Supplementary Information (SI) for Polymer Chemistry.

Supplementary Information

Transformation of Semicrystalline Polymer Mechanics by Cyclic Polymers

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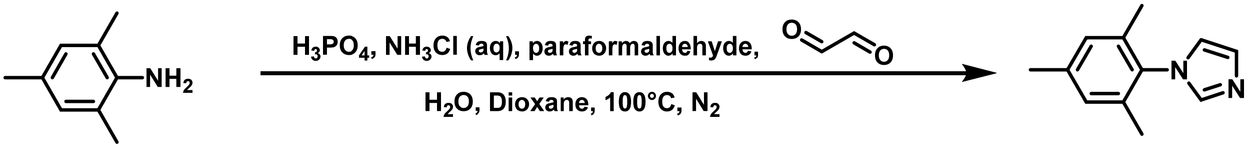
Synthesis of 1-mesityl-1H-imidazole:



In a 500 mL two necked round bottom flask equipped with a stir bar, reflux condenser, nitrogen inlet, and outlet 2,4,6-trimethylaniline (20 g, 0.15 mol) was added. 100 mL DI water and 11 mL of phosphoric acid (85.5%) was added (pH ≈2) and the reaction was stirred for 2 hours. 200 mL dioxane and 100 mL of DI water was added to the flask followed by paraformaldehyde (4.44 g, 0.15 mol) and glyoxal (aq.) (21.45 g, 0.15 mol). Ammonium chloride (7.9 g, 0.15 mol) was dissolved in 80 mL of DI water and added to the reaction flask and the reaction was refluxed at 105 °C. The color changed from yellow to brown over 6 hours. The reaction was then cooled to 0 °C in an ice bath and neutralized carefully with 1 M NaOH until the pH > 10. The reaction was then extracted 3 x 500 mL hexane and the organic layer was dried with magnesium sulfate and filtered. The brown solution was then concentrated via rotary evaporation to give a dark brown sludge. The material was then purified via flash column chromatography on silica with a mobile phase consisting of DCM:MeOH (90:10). Three compounds were separated, the last of which was the desired product obtained as a brown solid with a yield of 15%.

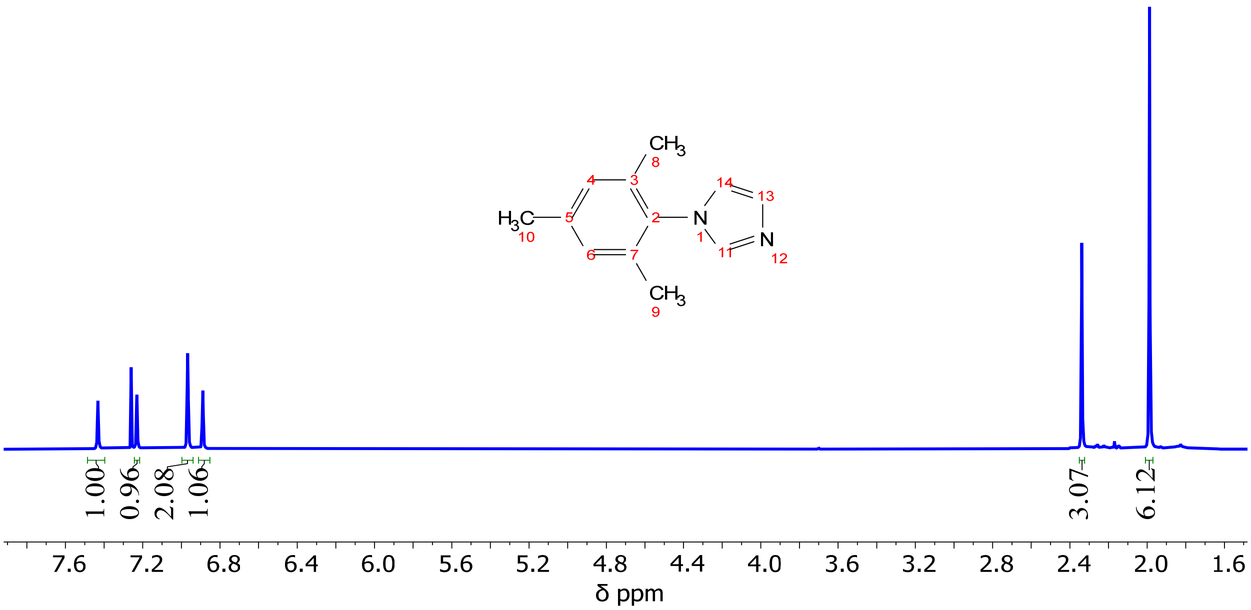


Figure S1. ^{1}H NMR spectrum of 1-mesityl-1H-imidazole.

