

# Post-functionalization and Mechanical Properties of Poly(lactide-cyclohexadiene oxide) Block Copolymers

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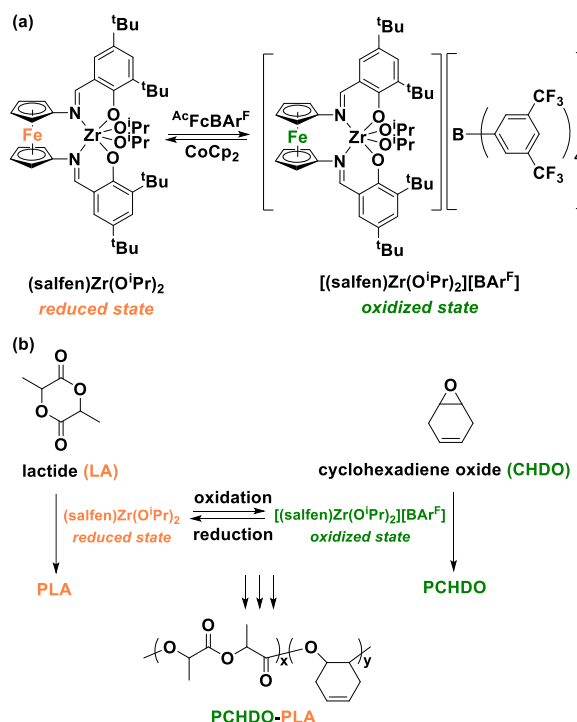
A series of lactide (LA) and cyclohexadiene oxide (CHDO) multiblock copolymers was synthesized using a redox switchable complex, (salfen)Zr(O<sup>i</sup>Pr)<sub>2</sub> (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine), with LA being polymerized by the reduced state, while CHDO was polymerized by the oxidized state of the catalyst. Diblock (PCHDO-PLA) and triblock (PLA-PCHDO-PLA and PCHDO-PLA-PCHDO) copolymers were prepared, and all the copolymers were post-functionalized using a thiol-ene click reaction. Dynamic mechanical analysis showed that both triblock copolymers have a better elasticity than the diblock copolymer, and all the functionalized copolymers have a better elasticity than the corresponding non-functionalized copolymers.

## Introduction

Polyesters and polyethers are biodegradable polymers that can help reduce the worldwide plastic waste and mitigate the “white pollution” issue.<sup>1-5</sup> In order to improve the properties of biodegradable polymers, the synthesis of polyether-*block*-polyesters allows tuning of their properties to adjust elasticity and hydrophilicity to meet the requirements of a specific material.<sup>6-8</sup> Furthermore, post-functionalization of copolymers with unsaturated functionalities in their structure allows additional improvements of their properties.<sup>9-12</sup>

Epoxides are valuable co-monomers for the formation of polycarbonates and polyesters, usually obtained from their ring opening copolymerization with CO<sub>2</sub> or cyclic anhydrides, respectively.<sup>13-18</sup> Switchable polymerization methods<sup>19-25</sup> have expanded the use of epoxides to other types of block copolymers such as polyether-*block*-polyesters,<sup>26-28</sup> polyester-*block*-polyesters,<sup>29-30</sup> polyether-*block*-polycarbonates,<sup>31</sup> and polyester-*block*-polycarbonates.<sup>32</sup> Of these methods, redox switchable ring-opening copolymerization of cyclic esters and epoxides offers precise control over the formation of polyether-*block*-polyesters directly from epoxides and cyclic esters.<sup>33-53</sup> Our group uses zirconium, titanium, aluminum, yttrium, or zinc complexes bearing a ferrocene unit in the ligand backbone that can be oxidized and reduced reversibly; these compounds show different selectivity in the reduced and oxidized states. Of these compounds, a zirconium complex, (salfen)Zr(O<sup>i</sup>Pr)<sub>2</sub> (salfen = N,N'-bis(2,4-di-*tert*-butylphenoxy)-1,1'-ferrocenediimine),<sup>54</sup> was investigated, and it was found that, in its reduced form, it can polymerize cyclic esters, such as  $\epsilon$ -lactide (LA),  $\epsilon$ -caprolactone, and  $\delta$ -valerolactone, while in its oxidized form, it can polymerize epoxides such as cyclohexene oxide (CHO) and propylene oxide.<sup>55</sup> As a consequence, it proved to be a successful redox switchable copolymerization system, where diblock and triblock copolymers of LA and CHO were prepared.

