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Depolymerizable Olefinic Polymers Based on Fused-Ring Cyclooctene Monomers

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Abstract

The growing consumption of synthetic polymers and the accumulation of polymer waste have led to a pressing need for new routes to sustainable materials. Achieving a closed-loop polymer economy *via* chemical recycling to monomer (CRM) is one such promising route. Our group recently reported a new CRM system based on polymers prepared by ring-opening metathesis polymerization (ROMP) of *trans*-cyclobutane fused cyclooctene (*t*CBCO) monomers. This system offers several key advantages, including the ease of polymerization at ambient temperatures, quantitative depolymerization to monomers under mild conditions, and a broad range of functionalities and thermomechanical properties. Here, we outline detailed protocols for the preparation of *t*CBCO-based monomers and their corresponding polymers, including the preparation of elastic polymer networks and compression molding of linear thermoplastic polymers. We also outline the preparation of high ring strain *E*-alkene *t*CBCO monomers and their living polymerization. Finally, the procedures for the depolymerization of linear polymers and polymer networks are also demonstrated.

Introduction

The versatile and robust nature of synthetic polymers has made them a ubiquitous fixture of modern human existence. On the flip side, the same robust and environmentally resistant properties make polymer waste exceedingly persistent. This, together with the fact that a large fraction of all synthetic polymers ever made has ended up in landfills[1], has raised legitimate concerns about their environmental effects[2]. Additionally, the open-loop nature of the traditional polymer economy has caused a steady consumption of petrochemical resources and a mounting carbon footprint[3]. Promising routes to a closed-loop polymer economy are, thus, highly sought after.

Chemical recycling to monomer (CRM) is one such route. The advantage of CRM over traditional recycling is that it leads to the regeneration of monomers that can be used to manufacture pristine polymers, as opposed to mechanical recycling of materials with deteriorating properties over multiple processing cycles. Polymers based on ring-opening polymerizations have appeared as especially attractive routes to CRM materials[4]. The thermodynamics of polymerization

is typically an interplay between two opposing factors: the enthalpy of polymerization (ΔH_p, which is typically negative and favors polymerization) and the entropy of polymerization (ΔS_p, which is also typically negative but disfavors polymerization), with the ceiling temperature (T_c) being the temperature at which these two factors balance each other out[5]. For a polymer to be capable of CRM under practical and economically beneficial conditions, the right balance of ΔH_p and ΔS_p must be achieved. Cyclic monomers allow a convenient means to tune these factors *via* the selection of the appropriate ring size and geometry, since here, ΔH_p is primarily determined by the ring strain of the cyclic monomers[4,5]. As a result, CRM polymers with a wide variety of monomers have been reported of late[6,7,8,9,10,11]. Out of these systems, ROMP polymers prepared from cyclopentenes are particularly promising due to the rather cheap starting material required and the hydrolytic and thermal stability of the polymers. Additionally, in the absence of a metathesis catalyst, the depolymerization is kinetically unfeasible, affording high thermal stability despite a low T_c[12]. However, cyclopentenes (and other monomers based on small cyclic structures) pose a key challenge-they cannot be readily functionalized, as the presence of functional groups on the backbone can affect the thermodynamics of polymerization in drastic, and sometimes unpredictable, ways[13,14].

Recently, we reported a system that overcomes some of these challenges[15]. Inspired by examples of low-strain fused ring cyclooctenes in the literature[16,17], a new CRM system was designed based on ROMP polymers of *trans*-cyclobutane fused cyclooctenes (*t*CBCO) (**Figure 1A**). The *t*CBCO monomers could be prepared at a gram scale from the [2+2] photo cycloadduct of maleic anhydride and 1,5-cyclooctadiene, which could be readily functionalized to achieve a diverse set of substituents (**Figure 1B**). The resulting monomers had ring strains comparable to cyclopentene (~5 kcal·mol^{-1}, as calculated using DFT). Thermodynamic studies revealed a low ΔH_p (−1.7 kcal·mol^{-1} to −2.8 kcal·mol^{-1}), which was offset by a low ΔS_p (−3.6 kcal·mol^{-1}·K^{-1} to −4.9 kcal·mol^{-1}·K^{-1}), allowing the preparation of high molecular weight polymers (at high monomer concentrations) and near quantitative depolymerization (>90%, under dilute conditions) at ambient temperatures in the presence of Grubbs II catalyst (**G2**). It was also demonstrated that materials with diverse thermomechanical properties could be obtained while preserving the ease of polymerization/depolymerization. This ability was further exploited to prepare a soft elastomeric network (which could also be readily depolymerized), as well as a rigid thermoplastic (with tensile properties comparable to polystyrene).

One drawback with this system was the need for high monomer concentrations to access high molecular weight polymers. At the same time, due to extensive chain transfer and cyclization reactions, the polymerization was uncontrolled in nature. This was addressed in a subsequent work *via* photochemical isomerization of the *Z*-alkene in the *t*CBCO monomers to prepare highly strained *E*-alkene *t*CBCO monomers[18]. These monomers could be rapidly polymerized in a living manner at low initial monomer concentrations (≥25 mM) in the presence of Grubbs I catalyst (**G1**) and excess triphenylphosphine (PPh_3). The polymers could then be depolymerized to yield the *Z*-alkene form of the monomers. This has created opportunities to access new depolymerizable polymer architectures, including block copolymers and graft/bottlebrush copolymers.

In this work, detailed protocols are outlined for the synthesis of *t*CBCO monomers with different functional groups and their polymerization, as well as the depolymerization of the resulting polymers. Additionally, protocols for the preparation of dogbone samples of a soft elastomeric network and their depolymerization, as well as compression molding of the *N*-phenylimide substituted rigid thermoplastic polymer, are also described. Finally, protocols for the photoisomerization of a *t*CBCO monomer to its strained *E*-alkene *t*CBCO form and its subsequent living ROMP are also discussed.

Protocol

NOTE: The protocols outlined below are detailed forms of experimental procedures reported previously[15,18,19]. Characterization of the small molecules and polymers has been reported previously[15,18]. Additionally, syntheses of monomers and polymers and depolymerization of polymers should be performed inside a fume hood with appropriate personal protective equipment (PPE), including nitrile gloves, safety glasses, and a lab coat.

