Synthesis and Self-assembly of Limonene Oxide - Lactide Block Copolymers

Ruxi Dai,[a#] Shah Valloppilly,[b] Nethmi De Alwis Watuthanthrige,[c] Progyateg Chakma,[c] Shijie Deng,[a] Dominik Konkolewicz,[c] and Paula L. Diaconescu*[a]

The reaction of limonene oxide with a zirconium complex led to polymers with a molar mass up to 4.0 kDa, the largest limonene oxide homopolymer reported so far. Diblock, triblock, and tetrablock copolymers of limonene oxide and L-lactide were also prepared using a redox switchable catalyst based on the same zirconium complex; the obtained copolymers are the first-ever reported limonene oxide-lactide block copolymers. The solid-state self-assembly properties of the copolymers were characterized by small angle X-ray scattering and rheology measurements, giving a self-assembly domain radius of 11, 25, and 35 nm for the diblock, triblock, and tetrablock copolymers, respectively.

Introduction

Limonene oxide (LO, Figure 1a)[1-2] is a biorenewable material that can be used to synthesize green polymers, which can then be naturally depolymerized and minimize the current "white pollution".[3-4] LO can be easily prepared from limonene, an abundant terpene extracted from citrus that has already gained wide application as a solvent and insecticide.[5] LO is largely used as a monomer to be copolymerized with CO_2 to form poly(limonene carbonate) (PLC, Figure 1b),[6-13] or anhydrides to form polyesters.[14-18] However, few reports exist on the homopolymerization of LO. In 1985, poly(limonene oxide) (PLO) was prepared for the first time by a radiation-induced cationic polymerization,[19] with a molar mass averaging 2.0 kDa. Another study on the photoinitiated cationic polymerization of LO also reported homopolymers with molar masses lower than 1.7 kDa and high dispersity.[20] Recently, metal-catalyzed ring opening polymerization was used for PLO synthesis, giving a molar mass of 1.3 kDa but good control over dispersity.[21]

The limited number of reports available and the low molar mass of the PLO suggest that the homopolymerization of LO is difficult, also indicating that the preparation of LO based block copolymers other than alternating copolymers might not be straightforward. In order to determine if LO based block copolymers have value and potential applications,[22] preparation methods are needed.

We decided to use redox switchable copolymerization for the synthesis of LO block copolymers with L-lactide (LA, Figure 1c), another biorenewable monomer. Redox switchable catalysis is a novel method for synthesizing block copolymers; a metal catalyst can have orthogonal activity toward different monomers depending on its oxidation state.[23-28] Upon adding an external oxidant or reductant, different monomers can be selectively polymerized and added to the polymer chain, therefore, a block copolymer can be prepared.

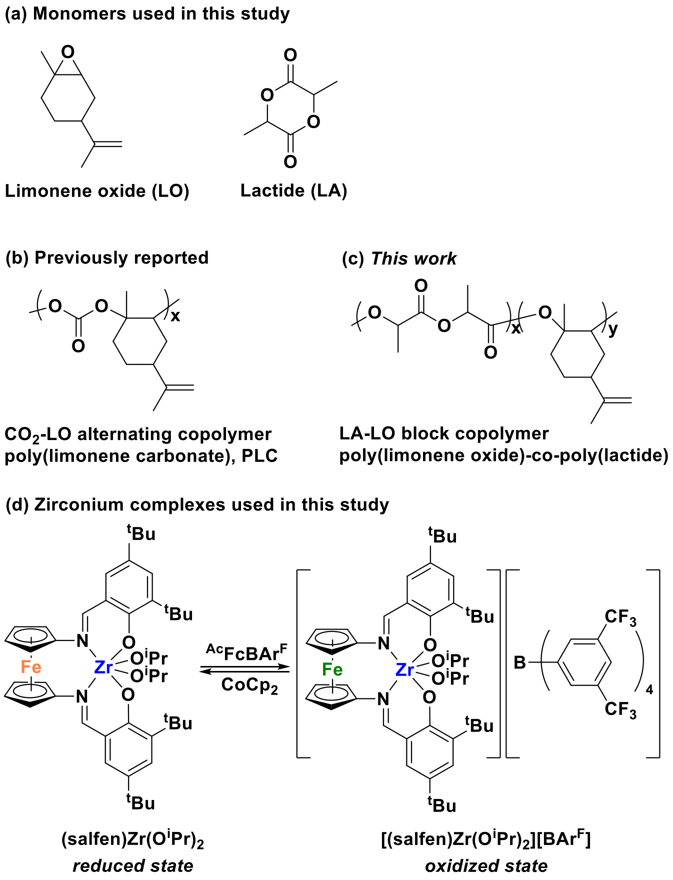


Figure 1 (a) Monomers used in this study: LO is (+)-limonene oxide, mixture of *cis* and *trans*, LA is L-lactide; (b) previously reported poly(limonene carbonate); (c) an example of a LO copolymer reported in this work; (d) redox switching of (salfen)Zr(O^iPr)$_2$.