LA is a promising biorenewable and biocompatible monomer. However, polylactide (PLA) is brittle, making it not versatile for many applications.<sup>56-58</sup>



**Scheme 1** (a) Redox switch of (salfen)Zr(O<sup>i</sup>Pr)<sub>2</sub>. (b) LA and CHDO monomers used in this study, and the flow chart of block copolymer preparation using redox switchable copolymerization in this work.

Given that LA can be polymerized in our redox switchable copolymerization system, we set out to investigate the formation of polylactide-polyether block copolymers. In particular, we chose cyclohexadiene oxide (CHDO, Scheme 1b), which is an unsaturated derivative of CHO. The unsaturated bond in CHDO can be used for post-functionalization<sup>59-61</sup> to tune further the mechanical property of the resulting copolymers. Herein, we report the synthesis of CHDO-LA block copolymers using the redox switchable method, along with their post-functionalization to study how those reactions would affect the mechanical property of the resulting copolymers.

## Results and Discussion

### CHDO homopolymerization

CHDO was synthesized from cyclohexadiene, following a published procedure.<sup>62</sup> (salfen)Zr(O<sup>i</sup>Pr)<sub>2</sub>, and its *in situ* oxidized

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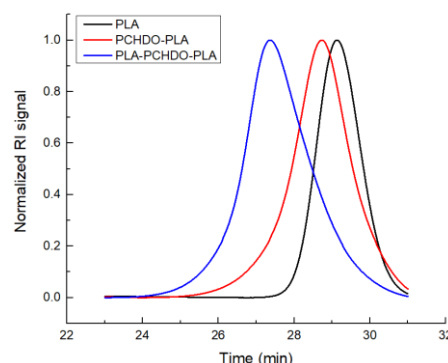
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

form,  $[(\text{salfen})\text{Zr}(\text{O}^i\text{Pr})_2][\text{BAR}^F]$  ( $\text{BAR}^F = \text{tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{-phenyl})\text{borate}$ ) were both tested as precatalysts for the homopolymerization of CHDO. Similar to CHO, CHDO can only be polymerized by the oxidized state of the precatalyst, with a 99% conversion (Table S2, entry 2). The reaction was monitored by NMR spectroscopy and size exclusive chromatography (SEC), with the conversion and molar mass data listed in Table S3; the conversion already reached 90.6% in 60 min (Table S3, entry 4).

### CHDO and LA copolymerization

Since CHDO can be polymerized by the oxidized form of the precatalyst, and LA can be polymerized by the reduced form, we decided to prepare copolymers in a redox switchable manner. First, a PCHDO-PLA diblock copolymer was prepared. The precatalyst  $(\text{salfen})\text{Zr}(\text{O}^i\text{Pr})_2$  was first added to a Schlenk tube in its reduced form, then LA was added to construct a PLA block. After the first reaction was completed, an equivalent of the oxidant  $\text{AcFcBAR}^F$  was added to oxidize the catalyst *in situ*, followed by the addition of CHDO to construct the PCHDO block.

The reaction was sampled after the preparation of each polymer block (Table 1, entry 1). The formula  $\text{CHDO}_{69}\text{-LA}_{40}$  was derived using the molar mass of each block divided by the molecular weight of the corresponding monomer. SEC traces (Figure S15) and diffusion ordered spectroscopy (DOSY, Figure S6) confirmed the formation of a copolymer.



**Figure 1** SEC traces for the formation of the PLA-PCHDO-PLA triblock copolymer showing that the molar mass increased as new blocks were added.