1. *t*CBCO monomer preparation[15]

1. [2+2] photoaddition
    1. To a quartz tube, add maleic anhydride (5.4 g, 55.1 mmol, 1 equiv.), cyclooctadiene (7.42 mL, 6.55 g, 61 mmol, 1.1 equiv.), and 150 mL of dry acetone.
    2. Seal the quartz flask with a rubber septum and insert a 6-in needle connected to the N_2 on a Schlenk line, and a smaller bleed needle. Stir the solution on a magnetic stir plate while bubbling with N_2 for ~30 min. Remove the needles following this.
    3. Equip the photoreactor with 300 nm lamps, and place the flask in it, clamped to a vertical support. Make sure to loosely cover the top of the photoreactor to shield the outside from UV radiation and turn on the cooling fan and UV lamps.
    4. After irradiating overnight, concentrate the mixture on a rotavap until most of the solvent is removed (heating bath of the rotavap set at ~40 °C, a vacuum of ~400-500 mbar). Some insoluble by-products may also be found attached to the wall of the quartz tube.
    5. Use the crude compound **1** obtained after solvent removal for the next step without further purification.
2. Methyl ester-acid **2**
    1. Suspend the crude compound **1** in 150 mL of methanol in a single neck round-bottom flask equipped with a condenser.
    2. Reflux the mixture in an oil bath over a stirring hotplate for 5 h and then allow it to cool down to room temperature (RT).
    3. Filter the resulting suspension and concentrate the filtrate on a rotavap (heating bath at ~45 °C, vacuum <300 mbar). During the reflux, the reaction suspension gradually becomes a homogeneous clear system with a chunk of insoluble side products.
    4. Purify the crude compound **2** through column chromatography using 3:7 ethyl acetate/hexane as the eluent (a general procedure for column chromatography is provided in section 2).
    5. Further, purify product **2** by recrystallization (recrystallization is performed using established techniques[20]) from a saturated solution in ethyl acetate (EA)/hexanes (~30% v/v EA) to remove isomers from the photoreaction, yielding the methyl

ester-acid **2** as a crystalline white powder (overall yield: 1.7 g, ~12.9%).

3. Dimethyl ester monomer **M1**

    1. To a 50 mL round-bottom flask equipped, with a stir bar, add methyl ester-acid **2** (600 mg, 2.52 mmol, 1 equiv.), 4-dimethylaminopyridine DMAP (61 mg, 0.5 mmol, 0.2 equiv.), methanol (0.2 mL, 0.161 mg, 5.04 mmol, 2 equiv.), and dry dichloromethane DCM (25 mL).
    2. Place the flask in an ice bath and add 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl; 966 mg, 5.04 mmol, 2 equiv.) into the solution.
    3. Allow the mixture to warm to RT and stir on a magnetic stir plate overnight.
    4. Dilute the mixture with dichloromethane (DCM), add to a 250 mL separatory funnel together with brine (about 1/2 the volume of the DCM solution), and agitate the mixture; collect the organic phase (this brine wash helps remove aqueous impurities and water in the organic phase).
    5. Dry over sodium sulfate (Na_2SO_4): Place the solution in a conical flask and add Na_2SO_4 in portions while swirling the flask; repeat this until any Na_2SO_4 added further does not clump together.
    6. Filter this solution *via* gravity filtration through a filter paper (grade 2, pore size ~8 µm) placed in a funnel. Concentrate the solution on a rotavap with the heating bath at 40 °C and under a vacuum of ~650-700 mbar (decrease the vacuum as the solution concentrates and solvent evaporation slows down but ensure that the solution does not boil aggressively to avoid splashing and contamination of the rotavap fixtures).
    7. Purify the crude product *via* column chromatography, using a 1:4 EA/hexanes mixture as eluent, and concentrate on a rotavap (heating bath at 40 °C, 240-300 mbar vacuum) to obtain compound **M1** as a white solid (509 mg, yield: 80%).

4. Diacid **4**

    1. To a 50 mL round-bottom flask equipped with a stir bar, add a solution of sodium hydroxide (NaOH) (1.68 g, 42 mmol, 16.7 equiv.) in water (20 mL) followed by 600 mg of methyl ester-acid **2** (600 mg, 2.52 mmol, 1 equiv.).
    2. Stir the reaction mixture at 60 °C for ~14 h.
    3. Once the reaction is complete, cool to RT and place the flask in an ice bath; add 3 M HCl until the solution is neutralized (as verified using a strip of pH paper).
    4. Extract the mixture with ~150 mL of EA (x5) in a separatory funnel and dry the organic layer over Na_2SO_4 (for the drying procedure, see the synthesis of **M1**).
    5. Remove the Na_2SO_4 by gravity filtration, and wash the residue trapped in the funnel with additional EA (x3).
    6. Concentrate on a rotavap (heating bath at ~40 °C, ~150-200 mbar vacuum, decreasing the vacuum to ensure a steady rate of solvent evaporation) to yield the diacid **3** as a white solid (yield: 470 mg, ~83.2%)

5. Dibutyl ester monomer **5**

    1. To a 50 mL round-bottom flask equipped with a stir bar, add diacid **4** (941 mg, 4.20 mmol, 1 equiv.), 4-dimethylaminopyridine (DMAP; 205.5 mg, 1.68

mmol, 0.4 equiv.), *n*-butanol (0.845.7 mL, 684.9 mg, 9.24 mmol, 2.2 equiv.), and dry DCM (60 mL).

2. Cool the flask in an ice bath and add EDC·HCl (3220.06 mg, 16.8 mmol, 4.0 equiv.) into the solution.
3. Allow the mixture to warm to RT and stir overnight (~12 h) for the completion of the reaction.
4. Dilute the mixture with ~120 mL of DCM, and wash with ~200 mL of brine in a 500 mL separatory funnel (to perform a brine wash, see the procedure for the synthesis of **M1**).
5. Dry over Na_2SO_4, filter (to dry and filter the solution, see the procedure for the synthesis of **M1**), and concentrate on a rotavap (heating bath at ~40 °C and a vacuum of ~600-700 mbar).
6. Purify the crude product mixture *via* column chromatography, using a 1:9 EA/hexanes mixture as eluent.
7. Remove the solvent on a rotavap (heating bath at ~40 °C, ~240-300 mbar vacuum) to obtain the product **M2** as a clear, colorless oil (yield: 540 mg, 38.3%).

6. Anhydride **1**
    1. To a 50 mL round-bottom flask equipped with a stir bar, add the diacid **3** (2.00 g, 8.92 mmol, 1 equiv.) and 20 mL of acetic anhydride.
    2. Heat the suspension to reflux (~140 °C) and keep it at that temperature overnight (around 14 h).
    3. To remove acetic anhydride, perform vacuum distillation.
        1. To the flask with the reaction mixture, attach a short path distillation apparatus with a receiving flask, and connect it to the vacuum (with the vacuum line closed initially). Place the reaction flask in an oil bath and turn on the vacuum (a vacuum below 1,000 mTorr is preferable).
        2. Collect any vapors that come over at RT, increasing the temperature gradually ~10 °C at a time (the upper limit will depend on the strength of the vacuum) until the reaction mixture is dry.
    4. Use the anhydride **1** for the next step directly without further purification.