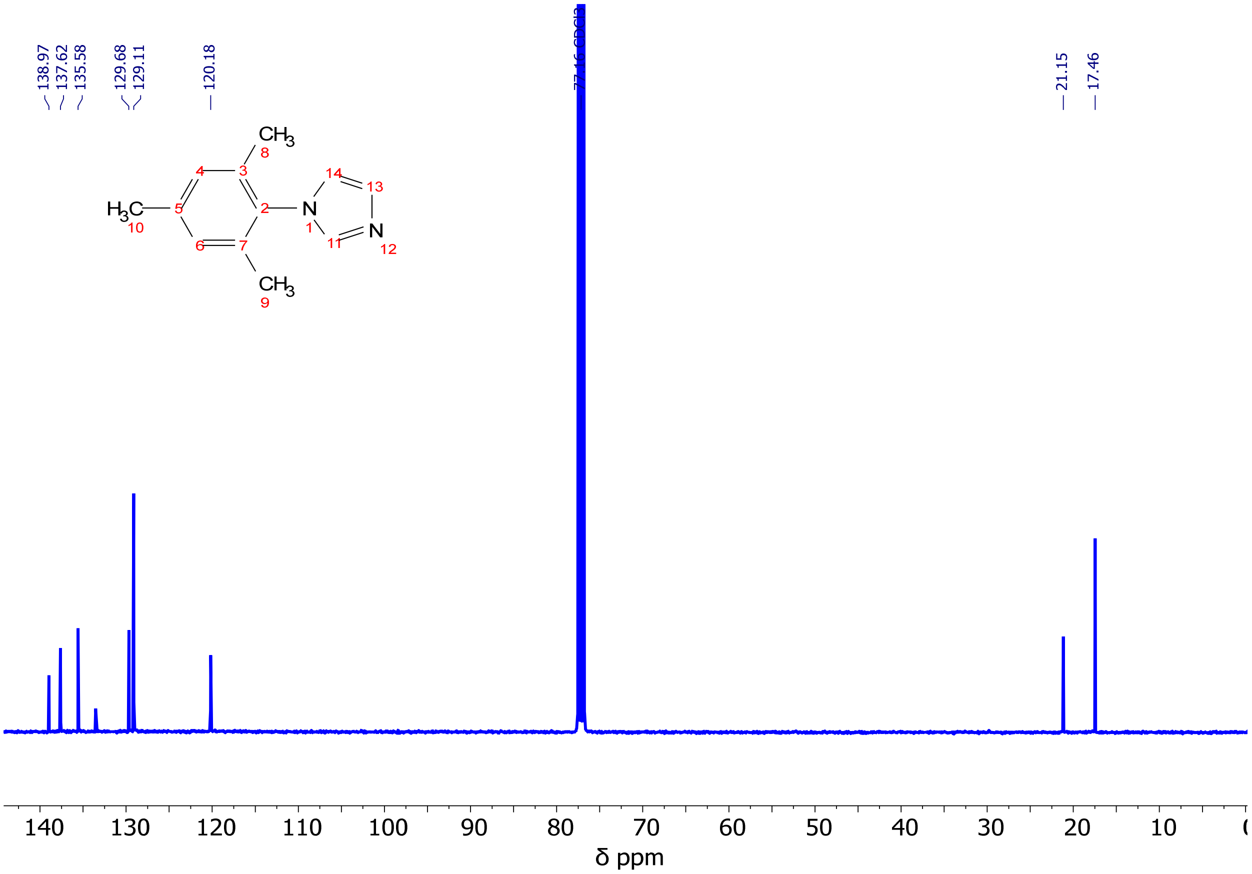
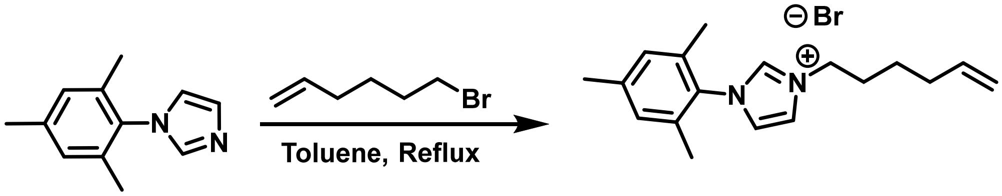


Figure S2. ^{13}C NMR spectrum of 1-mesityl-1H-imidazole.

Synthesis of 3-(hex-5-en-1-yl)-1-mesityl-1H-imidazol-3-ium bromide:



In a 100 mL two necked round bottom flask equipped with a stir bar, reflux condenser, nitrogen inlet, and outlet. 1-mesityl-1H-imidazole (1 g, 5.3 mmol) was dissolved in 15 mL toluene and added to the flask. 6-Bromo-1-hexene (1.05 g, 6.4 mmol) was added and the reaction was stirred under reflux at 110 °C overnight. The reaction was then cooled to room temperature and concentrated via rotary evaporation. The residual oily substance was dissolved in 1 mL of DCM and precipitated in diethyl ether 3 times. The brown solid was dried and stored under vacuum with a yield of 64%.