Our group has studied ferrocene-based metal complexes that can perform redox switchable ring opening polymerization.[29-43] The ferrocene unit in the ligand backbone is the redox center, while the other metal is the catalytic center (Figure 1d). For example, (salfen)Zr(O^iPr)$_2$ (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine) can polymerize lactones in the reduced state and epoxides in its oxidized state, and such redox switches can be repeated multiple times.[32] The compound was previously used to prepare LA and cyclohexene oxide copolymers, so we reasoned it could be a good candidate for LO polymerization. Herein, we report the use of (salfen)Zr(O^iPr)$_2$ to prepare large LO homopolymers, and the

---

[a] *Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095, USA*
[b] *Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, Nebraska 68588, USA*
[c] *Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, USA*
[#] *Current address: Sinochem Quanzhou Energy Technology Co., LTD, 398 Donghai Street, Quanzhou, Fujian Province, 362141, P. R. China*
**Corresponding author's email: pld@chem.ucla.edu*

† Electronic supporting information available online.

first LO block copolymers with LA. The self-assembly properties of the copolymers were probed by rheology measurements and small angle X-ray scattering (SAXS).

Table 1 LO homopolymerization studies.[a]

Entry	Monomer equiv.	Time (h)	Temp. (°C)	Solvent volume (mL)	Mn SEC (kDa) [b]	Mn calcd. (kDa) [c]	Đ
1	100	1	25	0.6	3.0	7.5	1.13
2	100	2	25	0.6	3.0	7.5	1.14
3	100	4	25	0.6	3.4	7.5	1.08
4	100	6	25	0.6	2.9	7.5	1.13
5	75	2	25	0.6	3.6	5.6	1.05
6	200	2	25	0.6	3.4	15.1	1.11
7	100	2	0	0.6	4.0	7.5	1.15
8	100	6	0	0.6	3.9	7.5	1.11
9	100	2	40	0.6	3.4	7.5	1.06
10	100	2	50	0.6	2.3	7.5	1.08
11	100	2	25	0.3	3.0	7.5	1.12
12	100	2	25	1.2	3.8	7.5	1.05

[a] All polymerization reactions were carried out with 4 µmol precatalyst, C_6D_6 was used as a solvent and hexamethylbenzene as an internal standard. All reactions achieved 100% conversion. [b] Molar masses were derived from SEC measurements. [c] The theoretical molar mass was calculated based on two initiating groups in the precatalyst.

Results and Discussions

LO Homopolymerization

[(salfen)Zr(O^iPr)$_2$][BAr^F] (BAr^F = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate), the precatalyst in the oxidized state, was used for the LO homopolymerization. The reactions reached 100% conversion within 1 h (Figure S1), but the molar mass obtained from the size exclusion chromatography (SEC) was less than the theoretical value. Therefore, we tried to optimize the reaction conditions by modifying the reaction time, temperature, monomer to precatalyst ratio, and concentration (Table 1). The molar mass of the homopolymers did not vary too much among the 12 entries in Table 1, falling in the range of 2.9 to 4.0 kDa. The reaction time did not have a significant impact on the molar mass of the homopolymers (Table 1, entry 1-4), nor did the amount of monomer (Table 1, entry 5-6). The solvent volume, or the general concentration, did not show a great impact on the molar mass (Table 1, entry 11-12) either. The only factor that impacted the molar mass, though slightly, was the temperature. A temperature as low as 0 °C gave a higher molar mass (Table 1, entry 7-8), while an elevated temperature of 50 °C gave a lower molar mass (Table 1, entry 10) than the unoptimized reaction, respectively. We postulated that the LO homopolymerization is affected by some back-biting side reaction (Scheme S1), and the polymer chain gets "locked" at certain lengths. Thermodynamics may favor the back-biting over polymer propagation over a certain chain length, which is about 3-4 kDa in our case. The low temperature can slow down the back-biting, leading to a higher degree of polymerization, thus a higher molar mass.

A mixture of *cis*- and *trans*-(+)-limonene oxide was used during the studies. The reaction was monitored by ^1H NMR spectroscopy, and the spectra showed that both isomers reacted (Figure S2). The *cis* isomer reacted faster than the *trans* isomer. At the end of the polymerization, the *cis* isomer was almost fully consumed while 23% of the *trans* isomer was left unreacted.