7. Imide monomer **M3**
    1. Dissolve the anhydride **1** (1.84 g, 8.92 mmol, 1.0 equiv.) in acetone (8 mL), and add aniline (1.63 mL, 17.84 mmol, 2.0 equiv.) dropwise.
    2. Allow the reaction to proceed for about 3 h followed by suction filtration. To perform suction filtration, place a Büchner funnel on an Erlenmeyer flask with a barb and connect it to the vacuum. Turn on the vacuum and filter the reaction mixture as usual.
    3. Wash the solid with a small amount of acetone and dry in a vacuum to obtain the amic acid as a white solid (yield: 2.5 g, 72%).
    4. Add the amic acid along with sodium acetate (1.10 g, 13.38 mmol, 1.5 equiv.) to a 50 mL round-bottom flask, followed by 15 mL of acetic anhydride.
    5. Stir the resulting suspension at 100 °C overnight (it will gradually become clear).
    6. Pour the mixture into 100 mL of cold water and allow to stir for 30 min.
    7. Perform suction filtration and wash the white residue with 50 mL of water 3x, then redissolve it in 100 mL

of DCM and dry over Na_2SO_4 (to dry and filter the solution, see the procedure for the synthesis of **M1**).

8. After filtration and removal of the solvent using a rotavap (heating bath at ~40 °C and a vacuum of ~600-700 mbar), purify the crude product *via* column chromatography using DCM as eluent and further purify *via* recrystallization[20] from toluene solution to yield imide monomer **M3** as white crystals (yield: 1.2 g, ~47.6%).

8. Crosslinker **XL**

1. To a round-bottom flask equipped with a stir bar, add ester-acid 2 (624.0 mg, 2.62 mmol, 1.0 equiv.), DMAP (64.1 mg, 0.5 mmol, 0.2 equiv.), 1,4-butanediol (111.8 mg, 1.24 mmol, 0.47 equiv.), and dry DCM (50 mL).
2. Place the flask in an ice bath and add EDC·HCl (1000.0 mg, 5.22 mmol, 2.0 equiv.) into the solution.
3. Allow the mixture to warm to RT and stir overnight.
4. Dilute the mixture with ~100 mL of DCM, and wash with ~150 mL of brine in a separatory funnel (to perform a brine wash, look at the procedure for the synthesis of **M1**).
5. Dry over Na_2SO_4, filter (to dry and filter the solution, see the procedure for the synthesis of **M1**), and concentrate on a rotavap.
6. Purify the crude product mixture *via* column chromatography, using a 3:7 EA/hexanes mixture as eluent.
7. Remove the solvent on a rotavap and using a high vacuum (heating bath at ~40 °C, ~240-300 mbar vacuum) to obtain the crosslinker **XL** as a white solid (yield: 239 mg, ~32.0 %).

2. Column chromatography

NOTE: The following is a general procedure for column chromatography as performed for the compounds described herein.

1. Prepare the crude product for loading: Dissolve the crude product in a small amount of eluent, add ~2x-3x the weight of the crude product in silica, and rotavap to remove solvent until the mixture forms a free-flowing powder.
2. Clamp a glass column containing a 24/40 ground glass joint on the top vertically and add a cotton plug to it to prevent the silica from leaking.
3. Weigh out ~40x-60x the weight of the crude product in silica, prepare a slurry in the eluent, and pour this into the glass column.
4. Drain the column until the solvent reaches the top of the silica and gently tap the column to pack the silica.
5. Load the crude product mixture from step 2.1 into the column using a funnel and add the eluent into the column.
6. Collect the fractions in 20 mL test tubes and monitor with thin layer chromatography (TLC) to identify fractions containing pure isolated products[21].

   NOTE: The column size is determined by the amount of silica being used. For silica loading of ~40-100 g, a column with a 28 mm diameter is used. For larger loadings, a 40 mm diameter column is used.

3. Photochemical Isomerization[18]

NOTE: The photoisomerization was adapted from a literature procedure[22].

1. To a circulation column, add cotton and silver nitrate ($AgNO_3$)-impregnated silica gel[22] (2.84 g of $AgNO_3$, 16.72 mmol, 2 equiv.). Fill the rest of the column with untreated silica gel to prevent the $AgNO_3$ from leaking, followed by adding another piece of cotton.
2. Wrap the column with aluminum foil and connect with tubing on either end. Connect one end of the column to a metering pump for circulation, with another piece of tubing coming out of the metering pump.
3. Put either end of the tubing into a flask with 200 mL of 2:3 v/v Et_2O/hexane and circulate for 2 h to pack the column tight and check any possible leaking.
4. Meanwhile, dissolve **M1** (2.81 g, 8.36 mmol, 1 equiv.) and methyl benzoate (2.27 g, 16.72 mmol, 2 equiv.) in a 2:3 v/v diethyl ether (Et_2O)/hexane solvent mixture in a quartz tube. Equip the photoreaction chamber with 254 nm wavelength lamps.
5. After confirming that the column is not leaking, replace the flask with the quartz tube, place it in the photoreaction chamber, and continue circulation (flow rate of ~10 mL/min) with the quartz tube under irradiation for 16 h. The reaction setup at this stage is shown in **Figure 3**.
   NOTE: The circulation column should be oriented such that the reaction mixture flows first through the $AgNO_3$-impregnated silica gel, followed by the untreated silica gel sequentially.
6. Pull the tubing up above the solution level after turning off the photoreactor and circulate for an additional 1 h to dry the column. Meanwhile, pack another column with a silica gel layer at the bottom and the $AgNO_3$-impregnated silica gel (2.84 g) at the top.
7. Empty the circulation column and load its contents to the silica column packed in step 3.6. Collect and concentrate the solution from the quartz tube; also add this to the silica column packed in step 3.6.
8. Wash the column with 2:3 v/v Et_2O/hexane (5x the volume of the stationary phase) to collect methyl benzoate and **M1**, followed by washing with acetone (5x the volume of the stationary phase) to collect ***E*M1** silver ion complex.
9. After acetone is removed on a rotavap, add a mixture of 200 mL of DCM and 200 mL of concentrated aqueous ammonia to the residue and stir for 15 min.
10. Collect the organic phase, wash it with water and brine solution in a separatory funnel. Dry the organic phase over Na_2SO_4, filter, and concentrate the filtrate.
11. Purify the crude mixture *via* column chromatography using a 2:3 Et_2O/hexane mixture as the eluent. Remove the solvent on a rotavap and dry under a high vacuum while placed in a liquid nitrogen bath to obtain pure ***E*M1** as a white solid (yield: 0.93 g, ~33%).NOTE: The liquid nitrogen bath is used here to freeze-dry the monomer. A dry ice/acetone bath may also be used for this purpose; the use of cryoprotective gloves is advised.