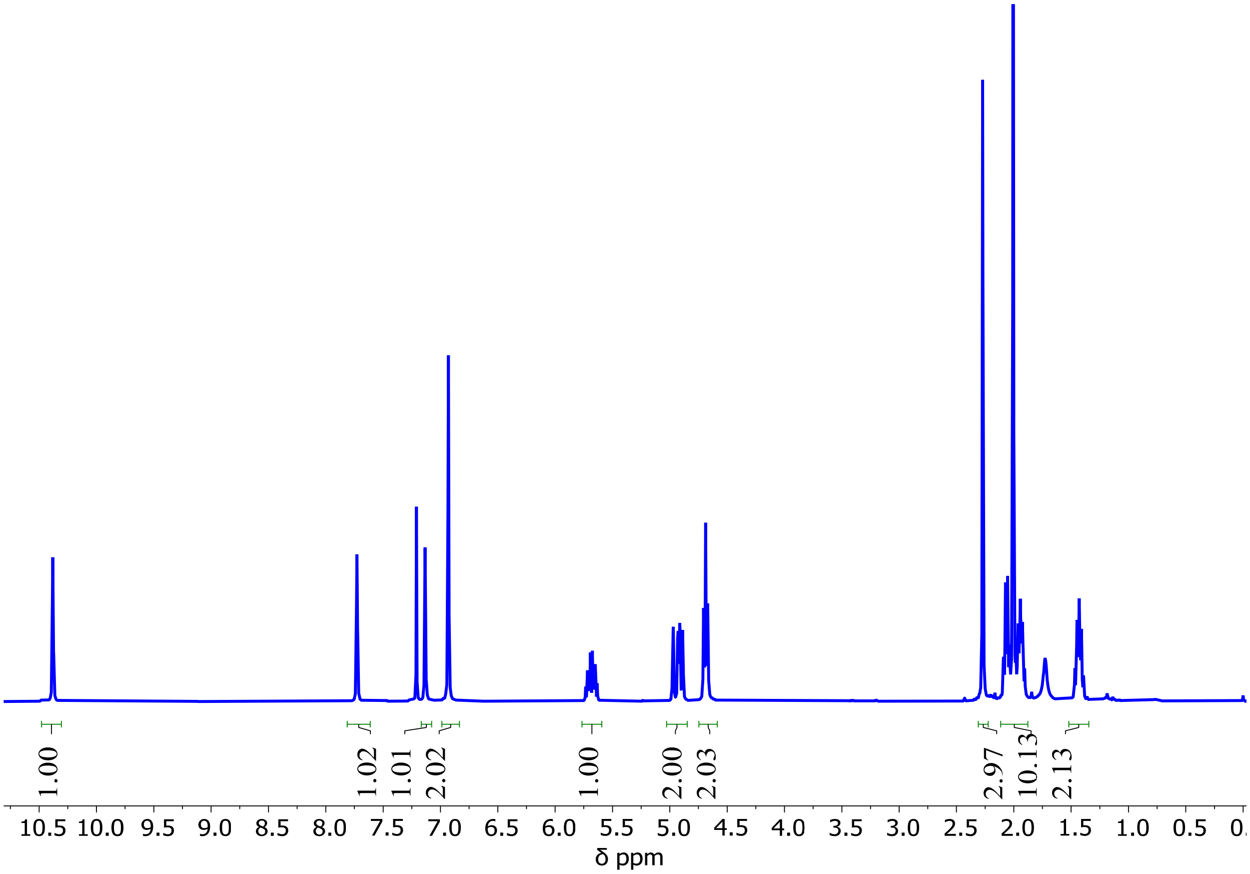


Figure S3. ^{1}H NMR spectrum of 3-(hex-5-en-1-yl)-1-mesityl-1H-imidazol-3-ium bromide.

