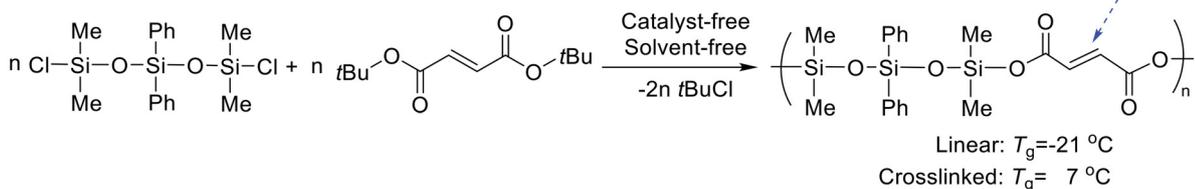
(a) Wooley, 1995 and 1998

R=Me, iPr, Ph

## (b) Tang, 2010

Crosslinking site

Linear: T_g=-21 $^\circ$C
Crosslinked: T_g= 7 $^\circ$C

Fig. 26 Synthesis of poly(silyl ester)s by catalyst-free polycondensation between AA/BB comonomers: (a) bis(trimethylsilyl ester)s and dichlorosiloxanes,[67,69] (b) 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyltrisiloxane and di-*tert*-butyl fumarate.[70]

methylsilyl ester of terephthalic acid yields a crystalline poly(silyl ester), whereas the *meta*-substituted isophthalic acid derivative yields an amorphous polymer.[67]

Another approach explored the polycondensation between *tert*-butyl esters of dicarboxylic acids and dichlorosilane, resulting in the by-product *tert*-butyl chloride.[70–74] Compared to bis(trimethylsilyl ester)s, di-*tert*-butyl esters exhibit improved storage stability and enhanced reactivity with dichlorosilane under the same polymerization conditions, in the absence of solvents and catalysts. For example, Tang *et al.* synthesized unsaturated poly(silyl ester)s by polycondensation between 1,5-dichloro-1,1,5,5-tetramethyl-3,3-diphenyl-trisilox-ane with di-*tert*-butyl fumarate under nitrogen at 100 °C for 3 days. The volatile *tert*-butyl chloride was simultaneously removed by evaporation (Fig. 26b).[70] The resulting viscous poly(silyl ester) was then subjected to a crosslinking process initiated by 2,2′-azobisisobutyronitrile through a free radical crosslinking reaction. By restricting the polymer chain mobility, the solid crosslinked poly(silyl ester) exhibits improved thermal performance compared to the original linear one. Specifically, the linear poly(silyl ester) had a T_g well below zero (T_g = −21 °C), while the crosslinked poly(silyl ester) showed an elevated T_g of 7 °C. Moreover, in the first step of thermal decomposition, the maximum weight loss velocity of the cross-linked product is obtained at a temperature of 234 °C, which is

significantly higher than the 194 °C value observed for the linear poly(silyl ester).

As mentioned above, the use of AB monomers helps to over-come various challenges encountered with AA/BB comonomers during the step-growth polymerization process. Thus, Wooley' group synthesized poly(silyl ester)s *via* the self-polycondensa-tion or self-polyaddition of AB monomers, relying mainly on the dehydrogenative cross-coupling reaction, transsilylation reaction and hydrosilylation reaction.[75,76] For example, they synthesized two bifunctional monomers containing Si–H and –COOH groups, and then synthesized poly(silyl ester)s *via* a Pd-catalyzed dehydrocoupling reaction involving these two AB-type monomers (Fig. 27a).[76] The AB monomer with a SiMe$_2$ moiety shows higher relative chain propagation rates in polymerization than the monomer with a Si(iPr)$_2$ fragment. However, the M_n of the methyl-substituted monomer is lower than that of the isopropyl-substituted monomer. Meanwhile, they also extended this method to synthesize hyperbranched poly(silyl ester) from AB$_2$-type monomer containing two Si–H groups and one –COOH group under the same reaction con-ditions, with the degree of branching of the resulting hyper-branched poly(silyl ester) reaching 51%. In addition to the dehydrogenative cross-coupling reaction, Wooley *et al.* syn-thesized poly(silyl ester)s by the transsilylation reaction of tri-methylsilyl ester and chlorosilane-functionalized AB-type