4. Polymer synthesis

1. Synthesis of linear polymers by conventional ROMP[15]
   NOTE: Polymers were synthesized through ring-opening metathesis polymerization (ROMP) of corresponding monomers *via* an identical procedure. The procedure is described below using **P1** as an example.

1. Dissolve dimethyl ester monomer **M1** (459 mg, 1.82 mmol, 1 equiv.) in DCM (400 µL) in a 3-dram vial equipped with a stir bar.
2. To the monomer solution, add 59 µL of a Grubbs II catalyst (**G2**) stock solution (concentration: 52.37 mg/mL, amount of **G2**: 3.09 mg, 0.00364 mmol, 0.002 equiv.) in DCM.
3. Allow the mixture to stir for 6 h at RT and quench by adding ethyl vinyl ether (300 µL) and stirring for another 30 min.
4. Dilute the mixture with 5 mL of DCM and add the catalyst scavenger (see the **Table of Materials** for details) particles (350 mg).
5. After stirring overnight, filter the suspension through a Celite plug and concentrate on a rotavap (water bath at ~40 °C, 600-700 mbar vacuum).
6. After precipitating twice in cold methanol and drying in a vacuum, obtain isolated polymer **P1** as a white solid.

2. Synthesis of linear polymers by living ROMP[18]

NOTE: Polymerization is conducted in an N_2-filled glovebox. Stock solutions of ***E*M1**, PPh_3 (triphenylphosphine), and **G1** in THF (tetrahydrofuran) are prepared in the glovebox. All vials and stir bars should be dried in an oven overnight before polymerization. Also, ensure that the working surfaces are free of **G1** since even small amounts of the catalyst may lead to unintended initiation of polymerization.

1. Prepare stock solutions for ***E*M1**, PPh_3, and **G1** in THF, respectively.
2. To a vial with a stir bar, add ***E*M1** (517 mg, 1.19 mmol, 1.0 equiv.) and PPh_3 (60.5 mg, 0.18 mmol, 0.15 equiv.) from their stock solutions, respectively.
3. Add additional THF such that the monomer concentration is 0.25 M.
4. Add **G1** (3.16 mg, 2.97 µmol, 0.0025 equiv.), and allow the mixture to stir for 10 min.
5. Add ethyl vinyl ether (1 mL) to quench the polymerization and stir the mixture for an additional 30 min. Precipitate the polymer thrice in methanol and dry on a vacuum line overnight.

3. Synthesis of polymer network **PN1**[15]

1. Add *t*CBCO monomer **M2** (660 mg, 1.8 mmol, 1 equiv.) and crosslinker **XL** (106.2 mg, 0.2 mmol, 0.11 equiv.) to a 4-dram glass vial. Add DCM (500 µL) to this and dissolve using a vortex mixer.
2. Add **G2** (3.4 mg, 0.004 mmol, 0.0022 equiv.) to this and agitate manually to ensure dissolution.
3. Using a glass pipette, add the solution to a polytetrafluoroethylene (PTFE) mold with six cavities (overall cavity dimensions: length 25 mm, width 8.35 mm, and depth 0.8 mm; gauge dimensions: length 5 mm, width 2 mm) (**Figure 4B**). Allow the network to cure at RT (24 h) and at −6 °C for 24 h.
4. Carefully remove the sample from the mold (a spatula may be used to pry a corner of the sample out of the cavity, and a pair of tweezers may be used to remove it). Submerge the sample in a 20 mL vial with ~5 mL of ethyl vinyl ether for 4 h.
5. Place the prepared sample in a cellulose thimble and place it in a Soxhlet extraction apparatus.

6. Affix the Soxhlet extractor onto a 500 mL round-bottom flask with 250 mL of $CHCl_3$ (chloroform) and place it in an oil bath. Attach a condenser to the top of the Soxhlet extractor.

7. Cover the arm of the extractor directing the flow of vapors from the flask to the condenser with aluminum foil for insulation. Allow the solvent to reflux for 14 h

8. Remove the sample from the thimble, place it on a piece of paper towel placed on a clean surface, cover (a small box with a lid may be used for this purpose), and allow the solvent to evaporate under ambient conditions for ~6 h.
   NOTE: Covering the sample is important to ensure gradual evaporation and prevent cracking of the sample as it dries.

9. Place the sample in a 20 mL vial and place it under a vacuum to dry completely, weighing periodically until no weight loss is detectable.

5. Depolymerization

1. Depolymerization of linear polymer (**P1**)[19]
   NOTE: Below is the general procedure for the depolymerization of linear *t*CBCO-based polymers.
   1. Place the polymer **P1** (30 mg, 0.119 mmol., 1 equiv.) in a 3-dram glass vial and dissolve it in 4706 µL of $CDCl_3$ (deuterated chloroform).
   2. Weigh **G2** (3 mg, 0.0035 mmol., 0.0297 equiv.) in a 1-dram glass vial and add 148.6 µL of $CDCl_3$ to dissolve it.
   3. Using a micropipette, add 50 µL of the solution of **G2** to the solution of **P1**. The total concentration of olefinic groups must be 25 mM. Split the vial's contents into three different vials, corresponding to three replicates.
   4. Place the vials in a water bath at 30 °C for ~16 h. Then, add 50 µL of ethyl vinyl ether to this to quench **G2**
      NOTE: The extent of depolymerization may be obtained using ^1H NMR spectroscopy from the ratio of the integration of the monomer olefin signal (5.5-5.8 ppm) to the sum of monomer and polymer/ oligomer olefin signals (5.2-5.3 ppm).

2. Depolymerization of the polymer network (**PN1**)[15]
   1. Calculate the olefinic groups per gram of polymer network. In the below example, the material consists of 90 mol% butyl ester monomer **M2** (M.W. = 366.47 g/mol) and 10 mol% crosslinker **XL** (M.W. = 530.65 g/mol). This results in **PN1** with 382.9 g/mol of olefin groups (or 2.61 mmol olefin groups per gram of **PN1**).
   2. Place the polymer network **PN1** (17.7 mg, 0.046 mmol, 1 equiv.) in a 1-dram glass vial and add 1.8 mL of $CDCl_3$ to it.
   3. Weigh **G2** (5 mg) in a 1-dram glass vial and add 256.1 µL of $CDCl_3$ to dissolve it.
   4. Add 40 µL of the solution of **G2** (corresponding to 0.92 µmol or 2 mol% of **G2**) to the vial with **PN1** submerged in $CDCl_3$. The total concentration of olefinic groups must be 25 mM.
   5. Place the vial with **PN1** and **G2** in a water bath at 50 °C for ~2 h. Then, add 100 µL of ethyl vinyl ether to this mixture to quench **G2**.