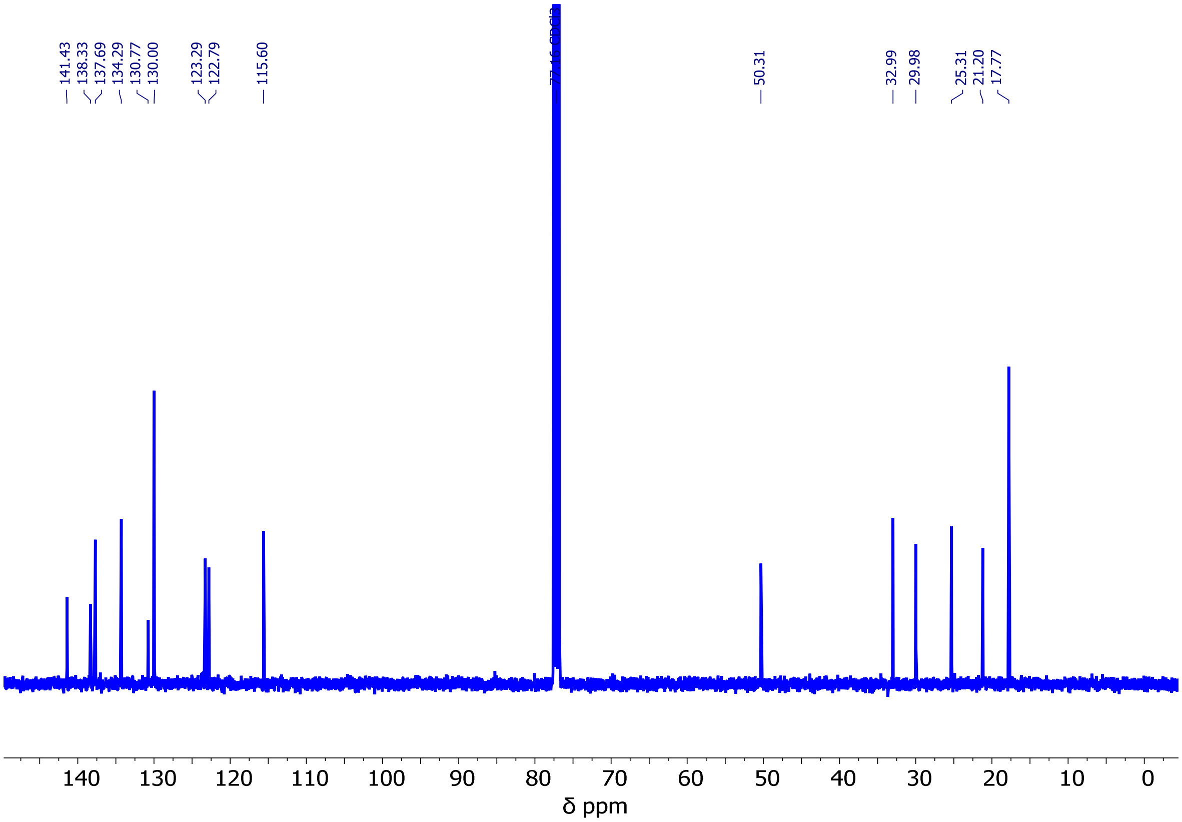
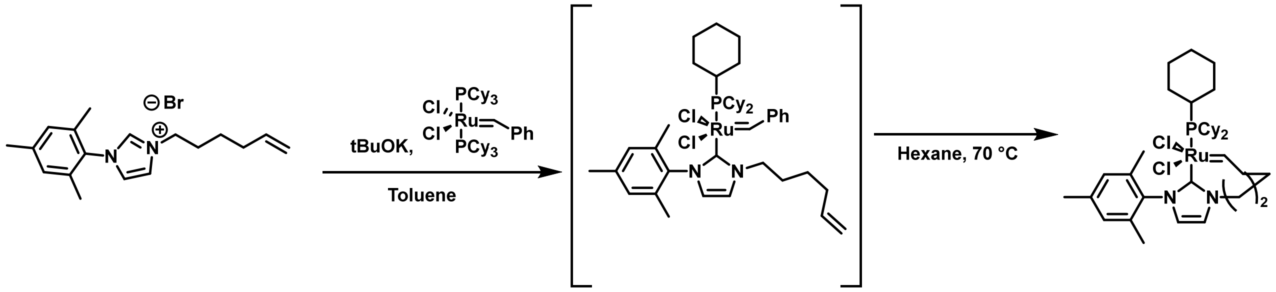


Figure S4. ^{13}C NMR spectrum of 3-(hex-5-en-1-yl)-1-mesityl-1H-imidazol-3-ium bromide.

Synthesis of REMP Grubbs Catalyst:



In a nitrogen filled glovebox, 3-(hex-5-en-1-yl)-1-mesityl-1H-imidazol-3-ium bromide (200 mg, 0.57 mmol) was weighed into a 50 mL Schlenk vial with a stir bar. Potassium tertiary butoxide (64 mg, 0.57) and 5 mL toluene were added, and the reaction was sonicated for 1 hour outside the glovebox. Then the reaction was stirred for another hour and Grubbs catalyst first generation (253 mg, 0.29 mmol) was weighed and added inside the glovebox to the flask. After 2 hours, the reaction was added to a pad of silica (10 g) and eluted with 5 mL of diethyl ether into a 500 mL Schlenk flask. The solvent was removed under a high vacuum to reveal a pinkish solid. The solid was dissolved in 2 mL toluene and then suspended in 300 mL hexanes. The reaction was refluxed at 70 °C outside the glovebox for one hour and a color change to light brown was observed. The reaction was brought into the glovebox and filtered. The filtrate was concentrated under vacuum and the remaining solid was washed with hexane:diethyl ether (4:1). The remaining solid was dried under high vacuum to give a dark green solid with a yield of 54 mg.

