

Supporting information:

Copper Mediated Controlled Radical Ring Opening Polymerization (RROP) of a vinyl cycloalkane

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Materials and Characterizations:

† 1, 1 bis (ethoxy carbonyl)-2-vinylcyclopropane, the monomer was synthesized from dibromo-2-butene and diethyl malonate in presence of NaH in THF solvent (see the supplementary information for details).

‡ ¹H NMR were recorded at 25^oC in CDCl₃ on a 200 MHz Bruker NMR spectrometer.

§ GPC analysis was performed on a Viscotek GPC chromatography equipped with a refractive index detector model VE 3580 and two ViscoGEL GPC columns GMHHR-H #17360 connected in series. THF was used as the eluent at a flow rate of 1.0 ml/min and calibration was carried out using low polydispersity polystyrene standards. Data acquisition and processing were performed using Viscotek OMNI-01 software.

¶ DSC analysis was recorded on a Pyris Diamond DSC, Perkin Elmer (UK) under nitrogen atmosphere from -100^oC to 150^oC at a heating rate of 20^oC/min. The glass transition temperature (T_g) was determined from the inclination point in the second heating curve.

≠ MALDI-TOF-MS analyses were carried out using a Perceptive Biosystems Voyager Elite MALDI-TOF mass spectrometer, equipped with a nitrogen laser (wavelength 337 nm). In this case 2,5-dihydroxybenzoic acid was used as a matrix and sodium trifluoroacetate was used as the cationic agent. The matrix, salt, and polymer solutions were premixed in THF in the ratio of 10/1/10.

Synthesis:

1. Preparation of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane: A solution of 1,4-dibromo-2-butene (12.84 mg, 0.06 mol.) and diethyl malonate (7.5 g, 0.06 mol.) in THF (50 ml) was added dropwise into NaH (2.8 g, 0.12 mol.) in THF (200 ml) at 0°C temperature. After the addition of NaH, the reaction mixture was refluxed at 70°C overnight. The resulting mass was filtered off and washed with ethanol twice. The combined filtrate was evaporated, and the residue was distilled under reduced pressure (65°C/4 mm Hg). The product was characterized by ¹HNMR and ¹³CNMR, elemental analysis and GC-MS. Yield: 18.5g (90%), purity: 100% (by GC and TLC). ¹HNMR: δ = 1.30 (t, 6H), 1.48–1.54 (m, 2H), 2.4–2.53 (m, 1H), 4.25 (q, 4H) and 5.15 – 5.52 (m, 3H) ppm. **Elemental analysis Calc.** C 62.26 H 7.55; Found C 62.57 and H 7.75. **GC-MS:** GC Ret. Time, 9.02 and MS MH⁺, 213 (NH₃).

2. ATRP of ECVCP: In a typical experiment 1.0 g (4.7 x 10⁻³ mol) of ECVCP and 2 ml of toluene were taken in a 25ml three neck round bottom flask. The flask was equipped with a condenser in one neck and a rubber septum in the other. Argon gas was passed through the solution for about 15 min to remove oxygen from the reaction mixture. CuBr (7.4 mg, 5.12 x 10⁻⁵ mol) and PMDETA (15 mg, 8.20 x 10⁻⁵ mol) were added to the flask. The polymerization was started by immersing the flask into oil bath already preheated at 90°C and by adding EBiB (20 mg, 1.03 x 10⁻⁴ mol) or PEBR (19 mg, 1.02 x 10⁻⁴ mol) as initiator. The samples were purified by passing through alumina column prior to the different analysis like GPC, ¹HNMR and DSC analysis. M_n GPC = 3033, PDI = 1.16, M_n MALDI = 2980, PDI = 1.32, ¹HNMR: δ = 1.10 (6H), 2.4 (4H), 4.2 (4H), 5.3 (2H)

3. General procedure for RROP of 1,1-bis(ethoxycarbonyl)-2-vinylcyclopropane (ECVCP) in solution and in bulk: In a polymerization ampoule ECVCP, AIBN and subsequently a dry solvent were introduced. The ampoule was cooled under liquid N₂, degassed several times by the freeze-pump thaw method and then was sealed off under vacuum. The polymerization was carried out at 60°C for 20 hours. The resulting mixtures was diluted with chloroform and poured into methanol/water mixture (4:1, by volume) to precipitate the polymer.

List of supplementary information:

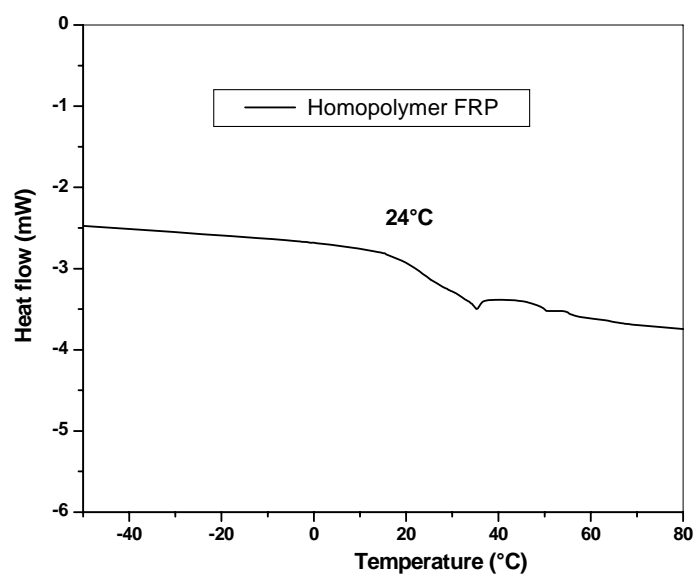
S₁ : DSC traces of PECVCP prepared by RROP