(a) Wooley, 2001
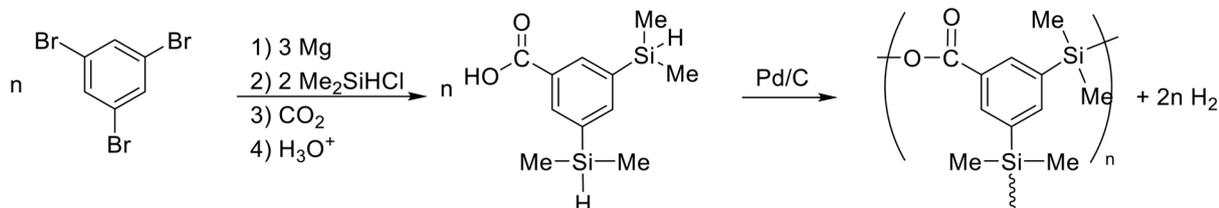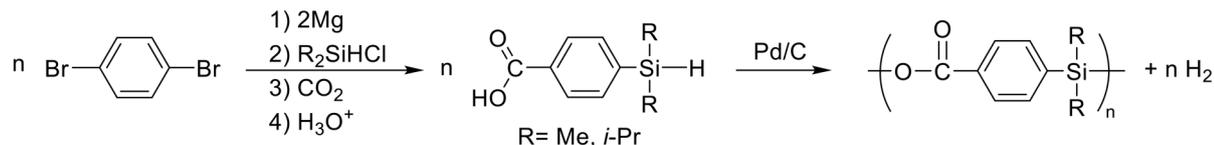
(b) Wooley, 2000
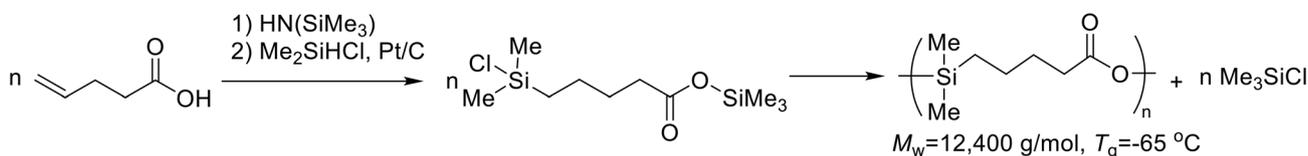
(c) Wooley, 2000
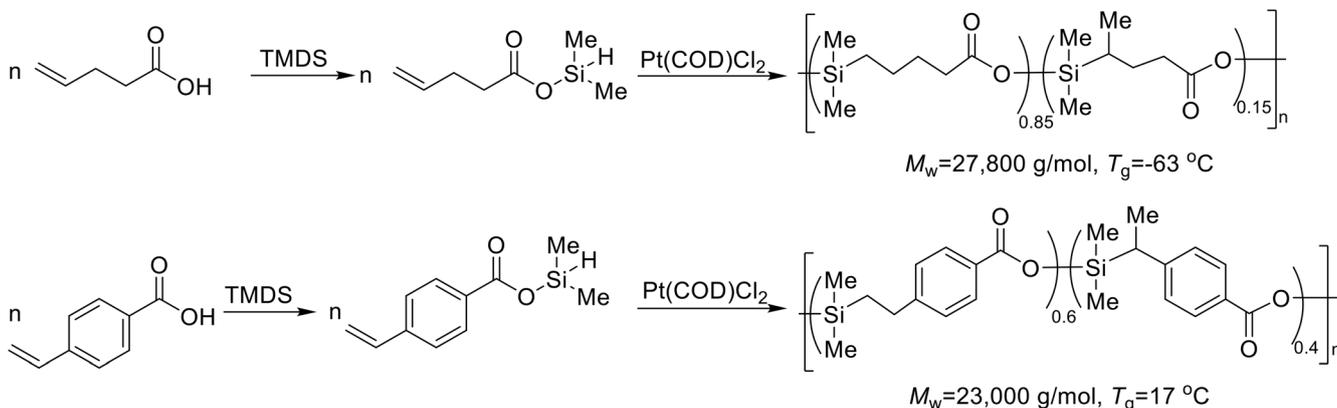
COD=1,5-cyclooctadiene