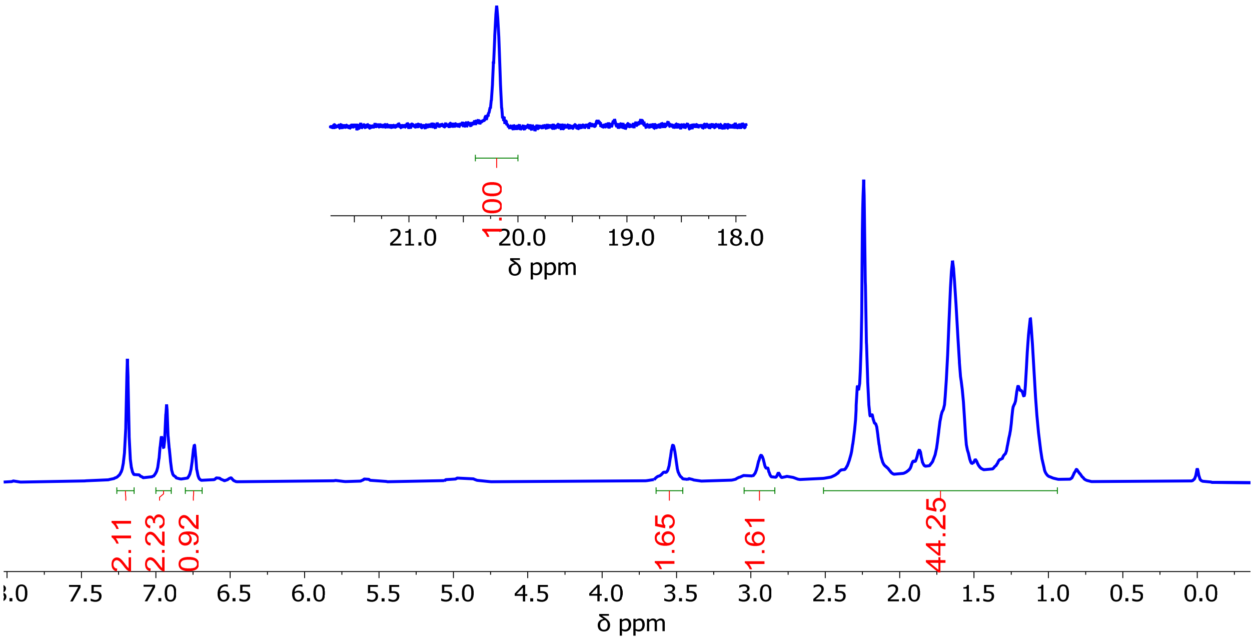


Figure S5. ^{1}H NMR spectrum of REMP catalyst.

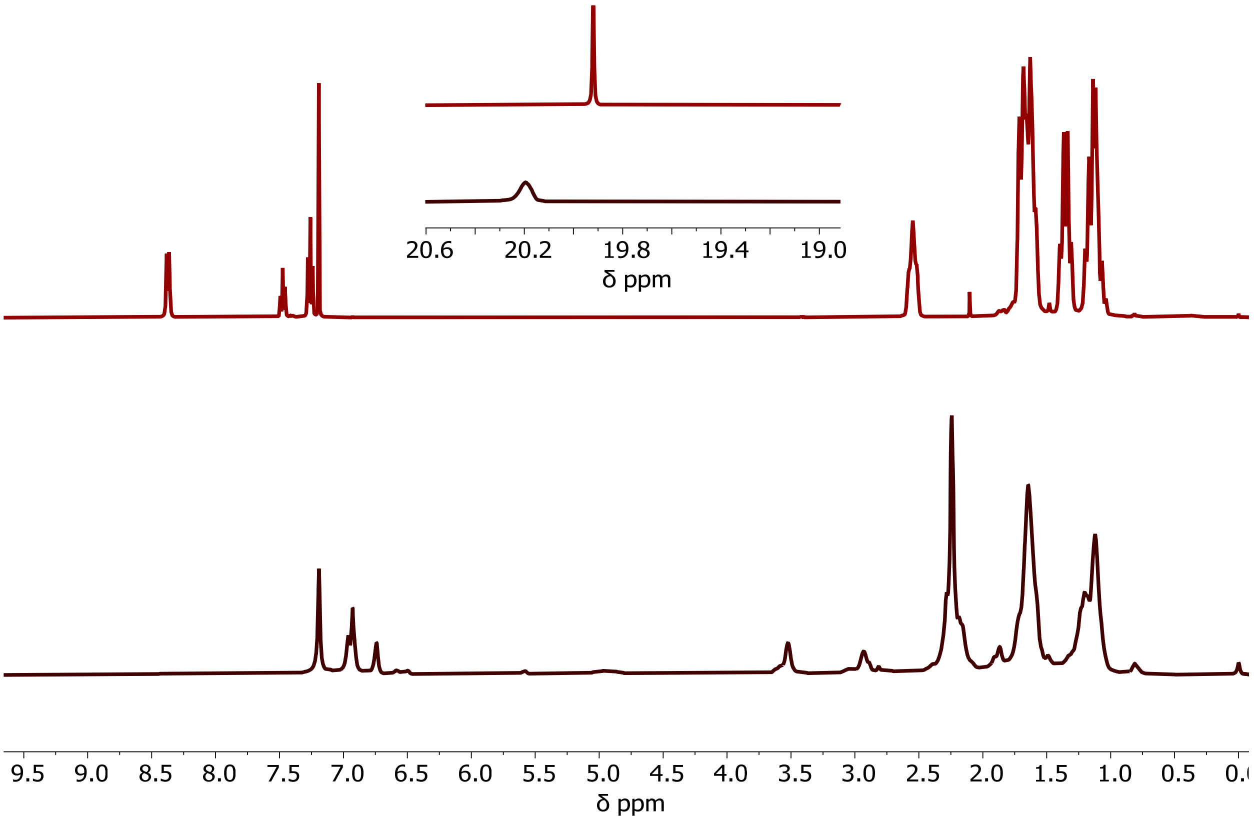
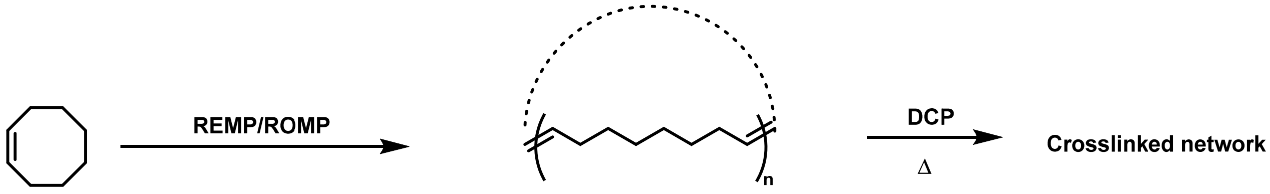


Figure S6. ^{1}H NMR spectrum of Grubbs first generation catalyst (top) and REMP catalyst (bottom).

Thiol-ene modification of polycyclocoetene

Cyclic polycyclooctene (100 mg, 0.91 mmol) was dissolved in 5 mL THF and sparged with nitrogen for 30 min. Methyl 3-mercaptopropionate (218 mg, 1.8 mmol) and DMPA (5 wt. %, 5 mg) were added and the reaction was exposed to UV light (355 nm) while stirring overnight. The next day the polymer was precipitated 3 times in methanol and dried under vacuum to afford a sticky white polymer.

Ring Opening Metathesis polymerization of cis-cyclooctene:



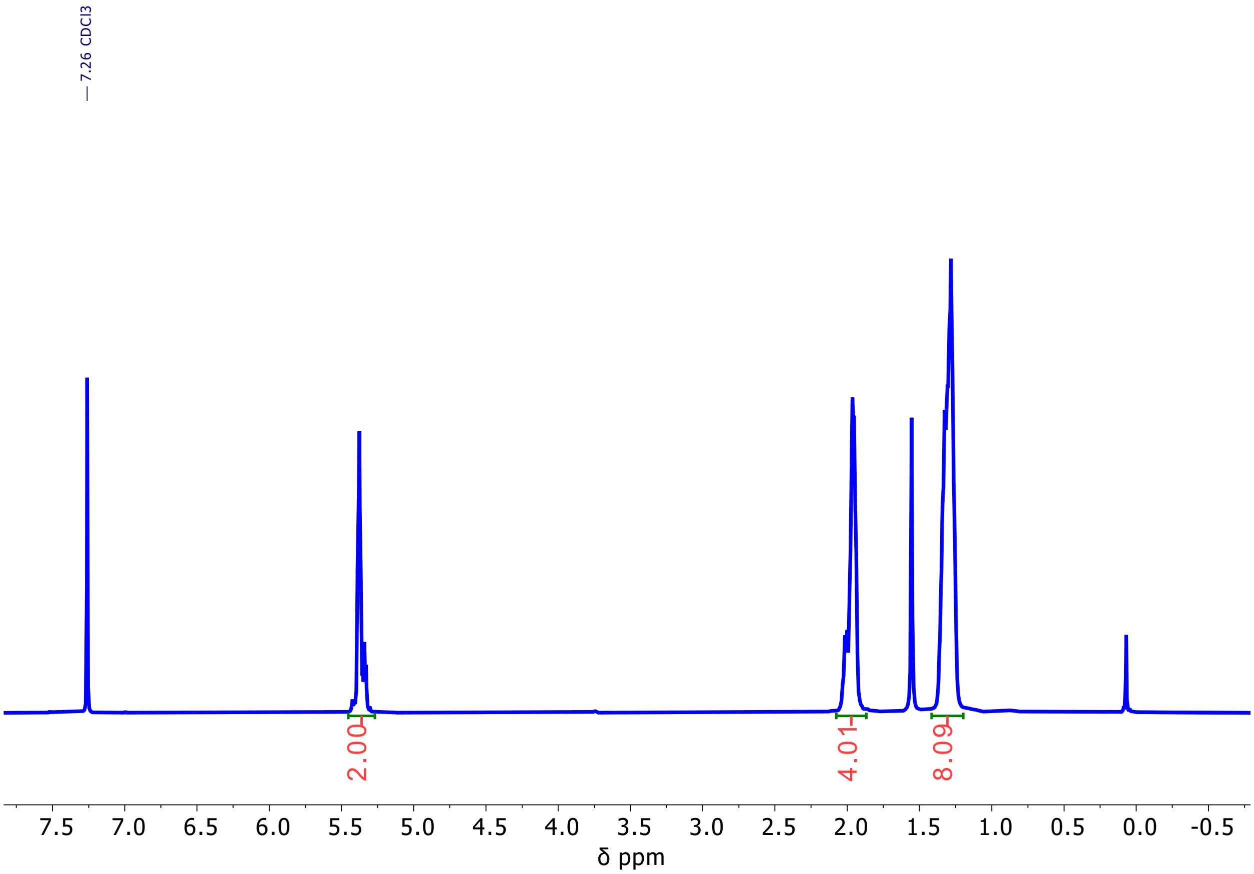


Figure S7. ^{1}H NMR spectrum of cyclic POCE.

