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Introduction

The precise control of monomer sequence in a macromolecule is an immediate and mostly unmet challenge in polymer synthesis.¹ Perfectly alternating copolymers are the most basic sequence-controlled polymers where comonomer pairs (M1 and M2) are incorporated with a strictly alternating sequence into poly(M1-*alt*-M2).² Precisely controlled alternating polymer sequences can affect the physical and mechanical properties of polymers and open the door to applications that are not achievable with corresponding homopolymers or gradient or block copolymers.³

Despite well-studied comonomer pairs such as styrene and maleic anhydride,⁴ aziridine and CO,⁵ epoxides and CO₂,⁶ epoxides and CO,⁷ epoxides and anhydride,⁸ alkenes and CO,⁹ and ethylene with other alkenes,¹⁰ perfectly alternating copolymerization is still a major challenge and has a limited scope of comonomer pairs. Alternating copolymerization of epoxides and lactones is rare. Endo and coworkers reported the anionic alternating copolymerization of bicyclic bis(γ -lactone) or 3,4-dihydrocoumarin with glycidyl ethers.¹¹ These “non-homopolymerizable” lactones can be alternately co-polymerized with epoxides to form oligomers ($M_n < 4$ kDa). Coates and coworkers reported the alternating copolymerization of dihydrocoumarin with epoxides to provide alternating polyesters with improved molecular weights and dispersities in presence of cocatalyst, PPNCl (M_n 7–19 kDa).¹²

The strategy to control the alternating sequence without using comonomer pairs is the polymerization of pre-sequenced

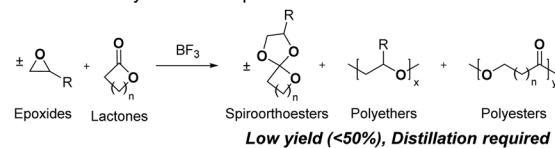
Temperature triggered alternating copolymerization of epoxides and lactones via pre-sequenced spiroorthoester intermediates†

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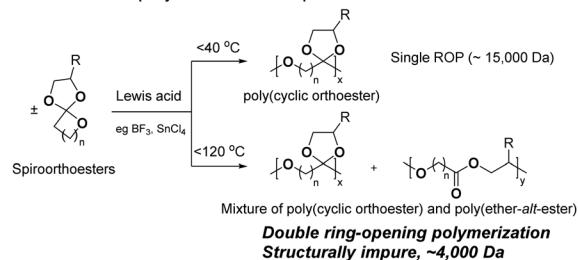
We report the alternating copolymerization of caprolactone and epoxide through the *in situ* formation of pre-sequenced spiroorthoester monomer. The reaction is catalyzed by the temperature triggered, bifunctional cationic indium complex (\pm -[(NNiO_tBu)_n](CH₂SiMe₃)][B(C₆F₅)₄] (1). 1 can catalyze the coupling of epoxide and lactone to form spiroorthoester at 60 °C and its double ring-opening polymerization at 110 °C to form poly(ether-*alt*-ester). The post-polymerization modification and degradation of the poly(ether-*alt*-ester) are further investigated.

monomers, however, the synthesis of such monomers can require multiple steps, and may suffer from low yields and limited functional group tolerance in the resulting polymers.¹³

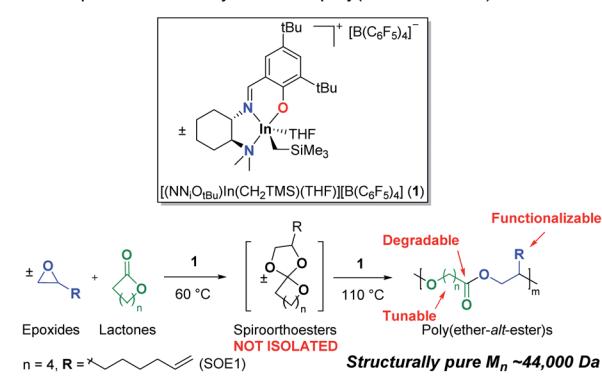
A. Conventional synthesis of spiroorthoesters



B. Conventional polymerization of spiroorthoesters



C. One-pot switchable synthesis of poly(ether-*alt*-ester) - *This Work*



Scheme 1 Synthesis and polymerization of spiroorthoesters.