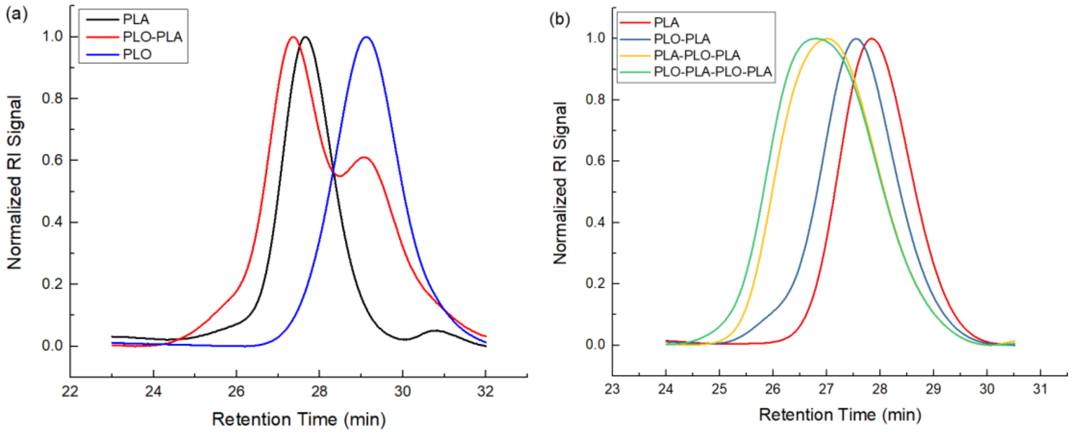


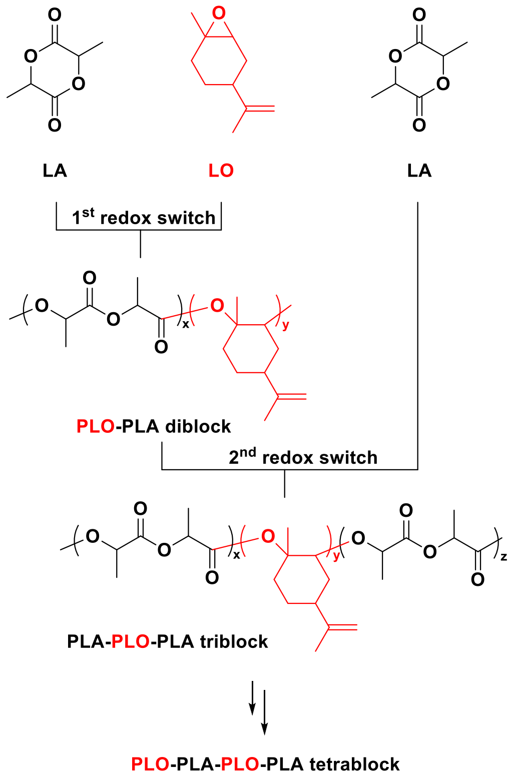
Figure 2 (a) SEC trace of an unsuccessful attempt of LO-LA copolymerization. The PLO-PLA trace was bimodal, with the right peak assigned as a PLO peak, and the left peak attributed to the new copolymer. (b) SEC traces of real-time monitoring of a tetrablock copolymer preparation.

The conversion of each isomer at different time points within 24 hours could be calculated from the integration of the NMR spectra (Table S1). Such reactivity was different than what was reported by Coates and coworkers[7] and Mosquera and coworkers.[21] The former reported in 2004 that during LO-CO$_2$ copolymerization only the *trans* isomer reacted, while the latter reported in 2020 that in their LO homopolymerization system only the *cis* isomer reacted. The PLO obtained from our reaction was regio-irregular, consistent with what Mosquera and coworkers reported. The regiochemistry of the polymer was confirmed by ^{1}H, ^{13}C, HSQC, and HMBC NMR spectroscopy (Figures S3-S6).

Copolymerization of LO and LA

The preparation of a LO-LA copolymer (Figure 1c), a fully bio-renewable and biodegradable block copolymer, was studied using the redox switchable polymerization method. The precatalyst, (salfen)Zr(O^{i}Pr)$_2$, can polymerize L-LA in its reduced state, and LO in the oxidized state, following the addition of an external oxidant, giving a PLO-PLA copolymer. The LO block polymerization time was first set at 5 h, since the (salfen)Zr(O^{i}Pr$_2$) catalytic system was reported to have a slower reaction rate of epoxide copolymerization compared to epoxide homopolymerization.[32] However, simply following the sequence “LA polymerization, catalyst oxidation, LO polymerization” gave a polymer mixture (Table S2, entry 1), with a bimodal SEC trace (Figure 2a). After comparing the SEC trace of the product to those of PLA and PLO homopolymers, we realized that a new PLO-PLA copolymer was made, but the PLO homopolymer was also generated. Such a PLO byproduct would also affect the further copolymerization to triblock and tetrablock copolymers. We reasoned that the LA polymerization was fine as the first block of the copolymerization. During the preparation of the second block, the LO block, the copolymerization was likely going well in the beginning, and then back-biting occurred, leading to the formation of extra PLO homopolymer byproduct. Therefore, the copolymerization conditions needed to be optimized, with the idea of stopping the LO polymerization before the back-biting point was reached.

First, the LO monomer feeding was reduced from 100 to 75 and then to 50 (Table S2, entry 1-3), with the idea that the back-biting would not occur before the monomer was fully consumed. The traces of the three copolymerization products were all bimodal, but the PLO homopolymer peak at around 29.3 min experienced a decrease in height (Figure S20). The trace for the copolymerization reaction with 50 equivalents of LO showed no legible shoulder, though the trace has a tail at the end. Finally, the LO polymerization time was optimized from 5 h to 2 h, then to 1 h (Table S2, entries 3-5). The SEC traces showed that a fine distribution was achieved in the 1 h LO polymerization product (Figure S21), meaning the PLO-PLA diblock copolymer could be made without any PLO homopolymer byproduct. DOSY studies supported the claim that the 1 h LO polymerization product was a copolymer, while the 2 h LO polymerization product was still a mixture of different polymers (Figures S10, S11). With the optimized conditions, a PLA-PLO-PLA triblock and a PLO-PLA-PLO-PLA tetrablock copolymer were prepared (Table 2, Scheme 1, Figures 2b, S12-S17).