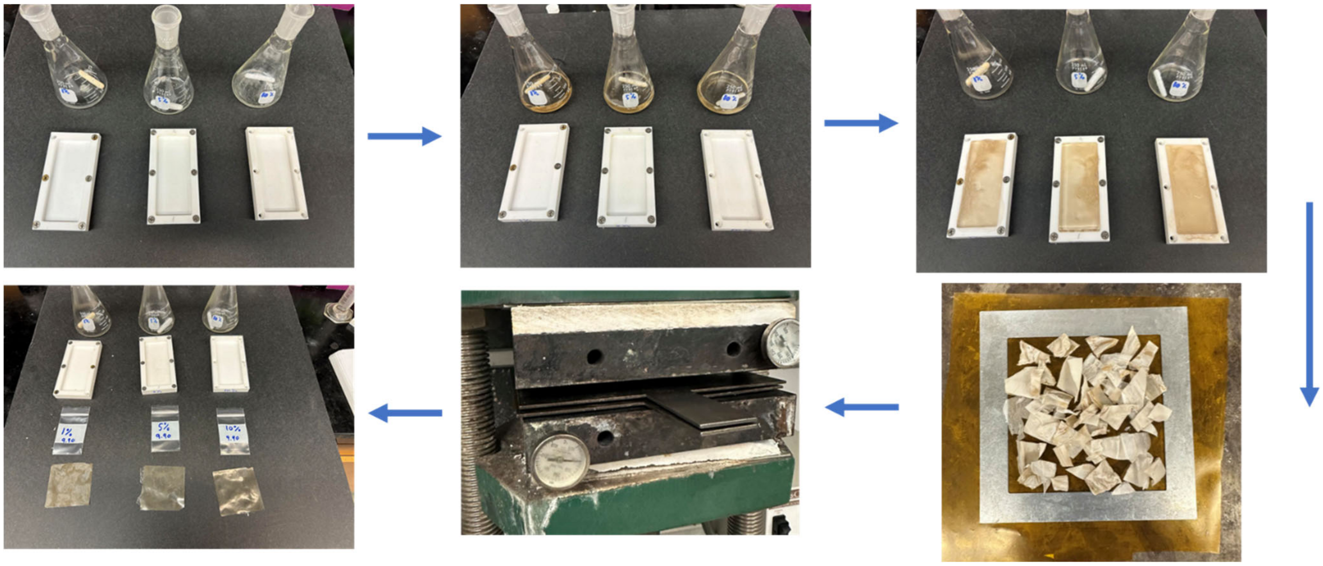


Figure S8. Optical images of the crosslinking process of PCOE into XL-PCOE.

Table S1. Polymerization results.

Sample	**Catalyst**	**[Cat.]:[CO]**	**Theoretical Mn (Da)**	**M_n (Da) (GPC)**	**Đ**
1	Grubbs-2	400	44080	67200	1.2
2		800	88160	91500	1.5
3		1200	132240	128000	1.4
4		5000	551000	660100	1.4
5		10000	1102000	999800	1.7
6		20000	2204000	Insoluble	-
7	Cyclic Grubbs	400	44080	62400	1.3
8		800	88160	92000	1.6
9		1200	132240	219000	1.5
10		5000	551000	598000	1.4
11		10000	1102000	884000	1.8

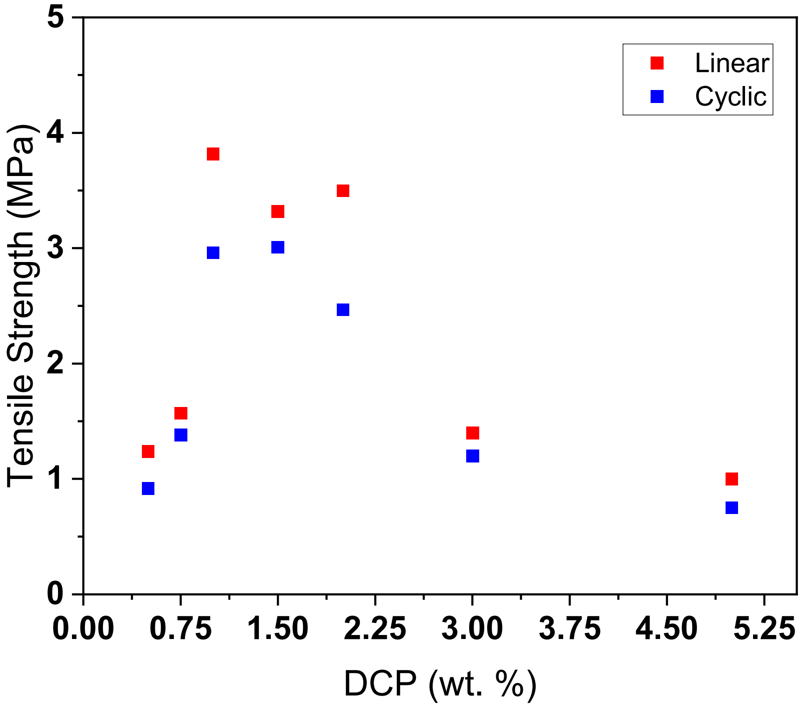
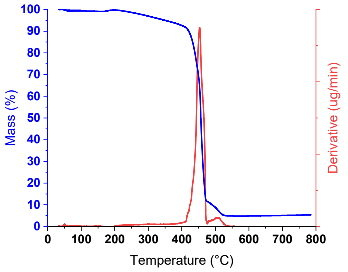
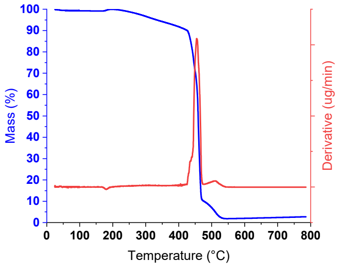
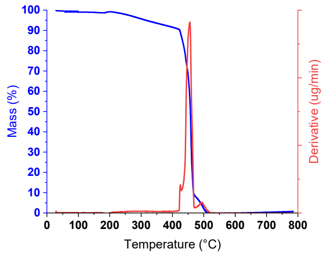