S₂ : DSC traces of PECVCP prepared by ATRROP

S₃ : MALDI-TOF-MS of ECVCP prepared by ATRROP

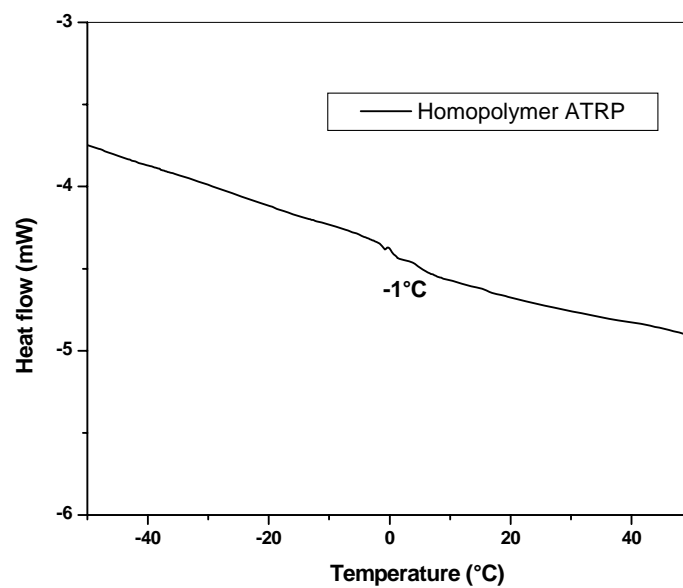
S₄: GPC traces of poly (ECVCP) prepared by ATRROP

4. DSC traces of PECVCP prepared by RROP



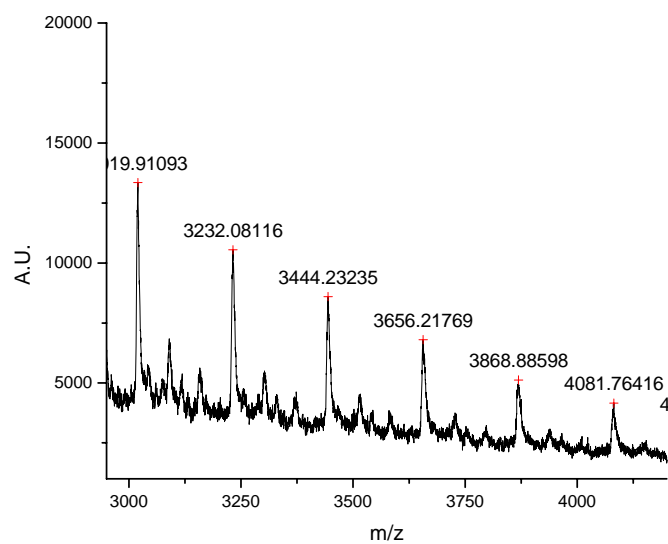
S1: DSC traces of PECVCP prepared by RROP

5. DSC traces of PECVCP prepared by ATRROP



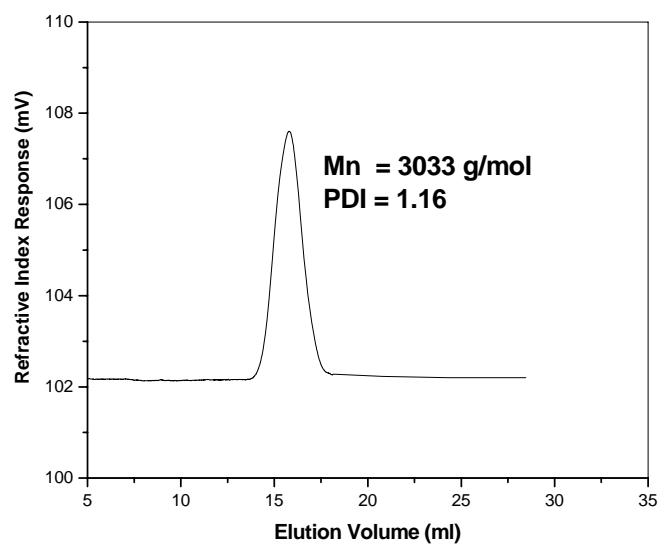
S2: DSC Traces of PECVCP prepared by ATRROP

6. MALDI-TOF-MS of ECVCP prepared by ATRROP



S3: MALDI-TOF-MS of PECVCP prepared by ATRROP

6. GPC traces of poly (ECVCP) prepared by ATRROP



S4: GPC traces of poly (ECVCP) prepared by ATRROP