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† Electronic supplementary information (ESI) available: It includes the experimental section as well as the characterization of polymers. See DOI: 10.1039/d1sc06634j



Namely, a wide range of spiroorthoesters (SOEs), a class of pre-sequenced monomer, can be synthesized through the coupling of epoxides and lactones (Scheme 1A).¹⁴ However, Lewis-acid-catalyzed formation and polymerization¹⁵ of spiroorthoesters to date have suffered from poor selectivity, resulting in the need for distillation, low monomer yields (<50%), low molecular weights, and high dispersities for the resulting polymers.¹⁶

The cationic ring-opening polymerization of spiroorthoesters consists of a single ring-opening polymerization of the lactone cyclic unit to form poly(cyclic orthoester), followed by the opening of the second ring to form poly(ether-*alt*-ester) (Scheme 1B).¹⁷ The mechanism of spiroorthoester polymerization and the temperature-dependent polymer structure have been reported previously (Scheme S2†).¹⁸ To date, polymers from double ring-opening polymerization of spiroorthoesters are either low molecular weight oligomers¹⁹ or a mixture of low molecular weight single and double ring-opened polymers (Scheme 1B).^{15b,18b,c,20} To the best of our knowledge, this is the first example of structurally pure, high molecular weight poly(ether-*alt*-ester)s.

We have reported a series of neutral²¹ and cationic²² indium(III) complexes for the highly controlled ring-opening homo- or copolymerization of cyclic esters and ethers.²³ In particular, we showed that cationic indium complex (\pm)-[$(\text{NN}_i\text{O}_{\text{tBu}})\text{In}(\text{CH}_2\text{SiMe}_3)_2$] $[\text{B}(\text{C}_6\text{F}_5)_4$] (1) catalyzes the coupling of an equimolar mixture of ϵ -caprolactone (ϵ -CL) and 1,2-epoxy-7-octene (EOE) to form 2-(hex-5-en-1-yl)-1,4,6-trioxaspiro[4.6]undecane (SOE1) in near quantitative isolated yield.²⁴ We showed that 5, 6, and 7-membered lactones as well as epoxides with a range of functionality are converted to the respective spiroorthoesters quantitatively.²⁴

Herein, we report a one pot formation of poly(ether-*alt*-ester) from ϵ -CL and EOE through the formation of pre-sequenced monomer SOE1 catalyzed by analogous cationic complex (\pm)-[$(\text{NN}_i\text{O}_{\text{tBu}})\text{In}(\text{CH}_2\text{SiMe}_3)_2$] $[\text{B}(\text{C}_6\text{F}_5)_4$] (1). This temperature triggered copolymerization involves coupling of the epoxide and lactone at 60 °C and polymerizing the spiroorthoester intermediate at 110 °C, resulting in high molecular weight poly(ether-*alt*-ester) (Scheme 1C). In contrast to the state of the art,²⁵ this is a simple and efficient strategy to synthesize functionalized aliphatic polyesters. We utilize the functionality in these polymers to prepare cross-linked materials. In addition, the ester linkages in these materials undergo hydrolytic degradation, offering a biodegradable alternative to conventional polymers.²⁶

Results and discussion

Complexes (\pm)-[$(\text{NN}_i\text{O}_{\text{tBu}})\text{In}(\text{CH}_2\text{SiMe}_3)_2$] $[\text{B}(\text{C}_6\text{F}_5)_4$] (1) and (\pm)-[$(\text{NN}_i\text{O}_{\text{tBu}})\text{In}(\text{CH}_2\text{SiMe}_3)_2$] $[\text{B}(\text{C}_6\text{F}_5)_4$] (2) were synthesized according to a previous report.^{23d} In a one pot reaction, the pre-sequenced monomer, SOE1, is synthesized *via* coupling of EOE and ϵ -CL with 1 in toluene at 60 °C for 24 h (Table 1, entry 1). Subsequently, the solvent is removed, resulting in a neat reaction mixture containing SOE1 and 1. This mixture is heated at 110 °C to form 100% double ring-opened product, the poly(ether-*alt*-ester) B, with molecular weights up to 18 000 Da (Fig. S8†).