Scheme 1 Copolymerization of LA and LO through the redox switchable polymerization method.

Thermal Properties of the Polymers

Differential scanning calorimetry (DSC) analysis was performed on the PLA homopolymer and the LO copolymers (Figure S22). The PLA block melting point was measured to be 158, 153, 160, and 159 °C for the PLA homopolymer, the diblock, triblock, and tetrablock copolymers, respectively (Table S3). A crystallization temperature of 118 °C was measured for the PLA homopolymer, and 99 and 104 °C for the triblock and tetrablock copolymers, respectively. The melting and crystallization temperatures were in accordance with previously reported values.[21, 39] A short and broad peak at 72 °C on the diblock copolymer DSC curve was observed as the glass transition temperature for the PLO block, similar to that reported by Mosquera and coworkers,[21] as the glass transition temperature (T_g) for a polyether block is usually a short and broad peak.[39, 44-45]

Rheology measurements

To investigate the self-assembly properties of the prepared block copolymers, a rheology study was conducted to test the phase separation or microphase domain in the solid state.[46-48] The diblock copolymer displayed a shorter rubbery plateau prior to the melting temperature, T_m (Figure S23a). Further, at 160 °C the material had a low storage and loss modulus that were similar to each other, suggesting a weakly structured material or one close to the boundary of rheological liquid and rheological solid. On the other hand, both triblock and tetrablock copolymers exhibited an extended rubbery plateau over the frequencies of 0.1-100 rad/s (Figure S23b and Figure 3). This extended rubbery plateau was observed even above the melting temperature of the material. The presence of the rubbery plateau suggests that the materials are phase separated into domains and display similar behavior as thermoplastic elastomers.[49-51] Even though these materials displayed a substantial decrease in G' and G" as a result of losing structural rigidity, they continued to display rubbery plateaus even at temperatures significantly greater than their T_m. This indicates that a microphase separated domain structure is retained even above the T_m of the hard block, an evidence of self-assembly in the solid state.

Table 2 Real-time monitoring of the tetrablock copolymer preparation.[a]

Block	Monomer of this block	Mn of the entire polymer so far (kDa) [b]	*Đ*	Mn of this block (kDa) [c]	Polymer formula [d]
1st block	LA	3.3	1.02	3.3	LA_{23}
2nd block	LO	5.5	1.09	2.2	LO_{15}-LA_{23}
3rd block	LA	6.8	1.08	1.3	LA_9-LO_{15}-LA_{23}
4th block	LO	7.9	1.12	1.1	LO_8-LA_9-LO_{15}-LA_{23}

[a] All polymerization reactions were carried out with 4 μmol precatalysts, C_6D_6 was used as the solvent and hexamethylbenzene as an internal standard. LA block polymerization: 100 equiv LA, heating for 20 h in 100 ºC; LO block polymerization: 50 equiv LO, 1 h at room temperature. Data points were taken at the end of the preparation of each block. [b] Molar masses were obtained from SEC measurements. [c] Molar masses were calculated from the total Mn of the current data point minus the total Mn of the last data point. [d] Formula for each block was calculated by the Mn of this block divided by the molar mass of the corresponding monomer.

Overall, the data suggests that the triblock and tetrablock copolymers contain mechanically percolated phase separated structures, which were not observed in the diblock copolymer. This is likely because the triblock and tetrablock structures can form microphase separated domains, where individual polymer chains straddle multiple domains and thereby create an extended, mechanically percolated structure.[52-53] The diblock copolymer, even if microphase separated, does not have an effective mechanical percolation and hence the mechanical properties above the melting temperature approximate a rheological liquid. Since the existence of the copolymer self-assembly is supported by the rheology test, SAXS measurements were performed to investigate further the size of the self-assembly domain (Figure 4).

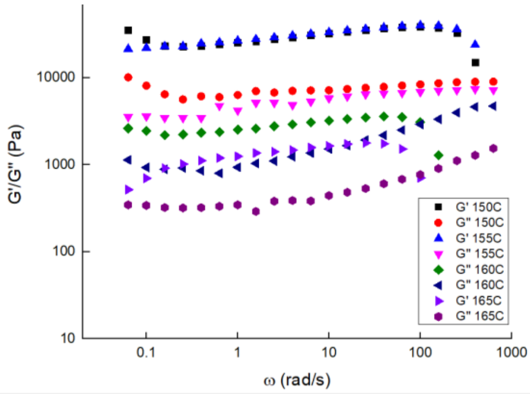


Figure 3 Storage (G') and loss (G") moduli of the PLO-PLA tetrablock copolymer at different temperatures.