**Table 1** Real-time monitoring of the formation of diblock and triblock copolymers <sup>a</sup>

Entry	Copolymer class	1 <sup>st</sup> block Mn (kDa) <sup>b</sup>	2 <sup>nd</sup> block Mn (kDa)	3 <sup>rd</sup> block Mn (kDa)	Total Mn (kDa)	$\bar{D}$	Copolymer formula <sup>c</sup>
1	PCHDO-PLA	5.7	6.6	--	12.3	1.2	$\text{LA}_{40}\text{-CHDO}_{69}$
2	PLA-PCHDO-PLA	4.2	3.8	4.1	12.1	1.3	$\text{LA}_{29}\text{-CHDO}_{39}\text{-LA}_{30}$
3	PCHDO-PLA-PCHDO	9.2	4.6	2.4	16.2	1.5	$\text{CHDO}_{25}\text{-LA}_{32}\text{-CHDO}_{96}$

<sup>a</sup> 100 equiv LA/CHDO monomer was used for preparing each block during the copolymerization. The polymerization was conducted at 25 °C for 1 h with the oxidized form of the precatalyst, and at 100 °C for around 20 h with the reduced form of the precatalyst. <sup>b</sup> Molar masses were derived from SEC. <sup>c</sup> The number of repeating units was calculated from the molar mass of each block, divided by the molecular weight of the corresponding monomer.

The triblock copolymers were prepared in a similar way. To prepare the PLA-PCHDO-PLA triblock copolymer (Table 1, entry 2), the reduced form of the precatalyst,  $(\text{salfen})\text{Zr}(\text{O}^i\text{Pr})_2$ , was firstly used to construct the first PLA block, then the catalyst was oxidized to synthesize the PCHDO block, and then it was reduced back to perform the second PLA block polymerization. In the case of preparing the PCHDO-PLA-PCHDO triblock copolymer (Table 1, entry 3), the precatalyst was first oxidized to  $[(\text{salfen})\text{Zr}(\text{O}^i\text{Pr})_2][\text{BAR}^F]$  *in situ* to polymerize the first PCHDO block, followed by a reduction to achieve the PLA block, then an oxidation for the second PCHDO block. The SEC traces for the formation of PLA-PCHDO-PLA (Figure 1) are all unimodal, and DOSY (Figure S9) also confirmed that PLA-PCHDO-PLA is a copolymer.

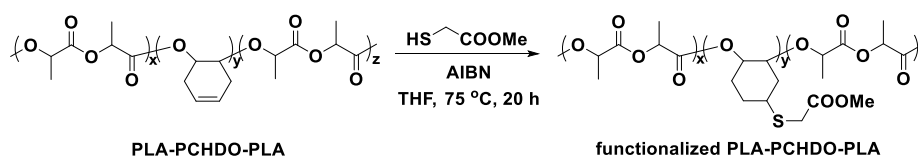
### Post-functionalization of the copolymers

All the copolymers were then post-functionalized using a thiol-ene click reaction. Azo-bis-*iso*-butyronitrile (AIBN) was used as a radical initiator to catalyze the addition of methyl thioglycolate to the C=C double bond of the CHDO units (Table 2). The reaction was sensitive to oxygen, so air was removed before the reaction started. The reaction was stirred at 75 °C for

20 hours in THF, followed by a workup in cold methanol. The molar mass of the functionalized copolymers was significantly higher than that of the corresponding plain copolymers (Table 2). In <sup>1</sup>H NMR spectra, the C=C double bond peak disappeared after post-functionalization, and new peaks were observed (Figure S13). The percentage of functionalized units was then calculated from the number of units functionalized divided by the number of CHDO units originally in the plain copolymer. In all cases, the post-functionalization rate was higher than 50%.

### Mechanical properties of resulting copolymers

Elasticity properties were measured by dynamic mechanical analysis for both the plain and the functionalized copolymers. For this study, we controlled the molar mass of every plain copolymer into the region of  $14.3 \pm 2.0$  kDa, and varied the LA ratio. Within each copolymer pair, i.e., functionalized and non-functionalized, two copolymers with a LA unit ratio of 0.2 and 0.4 were prepared (Table 3). All the copolymers were post-functionalized and characterized by SEC (Table S1). For dynamic mechanical analysis, each copolymer sample was dissolved in THF and cast into a film.

**Table 2** The molar mass of before and after functionalization of the copolymers, and the functionalization rate.<sup>a</sup>

Entry	Copolymer formula	Mn of the plain copolymer (kDa) <sup>b</sup>	Mn of the functionalized copolymer (kDa)	Number of functionalized units <sup>c</sup>	Post-functionalization (%) <sup>d</sup>
1	CHDO <sub>69</sub> -LA <sub>40</sub>	12.3	19.4	67	97%
2	LA <sub>29</sub> -CHDO <sub>39</sub> -LA <sub>30</sub>	12.1	15.7	34	87%
3	CHDO <sub>25</sub> -LA <sub>32</sub> -CHDO <sub>96</sub>	16.2	24.7	78	55%

<sup>a</sup> 1:200:10 of AIBN (Azo-bis-*iso*-butyronitrile) to methyl thioglycolate to C=C double bond ratio was used for the reaction. <sup>b</sup> All the molar mass data was derived from SEC measurement. <sup>c</sup> The number of functionalized units was calculated from subtracting the molar mass of the plain copolymer from that of the corresponding functionalized copolymer, then divided by the molecular weight of the methyl thioglycolate. <sup>d</sup> Calculated by the number of functionalized units divided by the number of CHDO units originally in the copolymer.

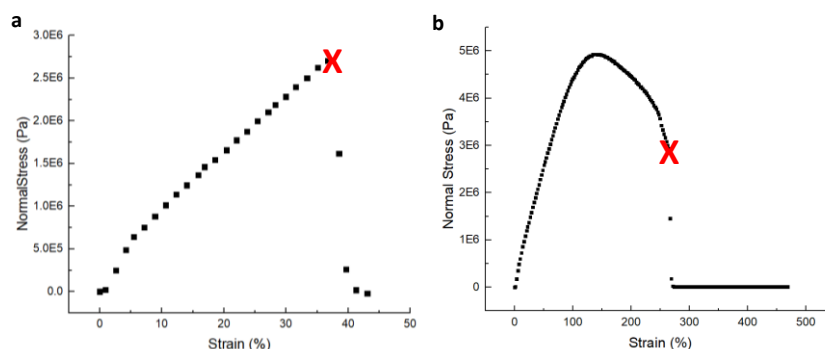
**Table 3** The dynamic mechanical analysis (DMA) of the plain and functionalized copolymers.

Entry	Copolymer class	LA unit ratio <sup>a</sup>	Plain (P) or functionalized (F)	Mn (kDa)	Young's modulus (MPa)	Max stress (MPa)	Elongation at break
1	PCHDO-PLA	0.2	P	14.3	9.0	2.8	36%
2			F	22.5	2.2	1.5	55%
3		0.4	P	12.3	1.2	2.5	21%
4			F	19.4	3.1	1.1	30%
5	PLA-PCHDO-PLA	0.2	P	14.8	6.5	1.5	330%
6			F	26.3	4.4	1.4	940%
7		0.4	P	14.5	4.2	2.7	130%
8			F	20.1	4.0	5.0	270%
9	PCHDO-PLA-PCHDO	0.2	P	16.2	5.1	1.3	170%
10			F	24.7	1.9	7.9	650%
11		0.4	P	15.9	2.1	1.6	72%
12			F	21.9	2.0	2.4	110%

<sup>a</sup> The LA unit ratio is calculated from the total number of LA units in the copolymer divided by the sum of LA units and CHDO units in the copolymer. This is not a mass ratio. The breakdown of the polymer formula and molar mass for individual blocks in each entry is listed in Table S1.

The Young's modulus was calculated, and the maximum stress and elongation at break point were read from the stress strain curve (Table 5, Figure 2 and S20-S31). We observed that all the copolymers, regardless of being functionalized, show the same magnitude of the Young's modulus and maximum stress, and no obvious trends can be deduced. However, the elongation percentage at break differed for each case, representing the difference in toughness (or the amount of energy it can absorb before breaking) between the copolymers. Furthermore, all functionalized copolymers had a larger elongation at break compared to the corresponding non-

functionalized copolymer, demonstrating that post-functionalization did alter the elasticity property of the corresponding copolymer. We also observed that, within the same copolymer class, a lower LA ratio resulted in a greater elongation at break, meaning that in the LA-CHDO copolymer system, LA is the "rigid monomer" and CHDO is the "soft monomer". Finally, for the non-functionalized copolymers from different classes but with the same LA unit ratio, the elongation at break is following the trend PCHDO-PLA < PCHDO-PLA-PCHDO < PLA-PCHDO-PLA. A similar trend was observed by us for copolymers of LA and trimethylene carbonate.<sup>63</sup>



**Figure 2** Stress strain curves of (a) PLA-PCHDO/0.2LA plain copolymer (Table 3, entry 1) and (b) PLA-PCHDO-PLA/0.4LA functionalized copolymer (Table 3, entry 8). The red cross marks the break point of the polymer film. The stress strain curves for other copolymers are in the SI.

## Conclusion

Three series of biodegradable copolymers, PCHDO-PLA, PLA-PCHDO-PLA, and PCHDO-PLA-PCHDO, were synthesized using a redox switchable copolymerization method. The copolymers were post-functionalized by a thiol-ene click reaction. Methyl thioglycolate was added to the CHDO units in the copolymer, as confirmed by the increase of the polymer molar mass and the disappearance of the olefinic peak in the corresponding NMR spectra. All plain and functionalized copolymers were characterized by dynamic mechanical analysis. The elongation percentage at break, or the toughness of the copolymer, is lower in the plain copolymers compared to the corresponding functionalized copolymers, and when the copolymer has a higher LA unit ratio. The general trend for the elongation at break is PCHDO-PLA < PCHDO-PLA-PCHDO < PLA-PCHDO-PLA. Our results indicate that the mechanical property of a copolymer can be improved by altering the composition of the copolymer and by post-functionalization. Overall, this study will open up new studies on the feasibility of using biodegradable polyesters and polyethers as daily plastics.

## Experimental Section

### General considerations

All experiments were performed in an Mbraun inert gas glovebox or under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were purified with a two-state solid-state purification system by the method of Grubbs and transferred to the glovebox inside a Schlenk flask without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use.  $^1\text{H}$  NMR spectra were recorded on Bruker 300, Bruker 500, or Bruker 600 spectrometers at room temperature in  $\text{C}_6\text{D}_6$ . Chemical shifts are reported with respect to the residual solvent peaks, 7.16 ppm ( $\text{C}_6\text{D}_6$ ) for  $^1\text{H}$  NMR spectra. CHDO were synthesized from cyclohexadiene following a published procedure<sup>62</sup> and brought into the glovebox without exposure to air. 1,2-difluorobenzene was distilled over  $\text{CaH}_2$  and brought into the glovebox without exposing to air. L-lactide (LA) and hexamethylbenzene were recrystallized from THF at least

twice before use.  $\text{CoCp}_2$  were purchased from Sigma-Aldrich and used as received.  $^{\text{AcFc}}\text{BAR}^{\text{F}}$  ( $^{\text{AcFc}}$  = acetoferrrocenyl,  $\text{BAR}^{\text{F}}$  = tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate)<sup>64</sup> and (salfen)Zr( $\text{O}^i\text{Pr}$ )<sub>2</sub><sup>54</sup> were synthesized following previously published procedures. Molecular weights of polymers were determined by size exclusion chromatography using a SEC-MALS instrument at UCLA. SEC-MALS uses a Shimadzu Prominence-i LC 2030C 3D equipped with an autosampler, two MZ Analysentechnik MZ-Gel SDplus LS 5  $\mu\text{m}$ , 300  $\times$  8 mm linear columns, a Wyatt DAWN HELEOS-II, and a Wyatt Optilab T-rEX. The column temperature was set at 40  $^\circ\text{C}$ . A flow rate of 0.70 mL/min was used and samples were dissolved in THF. The number average molar mass and dispersity values were found using the known concentration of the sample in THF with the assumption of 100% mass recovery to calculate  $\text{dn}/\text{dc}$  from the DRI signal.

Tensile tests were carried out on a TA RSA3 dynamic mechanical analyzer at a strain rate of 0.5  $\text{mm s}^{-1}$ . Samples with a measured thickness of 300  $\mu\text{m}$  were cut in 5-mm wide strips with a razor blade and loaded onto the thin film grips. At least three repetitive samples were tested for each formulation.

### NMR scale polymerizations with (salfen)Zr( $\text{O}^i\text{Pr}$ )<sub>2</sub>

Under an inert atmosphere, (salfen)Zr( $\text{O}^i\text{Pr}$ )<sub>2</sub> (4  $\mu\text{mol}$ ), the monomer,  $\text{C}_6\text{D}_6$  (0.6 mL), and an internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The reaction mixture was left at room temperature for 5 minutes while being shaken occasionally. The tube was sealed and brought out of the glovebox and heated to the specified temperature with an oil bath. The NMR tube was taken out of the oil bath and analyzed periodically by  $^1\text{H}$  NMR spectroscopy. When the reaction was done,  $\text{CH}_2\text{Cl}_2$  was added to the mixture and then the resulting solution was poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged for 3  $\times$  5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

### NMR scale polymerizations with [(salfen)Zr( $\text{O}^i\text{Pr}$ )<sub>2</sub>][ $\text{BAR}^{\text{F}}$ ]

Under an inert atmosphere, (salfen)Zr( $\text{O}^i\text{Pr}$ )<sub>2</sub> (4  $\mu\text{mol}$ ),  $\text{C}_6\text{D}_6$  (0.3 mL), and an internal standard (hexamethylbenzene) were added to a J-Young NMR tube. The  $^{\text{AcFc}}\text{BAR}^{\text{F}}$  solution (0.1 mL, 40 mM in 1,2-difluorobenzene) was added and the NMR tube was shaken for 5 minutes before adding the monomer. The tube was

sealed and brought out of the glovebox and left at room temperature. The NMR tube was monitored periodically by  $^1\text{H}$  NMR spectroscopy. When the reaction was done,  $\text{CH}_2\text{Cl}_2$  was added to the mixture and then the resulting solution was poured into 10 mL of cold methanol to precipitate the polymer. The mixture was centrifuged for 3 x 5 minutes, decanted, and dried under a reduced pressure to give the final polymer product.

#### Preparation of PLA-PCHDO diblock copolymer

Under an inert atmosphere, (salphen)Zr(O<sup>i</sup>Pr)<sub>2</sub> (16  $\mu\text{mol}$ ), LA (100 equiv),  $\text{C}_6\text{D}_6$  (2.5 mL) and an internal standard (hexamethylbenzene) were added to a 25 mL Schlenk tube. The reaction mixture was left at room temperature to stir for 5 minutes. The tube was sealed and brought out of the glovebox and heated to 100 °C with an oil bath. After heating for 20 h, the first block of the copolymer was made, and the tube was brought back into the glovebox. An  $^{13}\text{C}$ FcBAR<sup>F</sup> solution (0.4 mL, 40 mM in 1,2-difluorobenzene) was added and the Schlenk tube was shaken for 5 min before adding the CHDO (100 equiv). The tube was sealed and brought out of the glovebox, left at room temperature and shaken every 30 minutes. After 1 h reaction time, the polymerization was completed. The solution was poured into 20 mL cold methanol to precipitate the polymer. The mixture was centrifuged for 3 x 5 minutes, decanted, and dried under a reduced pressure to give the final polymer product. For real-time monitoring, a reaction aliquot was taken in the glovebox at the completion of each polymer block. The volume of the aliquot was carefully measured and the amount of subsequently added reagents was calculated accordingly.

#### Preparation of PLA-PCHDO-PLA triblock copolymer

Under an inert atmosphere, (salphen)Zr(O<sup>i</sup>Pr)<sub>2</sub> (16  $\mu\text{mol}$ ), LA (100 equiv),  $\text{C}_6\text{D}_6$  (2.5 mL) and the internal standard (hexamethylbenzene) were added to a 25 mL Schlenk tube. The reaction mixture was left at room temperature to stir for 5 minutes. The tube was sealed and brought out of the glovebox and heated to 100 °C with an oil bath. After heating for 20 h, the first block of the copolymer was made, and the tube was brought back into the glovebox. An  $^{13}\text{C}$ FcBAR<sup>F</sup> solution (0.4 mL, 40 mM in 1,2-difluorobenzene) was added and the Schlenk tube was shaken for 5 min before adding the CHDO (100 equiv). The tube was sealed, left at room temperature, and shaken every 30 minutes. After 1 h reaction time, the polymerization was completed. Then CoCp<sub>2</sub> solution (0.4 mL, 40 mM in  $\text{C}_6\text{D}_6$ ) was added to the reaction mixture. The tube was shaken for 5 minutes, then another 100 equiv LA was added. The tube was sealed and brought out of the glovebox and heated to 100 °C with an oil bath. After heating for 20 h, the third block of the copolymer was made. The solution was poured into 20 mL cold methanol to precipitate the polymer. The mixture was centrifuged for 3 x 5 minutes, decanted, and dried under a reduced pressure to give the final polymer product. For real-time monitoring, a reaction aliquot was taken in the glovebox at the completion of each polymer block. The volume of the aliquot was carefully measured and the amount of subsequently added reagents was calculated accordingly.

#### Preparation of PLA-PCHDO-PLA triblock copolymer

Under an inert atmosphere, (salphen)Zr(O<sup>i</sup>Pr)<sub>2</sub> (16  $\mu\text{mol}$ ),  $\text{C}_6\text{D}_6$  (2.5 mL) and an internal standard (hexamethylbenzene) were added to a 25 mL Schlenk tube. An  $^{13}\text{C}$ FcBAR<sup>F</sup> solution (0.4 mL, 40 mM in 1,2-difluorobenzene) was added and the Schlenk tube was shaken for 5 min before adding the CHDO (100 equiv). The tube was sealed, left at room temperature, and shaken every 30 minutes. After 1 h reaction time, the polymerization was completed. Then CoCp<sub>2</sub> solution (0.4 mL, 40 mM in  $\text{C}_6\text{D}_6$ ) was added to the reaction mixture. The tube was shaken for 5 minutes, then another 100 equiv LA was added. The tube was sealed and brought out of the glovebox and heated to 100 °C with an oil bath. After heating for 20 h, the second block of the copolymer was made. The tube was brought back into the glovebox. An  $^{13}\text{C}$ FcBAR<sup>F</sup> solution (0.4 mL, 40 mM in 1,2-difluorobenzene) was added and the Schlenk tube was shaken for 5 min before adding another 100 equiv CHDO. The tube was sealed, left at room temperature, and shaken every 30 minutes. After 1 h reaction time, the polymerization of third block was completed. The solution was poured into 20 mL cold methanol to precipitate the polymer. The mixture was centrifuged for 3x5 minutes, decanted, and dried under a reduced pressure to give the final polymer product. For real-time monitoring, a reaction aliquot was taken in the glovebox at the completion of each polymer block. The volume of the aliquot was carefully measured and the amount of subsequently added reagents was calculated accordingly.

#### Post-functionalization of the copolymer

Around 100 mg copolymers were added to 4.0 mL degassed THF in a Schlenk tube. 20 equiv methyl thioglycolate and 0.3 equiv AIBN were added and the reactor was sealed. The reactor was kept at 75°C and stirred for 20 h. Then the reaction mixture was concentrated and added to cold methanol for precipitation. The resulting polymer was dried under a reduced pressure.

#### Preparation of polymer film for dynamic mechanical analysis

A completely dried copolymer sample (around 100 mg) was dissolved into THF (2 mL) and stirred to make a transparent solution. About 5 drops of the copolymer solution were applied on a glass slide and spread to a 2 x 2 cm<sup>2</sup> square, and then air dried. The procedure was repeated until all the solution was consumed. The polymer film was cut the next day from the glass slide for dynamic mechanical analysis.

#### Conflicts of interest

There is no conflict of interest.

#### Acknowledgements

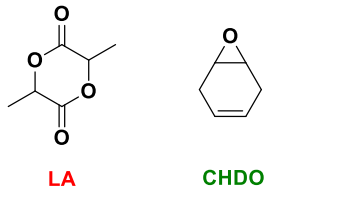
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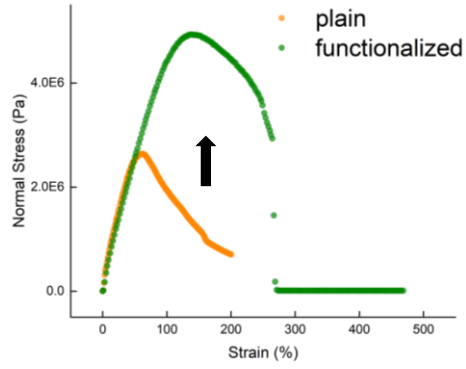
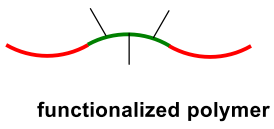
## TOC graph



redox switchable  
copolymerization



thiolene click  
post-functionalization



Enhanced mechanical property!