The exclusive formation of SOE1 is confirmed by the observation of the characteristic signals of the five-membered cyclic acetal (protons 7–8') in the ^1H NMR spectrum of the reaction mixture (Fig. 1a). After the double ring-opening polymerization, the ^1H NMR spectrum of poly(ether-*alt*-ester) shows that protons 1 and 1' in a seven-membered cyclic ether (3.56–3.60

Table 1 Homopolymerization and one-pot reaction of spiroorthoesters using 1^a

Complex	[SOE] : [initiator]	Temp. (°C)	Time (h)	Conv. ^b (%)	$M_{n,\text{GPC}}^c$ (g mol ⁻¹)	D^c	Yield (%)	A : B ^b
1 ^d	1	67	110	24	17 980	1.99	55	0 100
2 ^e	2	200	110	24	—	—	—	—
3 ^f	1	200	80	24	34	—	—	53 47
4	1	200	80	48	89	1.28	24	6 94
5	1	200	110	24	100	1.39	81	0 100
6	1	400	110	24	100	1.40	70	0 100
7 ^g	SnCl ₄	50	0	1	—	14 400	4.69	84
8 ^g	SnCl ₄	50	80	1	—	2840	4.53	82
9 ^g	SnCl ₄	50	120	1	—	1900	2.95	79
10 ^h	—	200	110	24	0	—	—	—

^a All reactions were performed twice under a nitrogen atmosphere in neat. Initiator = 0.008 mmol. ^b Determined by analysis of the crude material by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (151 MHz, C_6D_6 , 25 °C). ^c Determined by GPC measurements with polystyrene as the standard in THF and corrected by Mark–Houwink's corrections. ^d One-pot reaction. Spiroorthoester synthesis: [1] = 3.75 mM, [EOE] = 0.25 M, [ϵ -CL] = 0.25 M; spiroorthoester polymerization: performed in neat. ^e Initiated by the neutral indium complex (2). ^f Oligomeric product formed. ^g Data from ref. 18b. ^h Polymerization reaction without 1.



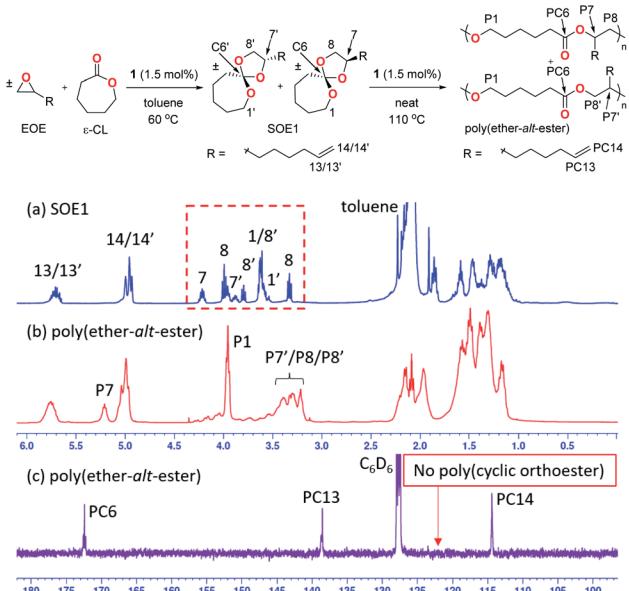


Fig. 1 One-pot synthesis of poly(ether-alt-ester) (Table 1, entry 1). ^1H NMR spectra of (a) crude intermediate product of SOE1, (b) poly(ether-alt-ester), and (c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of poly(ether-alt-ester) (400 MHz, C_6D_6 , 25 °C).

ppm) are shifted to P1 (3.95 ppm) and 7–8' (3.30–4.23 ppm) are shifted to P7–P8' (3.21–3.39 and 5.20 ppm) (Fig. 1b). The ratio of regioisomers is almost 50 : 50 (peak area: P7 : P7'–P8' \approx 1 : 5), meaning that intermediate poly(cyclic orthoester) undergoes the second ring-opening on either side of the cyclic acetal (Fig. S8 and S9 \dagger). A completely double ring-opened polymer structure is confirmed by the absence of the center carbon of SOE1 (C6 and C6'), the center carbon of poly(cyclic orthoester), and appearance of the ester carbonyl carbon of poly(ether-alt-ester) (PC6) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the product (Fig. 1c). 18b

FTIR spectroscopy confirms the formation of poly(ether-alt-ester) from double ring-opening polymerization. The most distinct difference between spiroorthoester/poly(cyclic orthoester) and poly(ether-alt-ester) is a strong C=O stretching absorption at 1732 cm $^{-1}$ that can be formed only by the double ring-opening polymerization. The $\nu_{\text{C}-\text{O}}$ frequencies of newly formed ether and ester linkages appear at 1094 and 1162 cm $^{-1}$, respectively (Fig. S10 \dagger).

Since we have investigated the formation of various spiroorthoesters in a previous publication, 24 we wanted to investigate the polymerization of isolated SOE1 with 1 to evaluate the impact of different reaction conditions on polymer characteristics. Importantly, as with SOE1 synthesis, neutral indium complex (2) was unreactive for the polymerization of SOE1 (Table 1, entry 2), and SOE1 was not polymerized in the absence of 1 (Table 1, entry 10).

Temperature impacts both the conversion and the selectivity of SOE1 polymerization. At 80 °C, polymerization of neat SOE1 reaches 34% conversion in 24 h. Importantly, the polymer products are a mixture of poly(cyclic orthoester) (A, 53%) and poly(ether-alt-ester) (B, 47%) (Table 1, entry 3). Increasing the

reaction time to 48 h yields higher conversion of SOE1 (89%), with the resulting polymer mixture containing a significantly higher proportion of double ring-opened product (A : B = 6 : 94) (Table 1, entry 4). In contrast, polymerization of SOE1 at 110 °C yields solely double ring-opened poly(ether-alt-ester) in 24 h (Table 1, entry 5). Increasing the SOE1 to catalyst ratio forms polymers with $M_n = 44\,000\text{ g mol}^{-1}$ (Table 1, entry 6). The molecular weight, dispersity, and degree of isomerization in this system are significantly superior to those reported by Endo and coworkers ($M_n = 2840\text{ g mol}^{-1}$; $D = 4.53$; B = 38%) (Table 1, entry 8). 18b

As these polymers are functionalizable, we investigated post-polymerization cross-linking *via* a thiolene reaction to transform the poly(ether-alt-ester) into a thermoset. The reaction of stoichiometric amounts of cross-linker 2,2'-(ethylenedioxy) diethanethiol (2SH) and the poly(ether-alt-ester) with M_n of 24 kDa (Table 1, entry 5) is initiated by 2,2'-azobis(2-methylpropionitrile) (AIBN). The transparent, flexible, and insoluble thiolene-cured polymer is generated in the shape of the mold in 5 minutes. FTIR spectroscopy shows that the cross-linked polymers lack the $\nu_{\text{S}-\text{H}}$ (2550–2600 cm $^{-1}$) and $\nu_{\text{C}=\text{C}}$ (910 and 1641 cm $^{-1}$) frequencies (Fig. 2). Crosslinking improves polymer thermal stability significantly: the cross-linked polymer has a decomposition temperature of 240 °C while the non-cross-linked polymer decomposes at 177 °C. A change in glass transition temperature (T_g) is also observed after crosslinking: the cross-linked polymer has a higher T_g at –52 °C compared to T_g of non-cross-linked polymer at –69 °C. In addition, crystallization of the cross-linked polymer is observed (120 °C), whereas non-cross-linked polymer remains amorphous (Fig. S18–S23 and Table S1 \dagger).

Finally, we investigated the base-catalyzed degradation behavior of the polymers. Subjecting 44 kDa poly(ether-alt-ester) (Table 1, entry 6) to a 0.1 M solution of tetrabutylammonium hydroxide for 2 h results in a significant decrease in molecular weight (Fig. 3a). FTIR spectra show that the

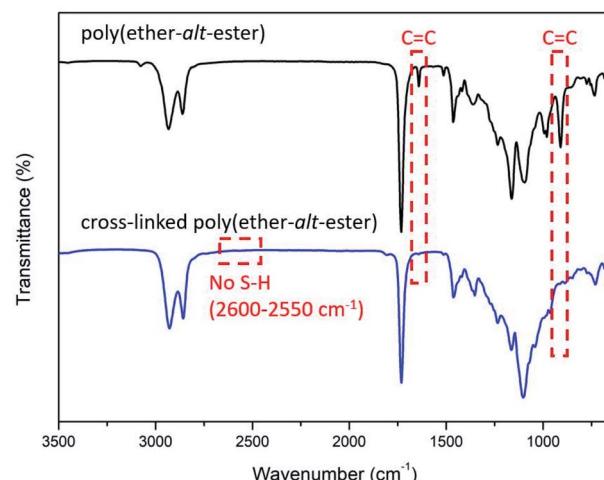


Fig. 2 Cross-linking of poly(ether-alt-ester) *via* thiolene reaction (top). FTIR spectra of poly(ether-alt-ester) and cross-linked poly(ether-alt-ester) (bottom).

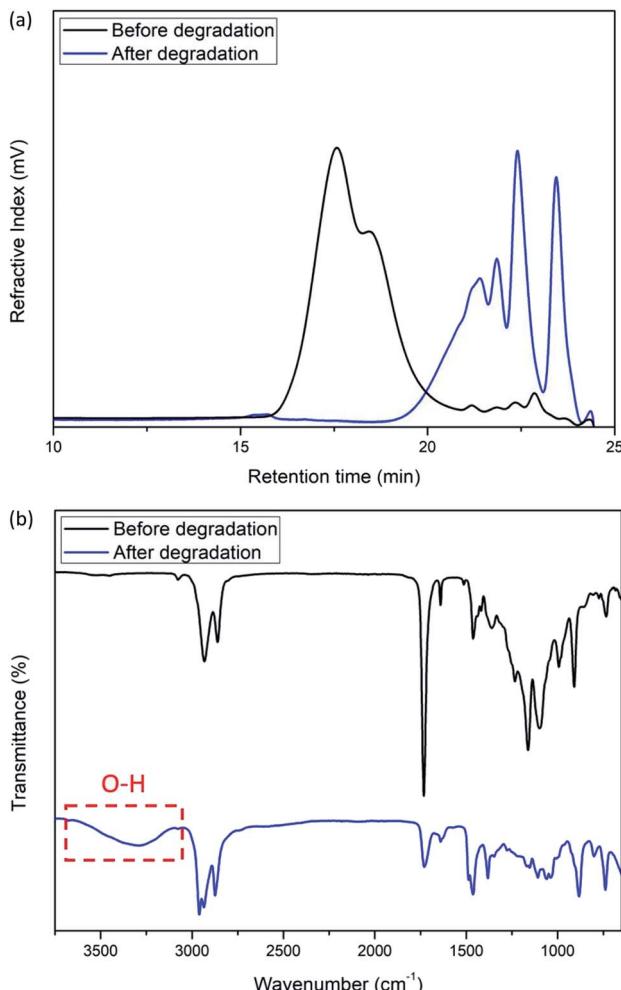


Fig. 3 Degradation of poly(ether-alt-ester). GPC trace (a, top) and FTIR spectra (b, bottom) of poly(ether-alt-ester) and degradation products (condition: 0.1 M tetrabutylammonium hydroxide in MeOH/DCM, room temperature, 2 h).

degradation products have a new $\nu_{\text{O-H}}$ frequency at 3700–3100 cm^{-1} which is consistent with the hydrolysis of the polymer (Fig. 3b). Importantly, there is a significant reduction in the $\nu_{\text{C=O}}$ peak, indicating degradation at the ester linkage. The degradation of cross-linked poly(ether-alt-ester) was also attempted under the same degradation condition. A significant reduction in molecular weight and $\nu_{\text{C=O}}$ peak were observed after 16 h (Fig. S27 and 28†).

1 is clearly different than other simple Lewis acids reported for this reaction. Spiroorthoester polymerization with other Lewis acids can achieve higher molecular weights at low temperatures to form single ring-opened polymers; however, when the temperature is increased to generate the double ring-opened poly(ether-alt-ester)s, molecular weights are significantly curtailed (Table 1, entry 7).^{18b} One reason for this difference may be the Lewis acidity of the respective catalysts.

The Lewis acidity of **1** was compared with other catalysts using a modified Gutmann–Beckett method with triethylphosphine oxide (TEPO) as a basic probe (Fig. 4).²⁷ **1** formed two

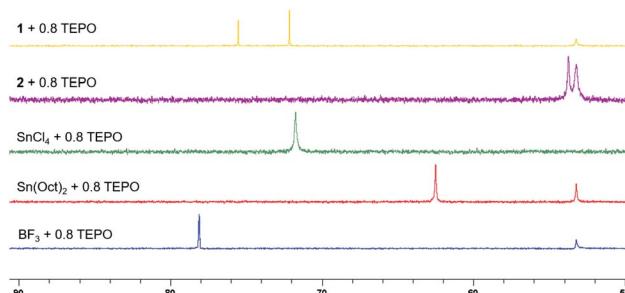


Fig. 4 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of TEPO showing the downfield shift with the increase in the Lewis acidity of the complexes (162 MHz, CDCl_3 , 25 °C).

species with TEPO due to the different solvations around indium metal centers.²⁸ Interestingly, **1** is less Lewis acidic than BF_3 and has similar Lewis acidity to SnCl_4 . Since spiroorthoester polymerization is not initiated by **2**, supporting the cationic polymerization mechanism (Scheme S2†), we must also consider the effect of the counter anion, which plays an important role in chain growth during the cationic polymerization.²⁹ With **1**, the growing chain ends can be stabilized by the bulky, stable, and non-coordinating anion $\text{B}(\text{C}_6\text{F}_5)_4$ so that chain transfer and termination reactions can be suppressed.³⁰ Thus, **1** provides a combination of moderate Lewis acidity and a stabilizing counter anion that enable selectivity in spiroorthoester formation and control in spiroorthoester polymerization.

Conclusions

In summary, we report the first example of a sequence controlled alternating copolymerization of epoxides and lactones *via* a one pot generation of a pre-sequenced spiroorthoester monomer. This reaction is temperature triggered: Spiroorthoester formation is the sole reaction at 60 °C, while spiroorthoester polymerization is the sole reaction at 110 °C. The resulting poly(ether-alt-ester)s are crosslinkable and degradable. We will be expanding the substrate range in this reaction and investigating the properties and applications of the resulting polymers. We will also be exploring new systems to control the stereo- and regioselectivity in these reactions.

Data availability

Additional data supporting this article were provided in ESI.†

Author contributions

P. M. supervised the project. H.-J. J. carried out most of the experiments and wrote the initial manuscript draft. C. G. assisted with the synthesis of complexes and conducted Lewis acidity study. P. M. and H.-J. J. revised the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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