NOTE: The extent of depolymerization may be obtained using ^{1}H NMR spectroscopy from the ratio of the integration of the monomer olefin signal (5.5-5.8 ppm) to the sum of monomer and polymer/ oligomer olefin signals (5.2-5.3 ppm).

6. Preparation of tensile testing specimens for P3 [15]

1. Dissolve **P3** (1 g) in dichloromethane (3 mL) with butylated hydroxytoluene (BHT) (500 ppm with respect to the polymer) added to it.
2. Place the solution on a Petri dish lined with a polytetrafluoroethylene (PTFE) sheet and allow it to dry under ambient conditions (8 h). Place the Petri dish in a vacuum oven at 70 °C under vacuum overnight (~16 h).
3. Remove from the oven and allow the Petri dish to cool to RT. Remove the polymer from the PTFE sheet and crush it into smaller pieces
4. Preheat the top and bottom plates of a carver press to 150 °C and allow the temperature to equilibrate for 20 min. To specify the temperature set-point, press and hold the * button and increase or decrease the set point using the buttons with the upward or downward pointing arrows, respectively. Release the buttons for the set point to be fixed.
5. Cover a steel plate (100 mm x 150 mm x 1 mm) with a PTFE sheet and place the steel dogbone mold (**F**) on this. Fill the cavities of the mold with the polymer **P3**.
   NOTE: Overall dimensions of the mold cavity: length 20 mm, width 7 mm, and depth 1 mm; gauge dimensions: length 10 mm, width 3 mm.
6. Cover the mold with a PTFE sheet and another steel plate of the same dimensions as step 6.5.
   NOTE: Underfilling the mold cavities can lead to bubbles or defects in the dogbone samples.
7. Place the above mold assembly in the heated carver press and apply a load of about ~7,000 lb using the hand crank on the carver press.
8. Allow the mold to reach the desired temperature for 10 min followed by another 10 min for compression molding to be complete. Release the platens of the press and remove the mold assembly.
   NOTE: The mold will be very hot; use heat-resistant gloves and tongs to handle it.
9. Cool the mold assembly by running under cold water; remove the mold from the steel plates and PTFE sheet. Push out the samples by hand.

Representative Results

Discussed here are representative results previously published[15,18,19]. **Figure 5** shows the GPC traces for polymer **P1** prepared by conventional ROMP with **G2** (red curve)[15] and living ROMP of ***E*M1** with **G1**/**PPh$_3$** (black)[18]. The polymer prepared by living ROMP has a much narrower molecular weight distribution (M_n = 114.9 KDa, $Đ$ = 1.17) versus the rather broad distribution seen for the polymer prepared by conventional ROMP with **G2** (M_n = 142 KDa, $Đ$ = 1.55).

^{1}H NMR spectra for the depolymerization of linear (**P1**) and crosslinked (**PN1**) polymers are given in **Figure 6**. The extent of depolymerization of **P1** is measured by calculating the ratio of the integral of the peaks corresponding to monomeric olefinic protons with respect to the sum of the peak integrals of the monomer and residual oligomer olefinic protons (as indicated in **Figure 6A**). Under the dilute conditions and in the presence of 1 mol% **G2**, **P1** is depolymerized nearly

quantitatively (~93%). The extent of depolymerization of **PN1** is calculated similarly and amounts to ~94% (**Figure 6B**). It must be noted here that, for **PN1**, "monomers" refers to the mixture of monofunctional monomer and crosslinkers (**M2** and **XL**, respectively) obtained after depolymerization.

Figure 7 shows the representative tensile curves (these data are from previously published work[15]) for polymer **P3** and networks **PN1**. The presence of the flexible butyl chains in **M2** causes **PN1** to be a soft, elastomeric material with an ultimate tensile strain of ~0.64 MPa, modulus of ~ 0.76 MPa, and strain at break of ~226%.

On the other hand, polymer **P3** with the rigid phenyl imide substituent behaves like a rigid glassy material with an ultimate tensile strength of ~41.4 MPa and strain at break of ~3.4%. Tensile testing was performed for **P3** with an Instron Universal Testing Frame, while that for **PN1** was performed with a homemade tensile tester, both at a crosshead speed of 5 mm·min^{-1}.