Small angle X-ray scattering (SAXS) measurements

The Debye model was used for the analysis of SAXS data. Unlike the familiar nanostructures that have well defined shapes, low molecular weight block copolymers are considered to have no specific shape and the scattering originates from shape independent two-phase regions of the polymer of different electron densities.[54-56] Even if the two phases have irregular shapes, the correlation length between the two domains can be obtained from the analysis.[57-58]

Figure 4 depicts the SAXS data and the best fits obtained using the Debye model (see the ESI for details). The correlation length (ξ), or self-assembly domain radius, obtained from the fits are given in the plot. The diblock, triblock, and tetrablock copolymers have a domain radius of 11, 25, and 35 nm, respectively. The domain radius value increased with the number of blocks, consistent with the fact that a larger polymer should have a larger self-assembly domain.[52, 59] The experimental data also showed an additional small peak around q = 0.008 $Å^{-1}$, corresponding to a length scale of 80 nm. The fractal parameter *h* from the fit for all the samples was around 0.35. Presumably due to their low molecular weight, the copolymers studied do not show classical morphologies of high order peaks.

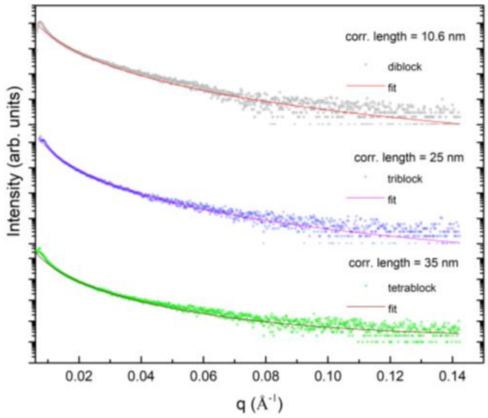


Figure 4 The log intensity vs. scattering vector (q) plots of the PLO-PLA diblock, triblock, and tetrablock copolymers.

Conclusions

PLO homopolymers, with a molar mass up to 4.0 kDa, the largest reported so far, were prepared using a zirconium complex. Furthermore, multiblock copolymers of LO and LA were prepared through redox switchable catalysis. Upon the optimization of polymerization conditions, a series of LO-LA diblock, triblock, and tetrablock copolymers was prepared for the first time. The self-assembly properties of the copolymers were investigated in the solid state. Rheology tests were consistent with phase separation in the triblock and tetrablock copolymers, suggesting the existence of a self-assembly domain. SAXS experiments were then performed to give a quantified measurement of the self-assembly domain. Using the Debye model, the correlation length, or the self-assembly domain radius were fitted to be 11, 25, and 35 nm for the diblock, triblock and tetrablock copolymers, respectively. This study marks a breakthrough in LO chemistry and indicates potential applications in nanoparticle and drug delivery based on the LO copolymer self-assembly properties.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the NSF (Grant CHE-1809116 to P. L. D., Grant No. DMR-1749730 to D. K. for rheological measurements, CHE-1048804 for NMR spectroscopy, ECCS-2025298 for X-ray scattering studies). R. D. is grateful for a Dissertation Year Fellowship from the University of California, Los Angeles. N. D. A. W. and P. C. thank the Miami University Dissertation Scholar Program. D. K. acknowledges support from the Robert H. and Nancy J. Blayney Professorship. X-ray scattering studies performed at NCMN were also supported by the Nebraska Research Initiative.

Notes and references

1. Meier, M. A. R.; Metzger, J. O.; Schubert, U. S., Plant oil renewable resources as green alternatives in polymer science. *Chem. Soc. Rev.* **2007,** *36* (11), 1788-1802.

2. Grignard, B.; Gennen, S.; Jérôme, C.; Kleij, A. W.; Detrembleur, C., Advances in the use of CO2 as a renewable feedstock for the synthesis of polymers. *Chem. Soc. Rev.* **2019,** *48* (16), 4466-4514.

3. Lau, W. W. Y.; Shiran, Y.; Bailey, R. M.; Cook, E.; Stuchtey, M. R.; Koskella, J.; Velis, C. A.; Godfrey, L.; Boucher, J.; Murphy, M. B.; Thompson, R. C.; Jankowska, E.; Castillo Castillo, A.; Pilditch, T. D.; Dixon, B.; Koerselman, L.; Kosior, E.; Favoino, E.; Gutberlet, J.; Baulch, S.; Atreya, M. E.; Fischer, D.; He, K. K.; Petit, M. M.; Sumaila, U. R.; Neil, E.; Bernhofen, M. V.; Lawrence, K.; Palardy, J. E., Evaluating scenarios toward zero plastic pollution. *Science* **2020,** *369* (6510), 1455-1461.

4. Borrelle, S. B.; Ringma, J.; Law, K. L.; Monnahan, C. C.; Lebreton, L.; McGivern, A.; Murphy, E.; Jambeck, J.; Leonard, G. H.; Hilleary, M. A.; Eriksen, M.; Possingham, H. P.; De Frond, H.; Gerber, L. R.; Polidoro, B.; Tahir, A.; Bernard, M.; Mallos, N.; Barnes, M.; Rochman, C. M., Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. *Science* **2020,** *369* (6510), 1515-1518.