Fig. 27   Synthesis of poly(silyl ester)s from AB-type monomers through (a) dehydrogenative cross-coupling reaction,[76] (b) transsilylation reaction,[75] (c) hydrosilylation reaction.[75]

monomer (Fig. 27b).[75] After a reaction time of 8 days, the resulting poly(silyl ester) synthesized from AB-type monomers exhibited a M_w (12 400 g mol^{-1}) higher than that obtained from similar polymerizations using the AA/BB comonomer system. While the increase in molecular weight is a significant advance, the transsilylation chemistry still requires several days of heating to produce poly(silyl ester)s. Therefore, they developed a faster synthetic method through [Pt(COD)Cl$_2$]-catalyzed hydrosilylation polymerization of hydridosilyl ester and vinyl-functionalized AB-type monomers at ambient temperature, with reaction times reduced down to 2 h (Fig. 27c).[75] Notably, there are two types of repeating unit structures along the prepared poly(silyl ester)s backbone, depending on different reaction mechanisms: α-addition and β-addition,

with the latter being the major one. However, since the hydrosilylation performed with silyl derivatives featuring bulky substituents is not efficient with this Pt-based catalytic system, the scope of poly(silyl ester)s was limited to those with Si-methyl side chain substituents.

3.2   Degradation behavior of poly(silyl ester)s

Compared to silyl ether groups, silyl ester (Si–O–C=O) groups are more susceptible to solvolysis, with hydrolysis occurring readily even in the absence of acidic or basic catalysts. Silyl ester groups can be cleaved by two different nucleophilic S_N2 attack mechanisms: either on the silicon atom or on the carbonyl carbon.[77] Nucleophilic attack on the silicon center is favored when it bears substituents with reduced steric hin-
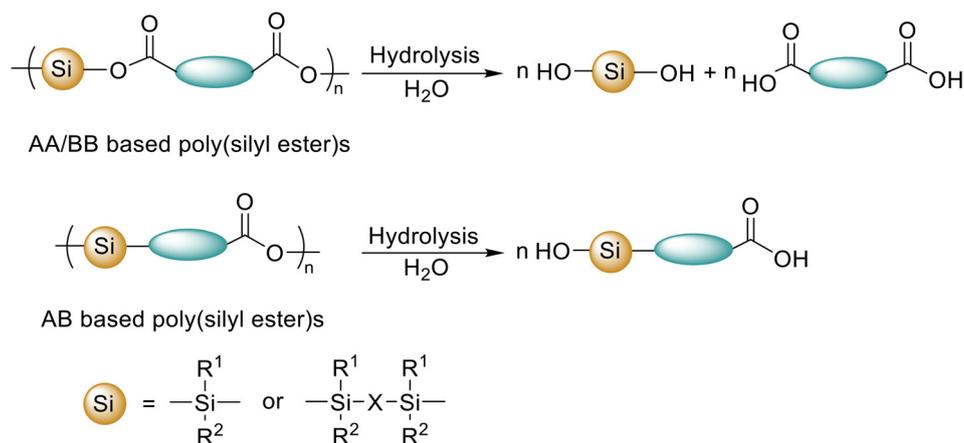
Fig. 28   Representative hydrolytic degradation routes of poly(silyl ester)s.

drance or with reduced electron donating abilities. Conversely, bulky substituents and electron-donating groups on the silicon center favor nucleophilic attack on the carbon atom of the carbonyl group. Hydrolysis of AA/BB type poly(silyl ester)s typically yields degradation products containing disilanol and dicarboxylic diacid (Fig. 28). On the other hand, the hydrolysis of AB-type poly(silyl ester)s results in the formation of degradation products containing silanol and carboxylic acid terminal groups. Based on the reported results, the chemical degradation rate of poly(silyl ester)s is mainly influenced by three categories of factors: chemical structure, physical properties, and degradation environment.

First, since the degradation behavior of poly(silyl ester)s depends mainly on their chemical structure (*i.e.*, the substituents attached to the silicon atoms and the carbonyl groups of the silyl ester linkage), Wooley and coworkers further conducted the hydrolytic degradation of their synthesized poly (silyl ester)s (Fig. 26a).[69] The Si-isopropyl-substituted polymer exhibited higher hydrolytic stability compared to the corresponding methyl- or phenyl-substituted polymers. This is mainly due to the fact that the isopropyl group has a higher steric hindrance and higher electron donating ability compared to the methyl and phenyl groups, respectively, which reduces the reaction probability of nucleophilic attack occurring at the silicon atom. The influence of the substituents attached to the carbonyl groups was also investigated during the hydrolysis process of their reported poly(silyl ester)s (Fig. 27c).[75] The ^{29}Si NMR analysis revealed that this nucleophilic attack reaction of the silyl ester bond occurred entirely at the silicon atom, and the poly(silyl ester) with the phenylene group attached to the carbonyl groups exhibited lower stability compared to the one with an aliphatic chain attached to the carbonyl groups. This is because the former is more susceptible to nucleophilic attack due to the greater stability and more favorable formation of the carboxylic acid anion attached to the phenyl group compared to that attached to the aliphatic chain. Within the carbonyl group, the carbon center is less electrophilic when attached to the electron-donating aliphatic group than to the electron-attracting aromatic moiety.

Second, the degradation behavior of poly(silyl ester)s is also influenced by their physical properties, which include factors such as hydrophobicity, solubility, crystallinity, and more. For example, the degradation rate of crystalline and amorphous poly(silyl ester)s in the solid state was compared under an environment of approximately 20 °C and 40% humidity (Fig. 26a).[78] Among the poly(silyl ester)s shown in Fig. 26a, the crystalline one, namely the one based on a *para*-terephthalic core, exhibited greater hydrolytic stability than the amorphous one (based on a *meta*-terephthalic framework), mainly due to the fact that the penetration of water molecules into the crystalline domains of the former is difficult, preventing further nucleophilic attack reaction.

Third, the external degradation environment can also influence the degradation rate of poly(silyl ester)s. The degradation rate of their synthesized poly(silyl ester)s as solids and in THF solution was also investigated, both under the same conditions of 20 °C and 40% humidity (Fig. 27c).[75] Notably, the degradation rate was found to be higher in the solid state than in solution. This difference can be attributed to an auto-acceleration effect within the solid state due to the increased hydrophilicity and polarity resulting from the accumulation of hydrolysis products. In conclusion, these results highlight the complex interplay of factors that influence the degradation of poly(silyl ester)s and contribute to a better understanding and facilitate the design of tailored degradable poly(silyl ester)s.

4   Siloxane-based polymers

Despite the numerous advantages of poly(silyl ether)s and poly(silyl ester)s, their processing can be challenging due to high hydrolytic sensitivity. In contrast, siloxane-based polymers exhibit improved stability. This is because siloxane linkages can undergo alcoholysis, hydrolysis, and siloxane exchange, with the hydrolysis rate of siloxane bonds being slower than that of silyl ether/ester bonds. Sander, McNeill, and Hartwig developed a series of siloxane-based polymers, and studied their degradation.[79] First, they synthesized two types of AA-
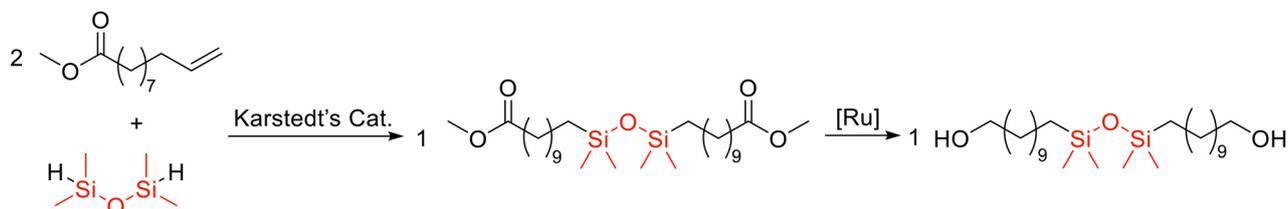
type siloxane-containing diesters and diols from bio-based methyl 10-undecenoate using Karstedt's and Ru-MACHO catalysts (Fig. 29a). Then, they performed step-growth polymerization of these two AA-type monomers with various BB-type monomers to obtain the corresponding siloxane-based polyurethane (PU), polyester, polyamide, and polycarbonate (Fig. 29b). For example, the siloxane-functional diol was polymerized with methylenediphenyl diisocyanate to form polyurethane using 1 mol% $[Sn(Oct)_2]$ as a catalyst. The resulting PU, with an M_n of 35 000 g mol^{-1} and a dispersity of 1.98,

exhibited excellent mechanical properties, including a tensile strength of 7.6 MPa and an elongation at break of 522%.

In addition to using linear monomers to synthesize siloxane-based polymers, cyclic monomers were also used to prepare siloxane-based ABA triblock copolyesters.[79] Siloxane-containing macrolactone was synthesized from bio-based methyl 10-undecenoate through a three-step process, including hydrosilylation, transesterification, and cyclization (Fig. 30a). Then, the ring-opening polymerization (ROP) of the siloxane-containing macrolactone was carried out in the presence of a

Sander, McNeill and Hartwig, 2024

(a) Monomer Synthesis
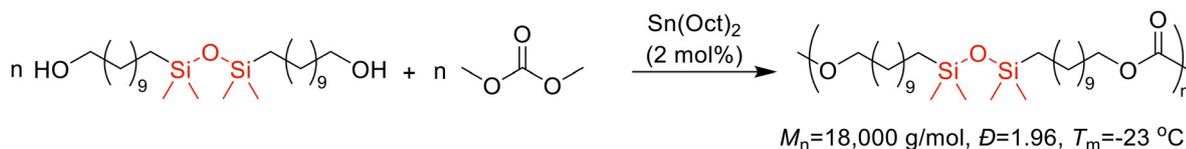

(b) Polymerization

M_n=35,000 g/mol, Đ=1.98, T_m=99 °C

M_n=58,000 g/mol, Đ=2.48, T_m=-10 °C

X=O, m=8,10
X=NH, m=3,10

M_n=18,000 g/mol, Đ=1.96, T_m=-23 °C
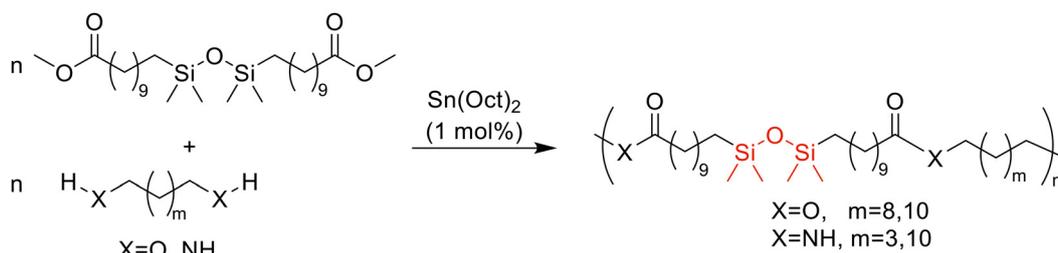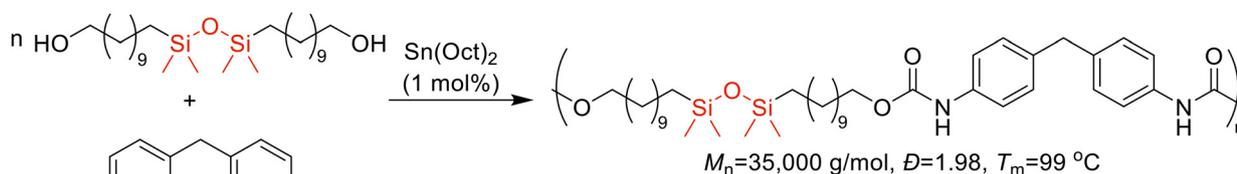
Fig. 29 Synthesis route of siloxane-based polymers.[79]

Sander, McNeill and Hartwig, 2024

(a) Monomer synthesis

(b) Polymerization

M_n=24,500 g/mol, Đ=1.68

M_n=31,400 g/mol, Đ=1.54
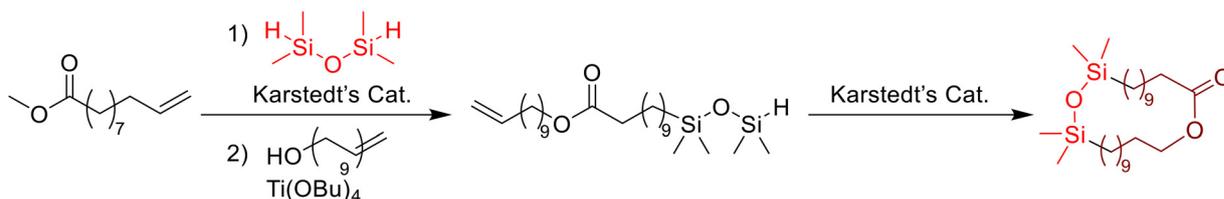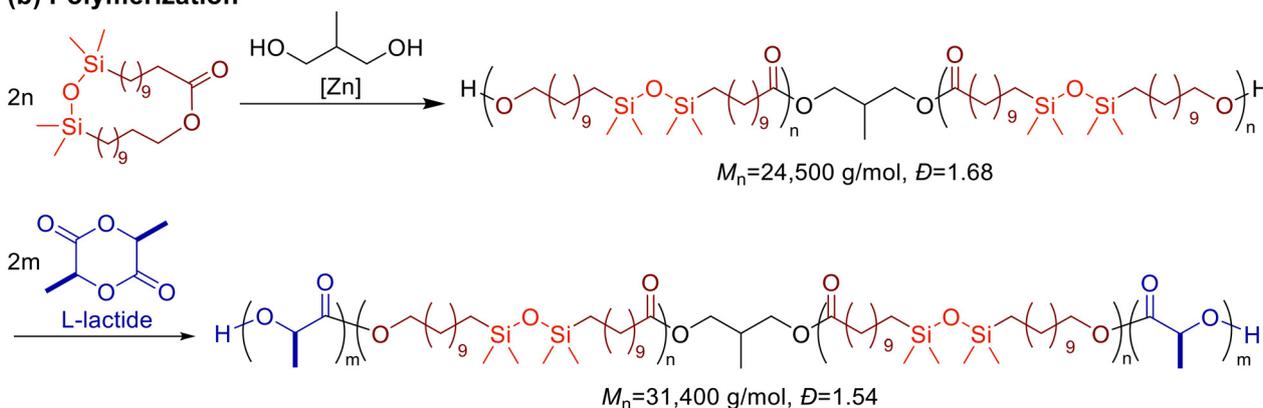
Fig. 30 Synthesis route of siloxane-based triblock copolyesters.[79]

Sander, McNeill and Hartwig, 2024
(a) Depolymerization

(b) Repolymerization

Original: M_n=10,500 g/mol, Đ=1.6
Repolymerized: M_n=10,500 g/mol, Đ=1.7

Fig. 31 Depolymerization and repolymerization route of siloxane-based polymers.[79]

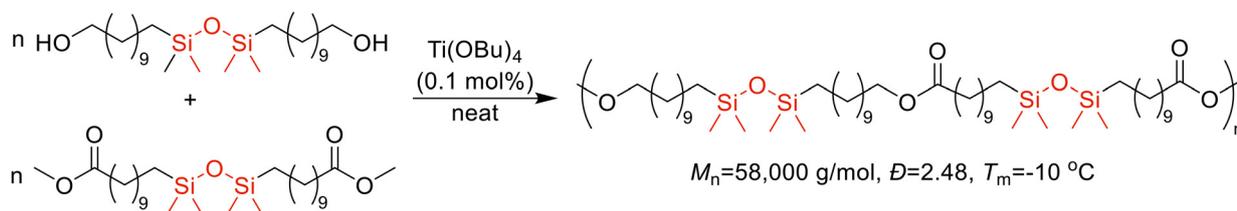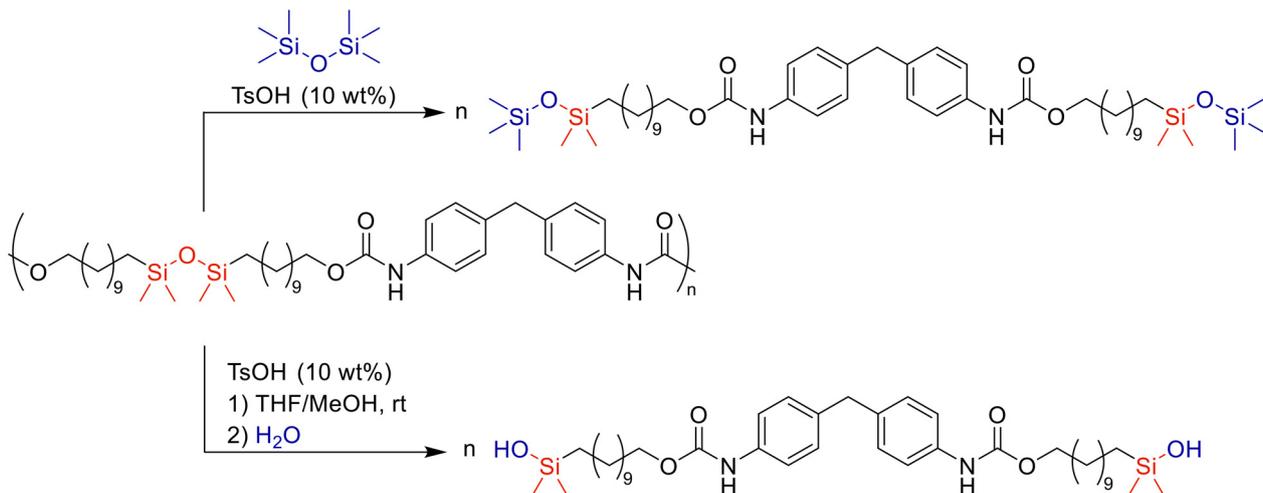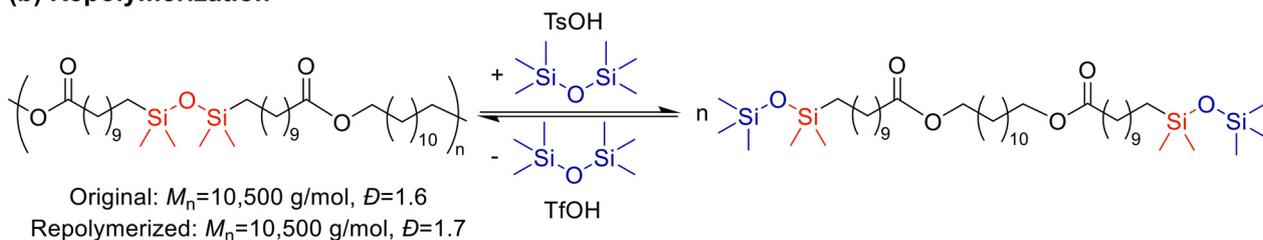Zn-based catalyst using 2-methyl-1,3-propanediol as an initiator (Fig. 30b). The resulting polyester chain with double-terminated hydroxyl groups was used as a macroinitiator for the ROP of L-lactide. The corresponding siloxane-based ABA triblock copolyesters, with an M_n of 31 400 g mol^{-1}, exhibited a T_m of −13 °C from the siloxane-based polyester segment, but no T_m was observed from the PLLA segments up to 200 °C.

Depolymerization of these siloxane-based polymers was performed *via* siloxane exchange and hydrolysis.[79] For example, a polyurethane was subjected to siloxane exchange with hexamethyldisiloxane (HMDSO) and TsOH as a catalyst in THF to produce the disiloxane-terminated monomer. The hydrolysis of PU was carried out in a mixture of THF and MeOH with the same catalyst, followed by the addition of water to give the silanol monomer (Fig. 31a). Repolymerization of the monomers was then performed to evaluate circularity, for example with a siloxane-based polyester. Using TfOH as a strong Brønsted acid catalyst, the disiloxane-terminated depolymerization product was repolymerized to polyester (10 500 g mol^{-1}) with the removal of HMDSO (Fig. 31b).

5   Outlooks and perspectives

In this review, we first highlighted two classes of silicon-based polymers, poly(silyl ether)s and poly(silyl ester)s, focusing on their synthetic strategies and degradation behavior. Despite significant advances in the synthesis of these polymers over the past two decades, their path to large-scale industrial production remains challenging. For example, most of the (co) polymers described in this review article are produced from hydrosilanes because Si–H bonds are relatively weak (SiH ≈ 330–380 kJ mol^{-1}) and can be easily converted into strong Si–O bonds (SiO ≈ 530 kJ mol^{-1}) by many different mechanisms.[80] Hydrosilanes are widely available as they are produced on an industrial scale using a direct (Rochow or Müller) process. In addition to the main product of this process (*i.e.* Me$_2$SiCl$_2$), small quantities of HSiCl$_3$, HMeSiCl$_2$, and HMe$_2$SiCl are produced. Although these compounds can be hydrolyzed and be incorporated into silicone polymers, they still pose environmental concerns due to their reactivity and the need for re-chlorination upon recycling. In addition, handling of pyrophoric and potentially toxic and/or gaseous hydrosilanes (*e.g.*, Me$_3$SiH or SiH$_4$) raises safety issues.[81] Future work should focus on developing chloride-free alternatives. One option to overcome these drawbacks is to use surrogates of hydrosilanes, as demonstrated by Oestreich and Cantat with silyl formates or silylated cyclohexa-1,4-dienes.[82,83]

Although laboratory studies have demonstrated encouraging results, the transition to industrial-scale production presents significant hurdles. The cost of catalysts and monomer availability must be considered, especially when transitioning to industrial-scale production. In comparison to conventional polymers such as polysiloxanes and polyethylene, poly(silyl ether)s and poly(silyl ester)s require more complex and costly production routes, involving expensive raw materials and intri-

cate processing techniques. However, these advanced materials offer distinct advantages, including enhanced recyclability and responsiveness to environmental stimuli. To unlock their full potential for widespread application, substantial efforts must be directed toward optimizing production efficiency and reducing overall costs. Several strategies have been proposed to address these issues. First, new and more affordable bio-based monomers can be used to replace traditional petroleum-based monomers, providing a more environmentally friendly and sustainable material life cycle. Second, earth-abundant metal and non-metal catalysts, such as Fe, Mn, Cu-based complexes and B(C$_6$F$_5$)$_3$, with lower loading or even catalyst-free systems, can be used instead of noble metal catalysts. Third, the development of more efficient production methods and technologies, such as one-pot catalysis with continuous production, can be pursued.[84] This approach allows the entire production process to take place in a single reactor, thereby increasing production efficiency, saving energy, and reducing material costs. Future advances will also lie in the development of novel copolymerization techniques to integrate poly(silyl ether)s and poly(silyl ester)s with other functional polymers, enabling improved properties and broader applications in high performance and biomedical fields. Expanding polymerization methods and routes to incorporate labile silyl linkages into a broader range of polymers could pave the way for the development of novel materials. Beyond degradability, the introduction of silyl ether linkages could affect the mechanical and thermal properties of the polymers compared to native difficult-to-degrade polymers. Therefore, it is crucial to design polymers that not only have better degradability, but also maintain or improve essential performance characteristics.

In summary, the development of these degradable silicon-based polymers holds great promise. Future innovations must prioritize sustainability by promoting the development of bio-based materials, thereby contributing to the creation of new polymer architectures that combine high performance and broad applicability. Achieving this will necessitate a deeper understanding of the structure-performance relationship, allowing for more refined structural modifications and functional enhancements. The versatility of these polymers, coupled with an increasing commitment to sustainability, positions them as key contributors in the quest for greener materials and a more sustainable future.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

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