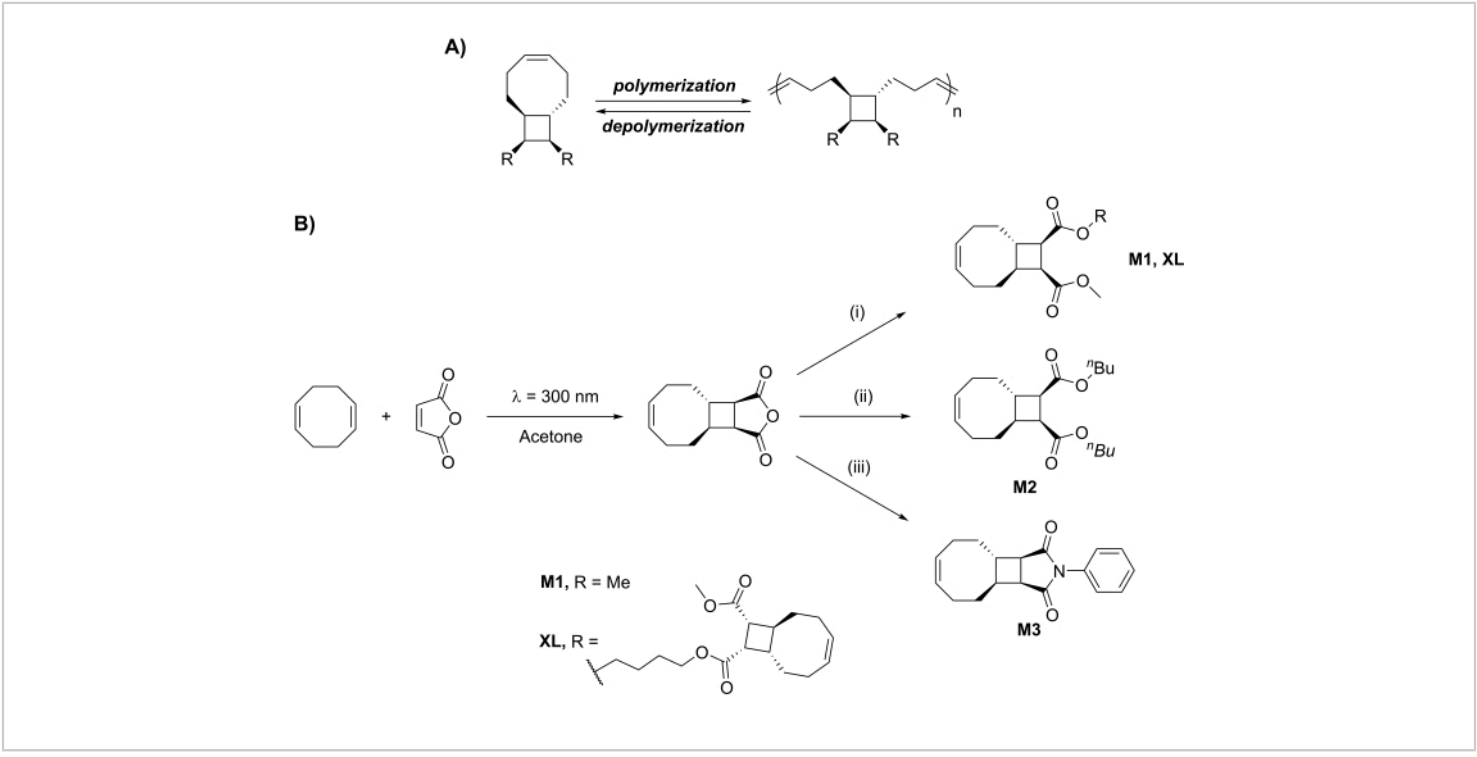

Figure 1: *t*CBCO monomers for depolymerizable olefinic polymers. (**A**) *t*CBCO monomers for chemically recyclable polymers. (**B**) Synthesis of *t*CBCO monomers. Photochemical [2 + 2] cycloaddition of 1,5-cyclooctadiene and maleic anhydride affords the anhydride **1**, which can be readily converted to **M1 and XL**, **M2**, and **M3** through conditions (i), (ii), and (iii), respectively. (i) **M1**: MeOH, reflux; MeOH, EDC, DMAP, DCM; **XL**: 1,4-butanediol, EDC, DMAP, DCM. (ii) **M2**: NaOH, H_2O, 60 °C; 1-butanol, EDC, DMAP, DCM. (iii) **M3**: aniline, acetone; sodium acetate, acetic anhydride, 100 °C. Please click here to view a larger version of this figure.

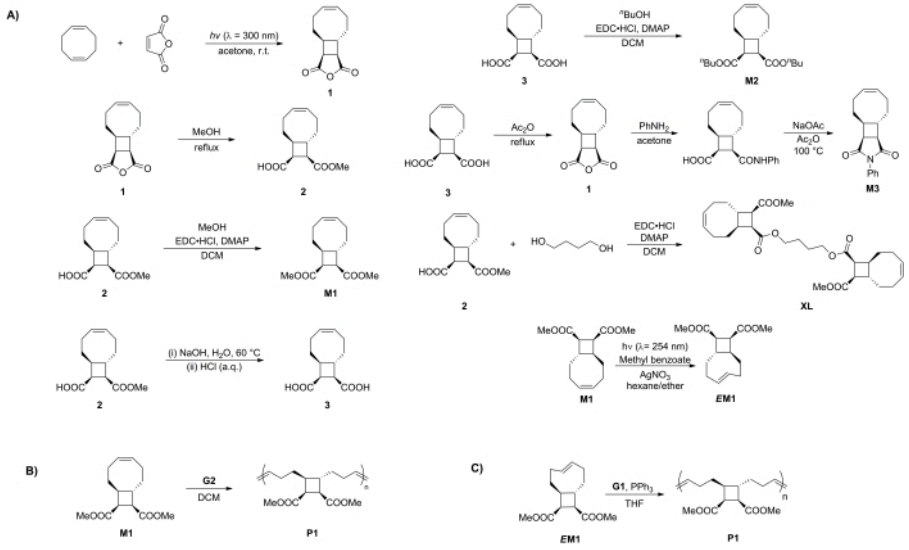

Figure 2: Reaction schemes for small molecule and polymer synthesis outlined in this work. (**A**) Synthesis of *t*CBCO small molecules and monomers. (**B**) Synthesis of **P1** by conventional ROMP. (**C**) Synthesis of **P1** by living ROMP. Please click here to view a larger version of this figure.

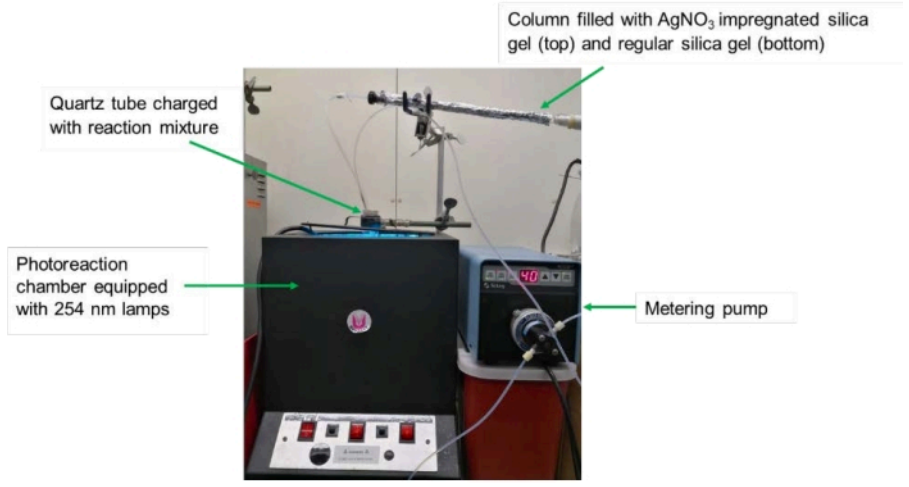

Figure 3. Reaction setup for photochemical isomerization of M1. The photoisomerization of **M1** to ***E*M1** involves irradiation under flow conditions, and the setup consists of a photoreactor housing the quartz reaction tube, a column packed with $AgNO_3$-impregnated silica (to trap the product), and a metering pump to enable the flow of the reaction mixture. Please click here to view a larger version of this figure.

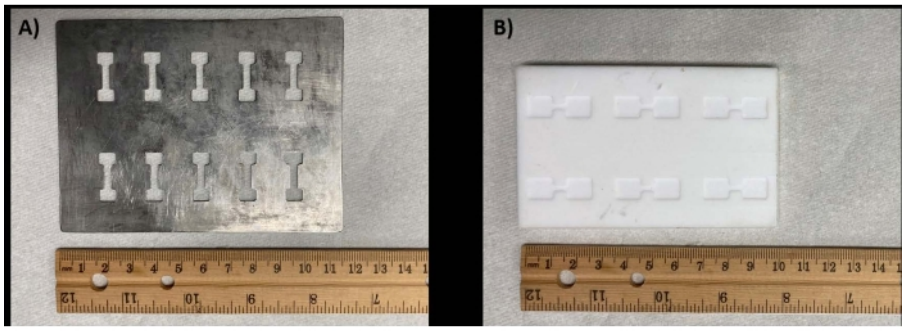

Figure 4: Molds used for compression molding of P3 and preparation of PN1. (**A**) Steel mold for compression molding of **P3** and (**B**) PTFE mold for curing elastomer network **PN1**. Please click here to view a larger version of this figure.

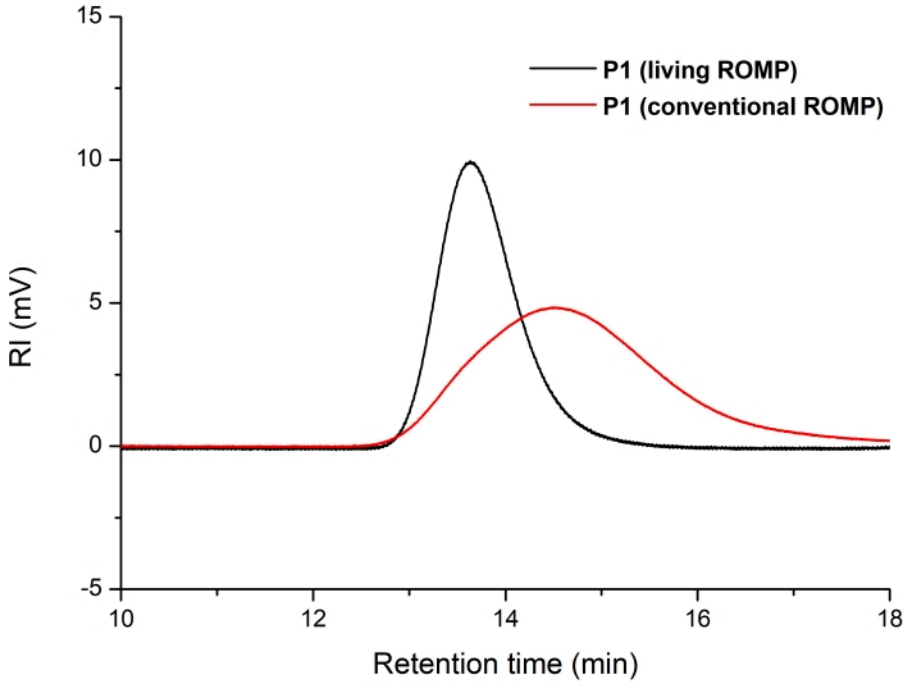

Figure 5: GPC traces for polymer. GPC traces for polymer **P1** prepared by living ROMP in the presence of **G1** and PPh_3 (black) and conventional ROMP in the presence of **G2** (red). This figure has been prepared from previously published data (red trace from Sathe *et al.*[15], black trace from Chen et al.[18]). Please click here to view a larger version of this figure.

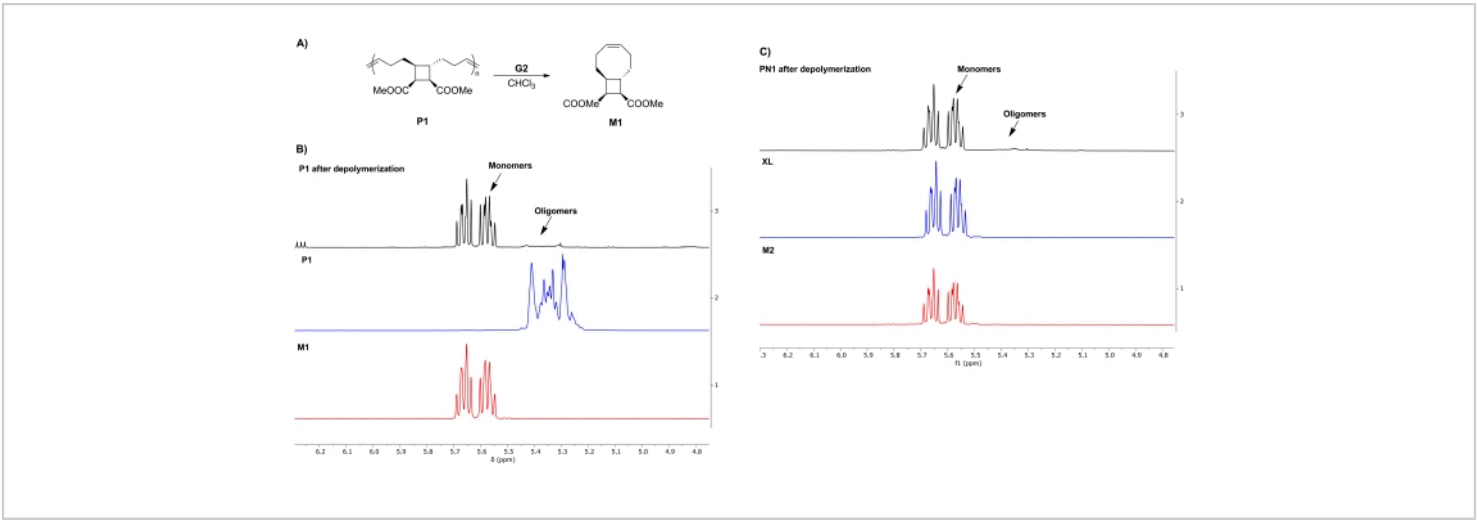

Figure 6: Depolymerization of *t*CBCO based polymers. (**A**) Depolymerization reaction scheme and stacked partial ^{1}H NMR spectra of (**B**) polymer **P1** after depolymerization (black), polymer **P1** before depolymerization (blue), and monomer **M1** (red) and (**C**) network **PN1** after depolymerization (black), crosslinker **XL** (blue), and monomer **M2** (red). This figure has been prepared from previously published data (data for B are from Sathe *et al.*[19], data for C are from Sathe *et al.*[15]). Please click here to view a larger version of this figure.

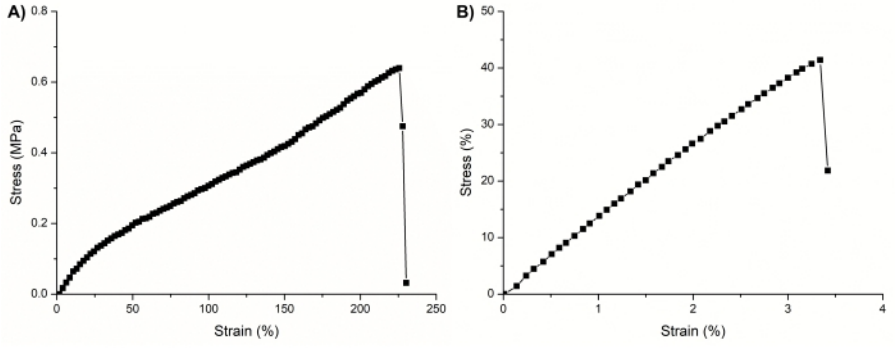

Figure 7: Stress vs. strain curves. (**A**) Polymer network **PN1** and (**B**) polymer **P3**. This figure has been prepared from previously published data from Sathe *et al.*[15]. Please click here to view a larger version of this figure.

Discussion

The *t*CBCO monomers can be prepared from a common precursor: the [2+2] photocycloadduct of maleic anhydride and 1,5-cyclooctadiene, anhydride **1**. Since the crude anhydride **1** is difficult to purify but can be hydrolyzed readily, the crude photoreaction mixture is subjected to methanolysis conditions to yield the readily isolable methyl ester-acid **2**. The recrystallization of **2** after column chromatography is key to obtaining the pure *trans*-cyclobutane isomer of **2**.

2 can be readily derivatized to prepare several different *t*CBCO monomers as outlined here, including the diester monomers **M1** and **M2**, imide monomer **M3**, and ester crosslinker **XL**. Additionally, the final esterification step in the preparation of **M2** and **XL** can lead to the formation of a side product that, we hypothesize, differs only in the relative stereochemistry of the ester groups (*cis*- for **M2** and **XL** vs. *trans*- for the side products). Being only slightly lower in polarity than the desired products, care must be taken during the purification of **M2** and **XL** so as to ensure efficient separation and minimize the loss of product. Typically, performing column chromatography under gravity (instead of flash chromatography) yields satisfactory results in this case.

The preparation of the highly strained monomer with the *trans*-cyclooctene, ***E*M1**, provides access to depolymerizable polymers with controlled molecular weight distribution. To achieve this, a photochemical isomerization method employing flow chemistry is utilized. This method shows higher yield and functional group tolerance compared to conventional batch-type photoisomerization. In this flow system, silver nitrate is used to immobilize ***E*M1** in a column. The constant removal of ***E*M1** drives the equilibrium in the irradiated reaction mixture toward ***E*M1** and prevents its photodegradation. Active silver nitrate and proper polarity of the solvent mixture are critical for optimal results. Additionally, the pressure buildup can cause leakages; thus, pre-circulation before irradiation is necessary to locate any leakages. Due to the silver nitrate silica gel and Et_2O/hexane solvent mixture, this method is limited to compounds with relatively low polarity and sufficiently high solubility in Et_2O/hexane. Further, the *trans*-olefins in these monomers are reactive and prone to dimerization/decomposition in the presence of acidic impurities[23]. Additionally, if the monomer is not isolable as a solid, it may be stored as a dilute solution or with a small amount of BHT (~3%-5%) added to prevent radical-induced side reactions; these *trans*-olefin monomers may also be refrigerated to further prevent degradation[24].

The *t*CBCO monomers can be polymerized to high molecular weights at ambient temperatures by ring-opening metathesis polymerization (ROMP) in the presence of **G2**. A rather high monomer concentration (~2 M) is needed to achieve this, owing to the low ring strain of the *t*CBCO monomers. If the monomers prove difficult to dissolve in the solvent at such high concentrations, sonication in an ultrasound bath may be helpful. Under these conditions, the polymerization can be performed to conversions >80% and high molecular weights (M_n > 100 kDa), albeit with broad dispersities ($Đ$ > 1.5)[15].

Monomer ***E*M1**, on the other hand, can be polymerized to a high conversion in a short time, even at low initial monomer concentrations. We attribute this to the high ring strain in ***E*M1,** resulting in a higher driving force for its polymerization. Depolymerization and cross-metathesis are suppressed by using an excess amount of PPh_3 with respect to **G1**, allowing polymerization to proceed to high conversions while maintaining low $Đ$ (<1.2). The polymerization shows a living character and can be applied for the synthesis of block copolymers[18]. The technique is fairly straightforward and robust enough that it can be conducted under ambient conditions by the simple addition of stock solutions. One important note, however, is that PPh_3 must be purified (to remove oxidized PPh_3 and other impurities) and stored under nitrogen (the purification may be done by recrystallization from ethyl acetate); additionally, care should be taken to dry the glassware before performing this polymerization.

The depolymerization of linear and crosslinked polymers based on this system under mild conditions is also demonstrated. It is interesting that this depolymerization is not

restricted to linear polymers only-polymer networks prepared with this system can also be readily depolymerized. This is likely because, while the local concentrations of olefinic groups in the swollen network may be high, chain scission events in the presence of catalyst aid in the degradation and dissolution of the network, following which the fragments further undergo depolymerization. It is critical to quench the catalyst with ethyl vinyl ether after depolymerization prior to evaporating the solvent since the extent of depolymerization may be affected if the active catalyst is still present in the system.

The versatility of this system is further cemented by the range of properties accessible. Here, the preparation of a soft rubbery network, as well as a rigid glassy plastic with the same depolymerizable core, is demonstrated. The preparation of network **PN1** may be challenging since it is rather fragile in the swollen state, requiring careful handling when removing it from the mold. Additionally, when performing Soxhlet extraction, highly volatile solvents (like dichloromethane) should be avoided since the rapid evaporation of such solvents may lead to warping and fracture of the sample. Additionally, to avoid such fracture, the swollen network should be allowed to dry in a covered container to slow the evaporation of the solvent. If the dissolution of **P3** in DCM during the preparation of dogbone samples proves difficult, an additional solvent may be added in small increments. Further, to avoid defects while preparing dogbone samples with **P3**, the underfilling of mold cavities should be avoided. High-temperature processing of **P3** can also lead to oxidative degradation due to the presence of olefinic groups in the backbone. To prevent this, butylated hydroxytoluene (BHT) may be added to the polymer.

The versatile nature of the *t*CBCO system lends itself to a diverse range of thermomechanical properties through facile functionalization, which can facilitate the introduction of chemical recyclability to areas where it has been as yet limited, like high-performance thermosets and composites. Additionally, the ability to access living polymerization with this system drastically expands the scope of depolymerizable polymer architectures that can be prepared, including block copolymers and bottlebrush and graft polymers.

Disclosures

A patent application (PCT/US2021/050044) has been filed for this work.

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