5. Ciriminna, R.; Lomeli-Rodriguez, M.; Demma Carà, P.; Lopez-Sanchez, J. A.; Pagliaro, M., Limonene: a versatile chemical of the bioeconomy. *Chem. Commun.* **2014,** *50* (97), 15288-15296.

6. Della Monica, F.; Kleij, A. W., From terpenes to sustainable and functional polymers. *Polym. Chem.* **2020,** *11* (32), 5109-5127.

7. Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W., Alternating Copolymerization of Limonene Oxide and Carbon Dioxide. *J. Am. Chem. Soc.* **2004,** *126* (37), 11404-11405.

8. Neumann, S.; Däbritz, S. B.; Fritze, S. E.; Leitner, L.-C.; Anand, A.; Greiner, A.; Agarwal, S., Sustainable block copolymers of poly(limonene carbonate). *Polym. Chem.* **2021,** *12* (6), 903-910.

9. Carrodeguas, L. P.; Chen, T. T. D.; Gregory, G. L.; Sulley, G. S.; Williams, C. K., High elasticity, chemically recyclable, thermoplastics from bio-based monomers: carbon dioxide, limonene oxide and ε-decalactone. *Green Chem.* **2020,** *22* (23), 8298-8307.

10. Bailer, J.; Feth, S.; Bretschneider, F.; Rosenfeldt, S.; Drechsler, M.; Abetz, V.; Schmalz, H.; Greiner, A., Synthesis and self-assembly of biobased poly(limonene carbonate)-block-poly(cyclohexene carbonate) diblock copolymers prepared by sequential ring-opening copolymerization. *Green Chem.* **2019,** *21* (9), 2266-2272.

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

12. Hauenstein, O.; Reiter, M.; Agarwal, S.; Rieger, B.; Greiner, A., Bio-based polycarbonate from limonene oxide and CO2 with high molecular weight, excellent thermal resistance, hardness and transparency. *Green Chem.* **2016,** *18* (3), 760-770.

13. Brandolese, A.; Kleij, A. W., Catalyst Engineering Empowers the Creation of Biomass-Derived Polyesters and Polycarbonates. *Acc. Chem. Res.* **2022,** *55* (12), 1634-1645.

14. Isnard, F.; Lamberti, M.; Pellecchia, C.; Mazzeo, M., Ring-Opening Copolymerization of Epoxides with Cyclic Anhydrides Promoted by Bimetallic and Monometallic Phenoxy–Imine Aluminum complexes. *ChemCatChem* **2017,** *9* (15), 2972-2979.

15. Chen, T. T. D.; Carrodeguas, L. P.; Sulley, G. S.; Gregory, G. L.; Williams, C. K., Bio-based and Degradable Block Polyester Pressure-Sensitive Adhesives. *Angew. Chem. Int. Ed.* **2020,** *59* (52), 23450.

16. Jeske, R. C.; DiCiccio, A. M.; Coates, G. W., Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. *J. Am. Chem. Soc.* **2007,** *129* (37), 11330-11331.

17. Nejad, E. H.; Paoniasari, A.; van Melis, C. G. W.; Koning, C. E.; Duchateau, R., Catalytic Ring-Opening Copolymerization of Limonene Oxide and Phthalic Anhydride: Toward Partially Renewable Polyesters. *Macromolecules* **2013,** *46* (3), 631-637.

18. Peña Carrodeguas, L.; Martín, C.; Kleij, A. W., Semiaromatic Polyesters Derived from Renewable Terpene Oxides with High Glass Transitions. *Macromolecules* **2017,** *50* (14), 5337-5345.

19. Aikins, J. A.; Williams, F., Radiation-Induced Cationic Polymerization of Limonene Oxide, α-Pinene Oxide, and β-Pinene Oxide. In *Ring-Opening Polymerization*, American Chemical Society: 1985; Vol. 286, pp 335-359.

20. Park, H. J.; Ryu, C. Y.; Crivello, J. V., Photoinitiated cationic polymerization of limonene 1,2-oxide and α-pinene oxide. *J. Polym. Sci. A Polym. Chem.* **2013,** *51* (1), 109-117.

21. Sessini, V.; Palenzuela, M.; Damián, J.; Mosquera, M. E. G., Bio-based polyether from limonene oxide catalytic ROP as green polymeric plasticizer for PLA. *Polymer* **2020,** *210*, 123003.

22. Diaz, C.; Mehrkhodavandi, P., Strategies for the synthesis of block copolymers with biodegradable polyester segments. *Polym. Chem.* **2021,** *12* (6), 783-806.

23. Lai, A.; Hern, Z. C.; Shen, Y.; Dai, R.; Diaconescu, P. L., Metal Complexes for Redox Switching and Control of Reactivity. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, Elsevier: 2021.