Figure S9. Comparison of the effects DCP has on tensile strength of cyclic and linear PCOE.







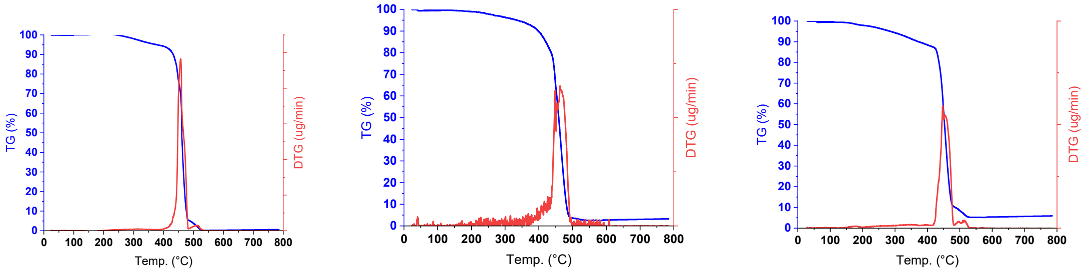


Figure S10. TGA curves for synthesized PCOE materials: (Top L to R) C-XL-0.75, C-XL-1.0, C-XL-1.5; (Bottom L to R) L-XL-0.75, L-XL-1.0, L-XL-1.5.

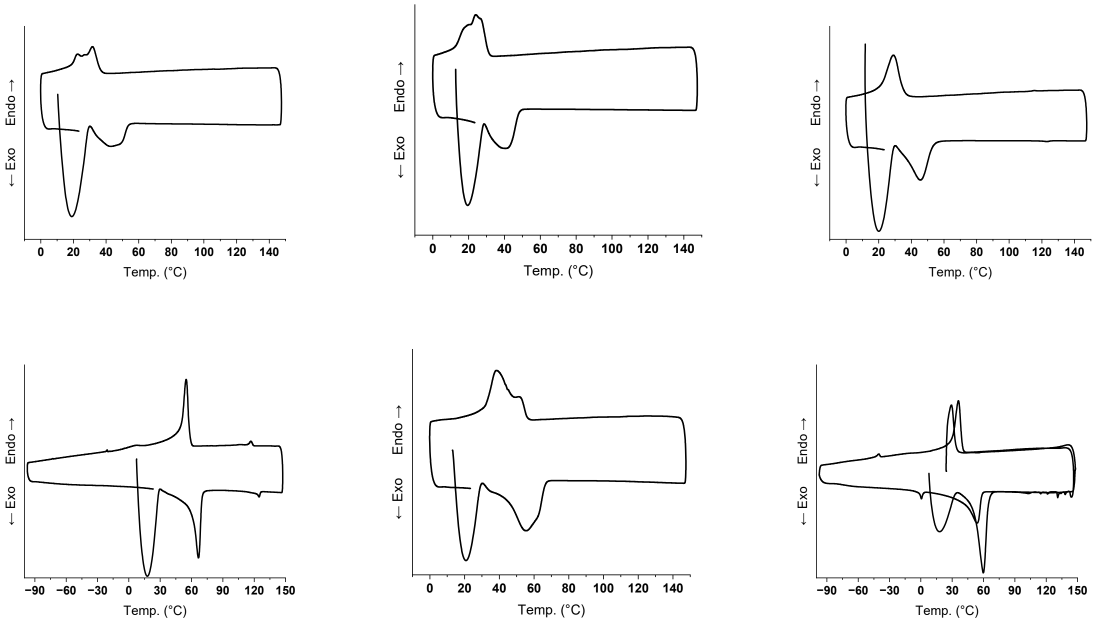


Figure S11. DSC curves for synthesized PCOE materials: (Top L to R) C-XL-0.75, C-XL-1.0, C-XL-1.5; (Bottom L to R) L-XL-0.75, L-XL-1.0, L-XL-1.5.