24. Wei, J.; Diaconescu, P. L., Redox-switchable Ring-opening Polymerization with Ferrocene Derivatives. *Acc. Chem. Res.* **2019,** *52* (2), 415-424.

25. Qi, M.; Dong, Q.; Wang, D.; Byers, J. A., Electrochemically Switchable Ring-Opening Polymerization of Lactide and Cyclohexene Oxide. *J. Am. Chem. Soc.* **2018,** *140* (17), 5686-5690.

26. Biernesser, A. B.; Delle Chiaie, K. R.; Curley, J. B.; Byers, J. A., Block Copolymerization of Lactide and an Epoxide Facilitated by a Redox Switchable Iron-Based Catalyst. *Angew. Chem. Int. Ed.* **2016,** *55* (17), 5251–5254.

27. Teator, A. J.; Lastovickova, D. N.; Bielawski, C. W., Switchable Polymerization Catalysts. *Chem. Rev.* **2016,** *116* (4), 1969-1992.

28. Hern, Z. C.; Quan, S. M.; Dai, R.; Lai, A.; Wang, Y.; Liu, C.; Diaconescu, P. L., ABC and ABAB Block Copolymers by Electrochemically Controlled Ring-Opening Polymerization. *J. Am. Chem. Soc.* **2021,** *143* (47), 19802-19808.

29. Xu, X.; Luo, G.; Hou, Z.; Diaconescu, P. L.; Luo, Y., Theoretical insight into the redox-switchable activity of group 4 metal complexes for the ring-opening polymerization of ε-caprolactone. *Inorg. Chem. Front.* **2020,** *7* (4), 961-971.

30. Lai, A.; Hern, Z. C.; Diaconescu, P. L., Switchable Ring-Opening Polymerization by a Ferrocene Supported Aluminum Complex. *ChemCatChem* **2019,** *11* (16), 4210-4218.

31. Lai, A.; Clifton, J.; Diaconescu, P. L.; Fey, N., Computational mapping of redox-switchable metal complexes based on ferrocene derivatives. *Chem. Commun.* **2019,** *55,* , 7021-7024

32. Dai, R.; Diaconescu, P. L., Investigation of a Zirconium Compound for Redox Switchable Ring Opening Polymerization. *Dalton Trans.* **2019,** *48*, 2996-3002.

33. Dai, R.; Lai, A.; Alexandrova, A. N.; Diaconescu, P. L., Geometry Change in a Series of Zirconium Compounds during Lactide Ring-Opening Polymerization. *Organometallics* **2018,** *37* (21), 4040-4047.

34. Abubekerov, M.; Wei, J.; Swartz, K. R.; Xie, Z.; Pei, Q.; Diaconescu, P. L., Preparation of multiblock copolymers via step-wise addition of l-lactide and trimethylene carbonate. *Chem. Sci.* **2018,** *9* (8), 2168.

35. Abubekerov, M.; Vlček, V.; Wei, J.; Miehlich, M. E.; Quan, S. M.; Meyer, K.; Neuhauser, D.; Diaconescu, P. L., Exploring Oxidation State-Dependent Selectivity in Polymerization of Cyclic Esters and Carbonates with Zinc(II) Complexes. *iScience* **2018,** *7*, 120-131.

36. Wei, J.; Riffel, M. N.; Diaconescu, P. L., Redox Control of Aluminum Ring-Opening Polymerization: A Combined Experimental and DFT Investigation. *Macromolecules* **2017,** *50* (5), 1847-1861.

37. Quan, S. M.; Wei, J.; Diaconescu, P. L., Mechanistic Studies of Redox-Switchable Copolymerization of Lactide and Cyclohexene Oxide by a Zirconium Complex. *Organometallics* **2017,** *36* (22), 4451-4457.

38. Lowe, M. Y.; Shu, S.; Quan, S. M.; Diaconescu, P. L., Investigation of redox switchable titanium and zirconium catalysts for the ring opening polymerization of cyclic esters and epoxides. *Inorg. Chem. Front.* **2017,** *4*, 1798-1805.

39. Quan, S. M.; Wang, X.; Zhang, R.; Diaconescu, P. L., Redox Switchable Copolymerization of Cyclic Esters and Epoxides by a Zirconium Complex. *Macromolecules* **2016,** *49* (18), 6768-6778.

40. Quan, S. M.; Diaconescu, P. L., High activity of an indium alkoxide complex toward ring opening polymerization of cyclic esters. *Chem. Commun.* **2015,** *51*, 9643 - 9646.

41. Wang, X.; Thevenon, A.; Brosmer, J. L.; Yu, I.; Khan, S. I.; Mehrkhodavandi, P.; Diaconescu, P. L., Redox Control of Group 4 Metal Ring-Opening Polymerization Activity toward l-Lactide and ε-Caprolactone. *J. Am. Chem. Soc.* **2014,** *136* (32), 11264-11267.

42. Broderick, E. M.; Guo, N.; Wu, T.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Cantat, T.; Diaconescu, P. L., Redox control of a polymerization catalyst by changing the oxidation state of the metal center. *Chem. Commun.* **2011,** *47*, 9897-9899.

43. Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L., Redox Control of a Ring-Opening Polymerization Catalyst. *J. Am. Chem. Soc.* **2011,** *133* (24), 9278–9281.

44. Durmaz, Y. Y.; Kukut, M.; Moszner, N.; Yagci, Y., Sequential photodecomposition of bisacylgermane type photoinitiator: Synthesis of block copolymers by combination of free radical promoted cationic and free radical polymerization mechanisms. *J. Polym. Sci. A Polym. Chem.* **2009,** *47* (18), 4793-4799.

45. Plommer, H.; Reim, I.; Kerton, F. M., Ring-opening polymerization of cyclohexene oxide using aluminum amine–phenolate complexes. *Dalton Trans.* **2015,** *44* (27), 12098-12102.

46. Bhatia, S. R.; Mourchid, A.; Joanicot, M., Block copolymer assembly to control fluid rheology. *Curr. Opin. Colloid Interface Sci.* **2001,** *6* (5), 471-478.

47. Newby, G. E.; Hamley, I. W.; King, S. M.; Martin, C. M.; Terrill, N. J., Structure, rheology and shear alignment of Pluronic block copolymer mixtures. *J. Colloid Interface Sci.* **2009,** *329* (1), 54-61.

48. Puig-Rigall, J.; Obregon-Gomez, I.; Monreal-Pérez, P.; Radulescu, A.; Blanco-Prieto, M. J.; Dreiss, C. A.; González-Gaitano, G., Phase behaviour, micellar structure and linear rheology of tetrablock copolymer Tetronic 908. *J. Colloid Interface Sci.* **2018,** *524*, 42-51.

49. Li, F.-J.; Tan, L.-C.; Zhang, S.-D.; Zhu, B., Compatibility, steady and dynamic rheological behaviors of polylactide/poly(ethylene glycol) blends. *J. Appl. Polym. Sci.* **2016,** *133* (4).

50. Veenstra, H.; Hoogvliet, R. M.; Norder, B.; De Boer, A. P., Microphase separation and rheology of a semicrystalline poly(ether-ester) multiblock copolymer. *J. Polym. Sci. B Polym. Phys.* **1998,** *36* (11), 1795-1804.

51. Pourmohammadi-Mahunaki, M.; Haddadi-Asl, V.; Roghani-Mamaqani, H.; Koosha, M.; Yazdi, M., Effect of chain extender length and molecular architecture on phase separation and rheological properties of ether-based polyurethanes. *Polym. Bull.* **2022,** *79* (10), 8653-8668.

52. Lin, F.-Y.; Hohmann, A. D.; Hernández, N.; Shen, L.; Dietrich, H.; Cochran, E. W., Self-Assembly of Poly(styrene-block-acrylated epoxidized soybean oil) Star-Brush-Like Block Copolymers. *Macromolecules* **2020,** *53* (18), 8095-8107.

53. Jørgensen, E. B.; Hvidt, S.; Brown, W.; Schillén, K., Effects of Salts on the Micellization and Gelation of a Triblock Copolymer Studied by Rheology and Light Scattering. *Macromolecules* **1997,** *30* (8), 2355-2364.

54. Manet, S.; Lecchi, A.; Impéror-Clerc, M.; Zholobenko, V.; Durand, D.; Oliveira, C. L. P.; Pedersen, J. S.; Grillo, I.; Meneau, F.; Rochas, C., Structure of Micelles of a Nonionic Block Copolymer Determined by SANS and SAXS. *J. Phys. Chem. B* **2011,** *115* (39), 11318-11329.

55. Czajka, A.; Armes, S. P., In situ SAXS studies of a prototypical RAFT aqueous dispersion polymerization formulation: monitoring the evolution in copolymer morphology during polymerization-induced self-assembly. *Chem. Sci.* **2020,** *11* (42), 11443-11454.

56. Stegelmeier, C.; Exner, A.; Hauschild, S.; Filiz, V.; Perlich, J.; Roth, S. V.; Abetz, V.; Förster, S., Evaporation-Induced Block Copolymer Self-Assembly into Membranes Studied by in Situ Synchrotron SAXS. *Macromolecules* **2015,** *48* (5), 1524-1530.

57. Hall, B. D., Debye function analysis of structure in diffraction from nanometer-sized particles. *J. Appl. Phys.* **2000,** *87* (4), 1666-1675.

58. Tsybulya, S. V.; Yatsenko, D. A., X-ray diffraction analysis of ultradisperse systems: The Debye formula. *J. Struct. Chem.* **2012,** *53* (1), 150-165.

59. Dao, T. P. T.; Vezenkov, L.; Subra, G.; Amblard, M.; In, M.; Le Meins, J.-F.; Aubrit, F.; Moradi, M.-A.; Ladmiral, V.; Semsarilar, M., Self-Assembling Peptide—Polymer Nano-Objects via Polymerization-Induced Self-Assembly. *Macromolecules* **2020,** *53* (16), 7034-7043.

TOC graph: