Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for:

An Entropy-Driven Ring-Opening Metathesis Polymerization Approach towards Main-Chain Liquid Crystalline Polymers

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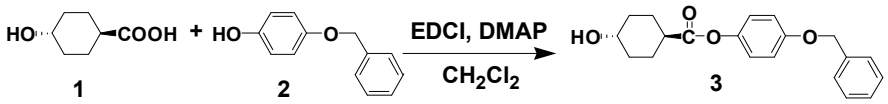
General considerations.

Grubbs 2nd generation catalyst and Grubbs 1st generation catalyst were purchased from Aldrich Inc. *Trans*-4-hydroxycyclohexanecarboxylic acid and 10-undecenoic acid was purchased from TCI Inc. 4-(Benzyloxy)phenol, palladium 10% on carbon, N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDCI), ammonium formate, and dimethylaminopyridine (DMAP) were purchased from Aladdin Inc. Dichloromethane and triethylamine were distilled from calcium hydride under nitrogen.. A Sigma 2K 15 centrifuge was applied to isolate the polymers from organic solvents.

All ^{1}H NMR spectra were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300) and recorded in $CDCl_3$ (internal reference 7.26 ppm). Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10°C /min. Thermogravimetric analysis (TGA) was measured by a Perkin-Elmer TGA7 under nitrogen atmosphere. The liquid crystalline textures were investigated by using an Olympus BX53P microscope, equipped with a Mettler PF82HT hot stage. Gel permeation chromatography (GPC) against polystyrene standards in THF was equipped with an HP 1100 HPLC, an HP 1047A refractive index detector and a Plgel MIXED-C column. X-ray scattering experiment was carried out by recording both wide-angle and small angle X-ray scattering simultaneously, the q range covered from 0.06 to 29 nm^{-1}. $q = 4\pi(\sin\theta)/\lambda$, λ is 0.1542 nm of Cu Kα radiation, the scattering angle is 2θ.

1. Synthesis of macrocyclic monomer by macrolactonization



4-Hydroxy-cyclohexanecarboxylic acid 4-benzyloxy-phenylester (3)

Dimethylaminopyridine (300 mg, 2.46 mmol), 4-benzyloxy-phenol **2** (1.46 g, 7.29 mmol) and *trans*-4-hydroxycyclohexanecarboxylic acid **1** (700 mg, 4.86 mmol) were dissolved in freshly distilled dichloromethane (30 mL) under nitrogen. This mixture was cooled down to -20 ºC. A mixture of triethylamine (740 mg, 7.32 mmol) and EDCI (1.40 g, 7.32 mmol) were dissolved in freshly distilled dichloromethane (20 mL) were added slowly into the above mixture. The reaction mixture was stirred at -20 ºC for 15 min and then stirred at room temperature for another 20 h. The resulting solution was washed with water and brine solution (3×30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude compound was purified by flash chromatography (hexane/EtOAc 1:1) to afford desired product **3** as a white solid (1.28 g, Yield: 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (m, 5H), 7.04 – 6.95 (m, 4H), 5.09 (s, 2H), 3.75 – 3.64 (m, 1H), 2.53 (m, 1H), 2.21 (m, 2H), 2.12 (m, 2H), 1.72 – 1.64 (m, 2H), 1.47 – 1.32 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.27, 156.44, 144.47, 136.86, 128.58, 128.00, 127.43, 122.21, 115.49, 77.26, 77.01, 76.75, 70.47, 69.70, 42.25, 34.40, 27.08.

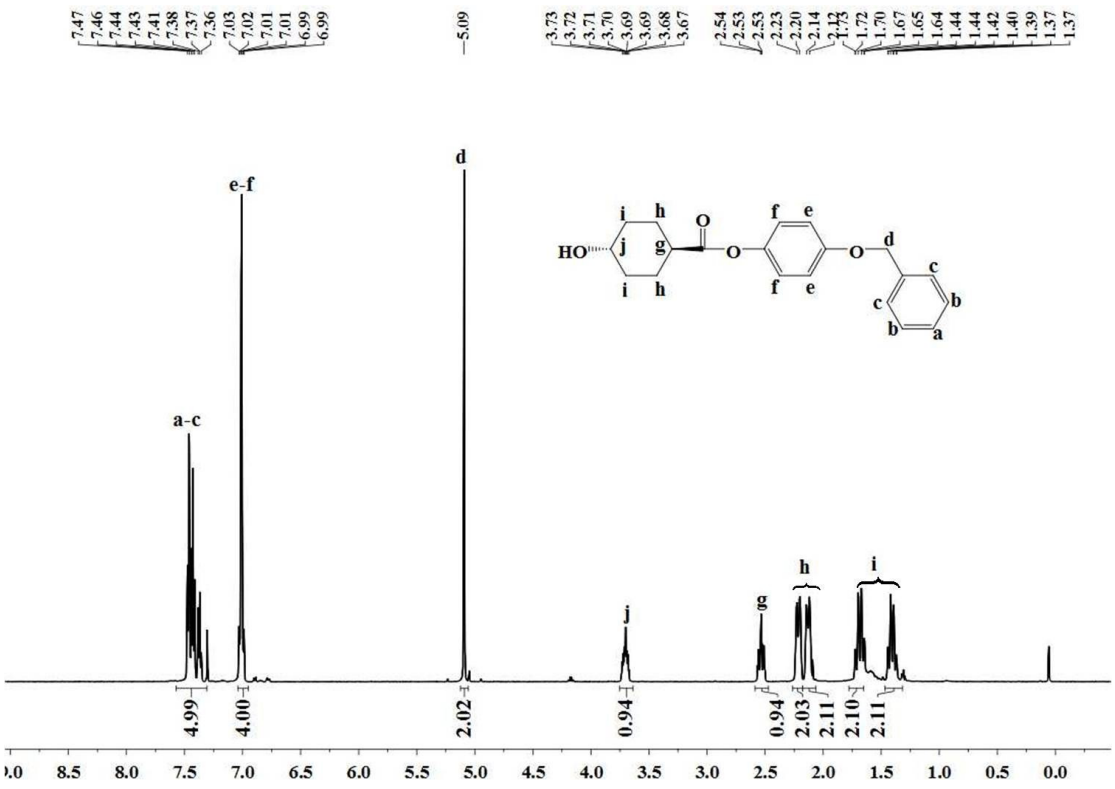


Figure S1. ^{1}H NMR spectrum of compound **3**.

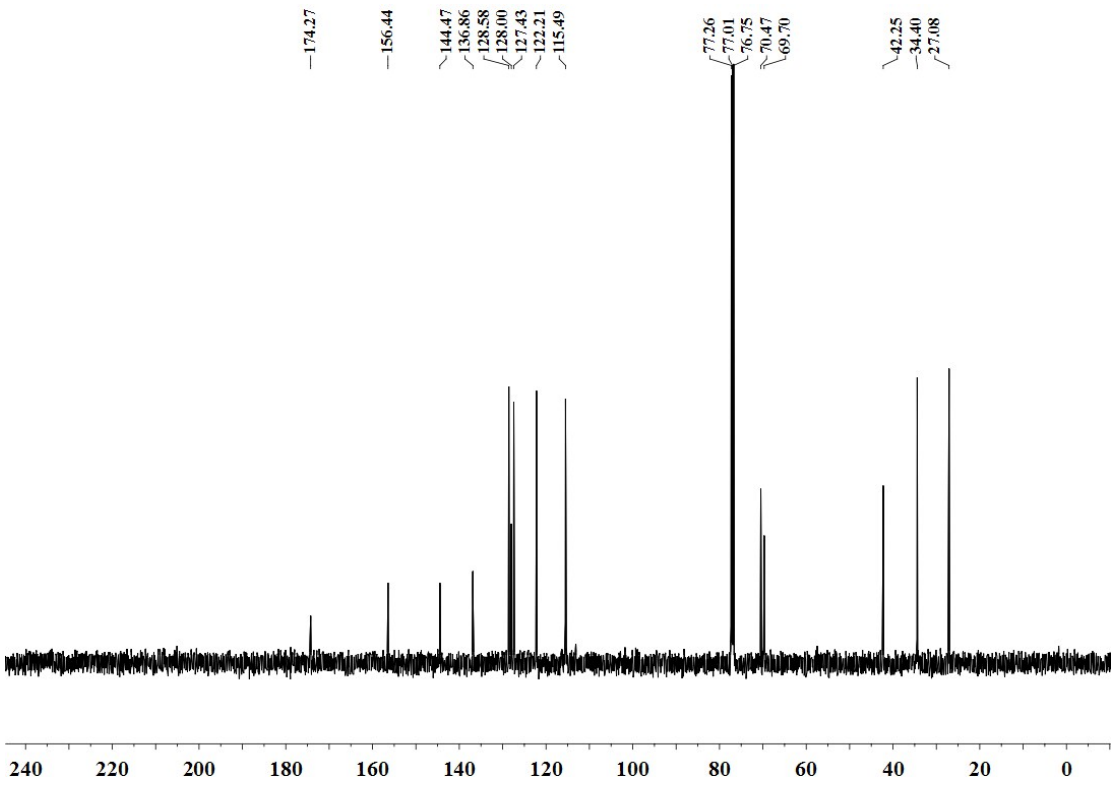
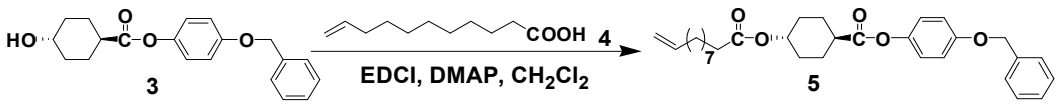


Figure S2. ^{13}C NMR spectrum of compound **3**



4-Undec-10-enoyloxy-cyclohexanecarboxylic acid 4-benzyloxy-phenyl ester (5)

Dimethylaminopyridine (280 mg, 2.29 mmol), compound **3** (2.50 g, 7.66 mmol) and undec-10-enoic acid **4** (1.41 g, 7.66 mmol) were dissolved in freshly distilled dichloromethane (40 mL) under nitrogen. This mixture was cooled down to -20 ºC. A mixture of triethylamine (1.16 g, 11.47 mmol) and EDCI (2.20 g, 11.47 mmol) in dissolved freshly distilled dichloromethane (30 mL) were added slowly into the above mixture. The reaction mixture was stirred at -20 ºC for 15 min and then stirred at room temperature for another 20 h. The resulting solution was washed with water and brine solution (3×40 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude compound was purified by flash chromatography (hexane/EtOAc 5:1) to afford desired product **5** as a white solid (3.09 g, Yield: 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.30 (m, 5H), 7.07 – 6.86 (m, 4H), 5.80 – 5.84 (m, 1H), 5.05 (s, 2H), 4.97 – 4.87 (m, 2H), 4.84 – 4.71 (m, 1H), 2.54 (m, 1H), 2.35 – 2.23 (m, 2H), 2.24 – 1.97 (m, 6H), 1.81 – 1.37 (m, 8H), 1.35 – 1.28 (m, 8H).

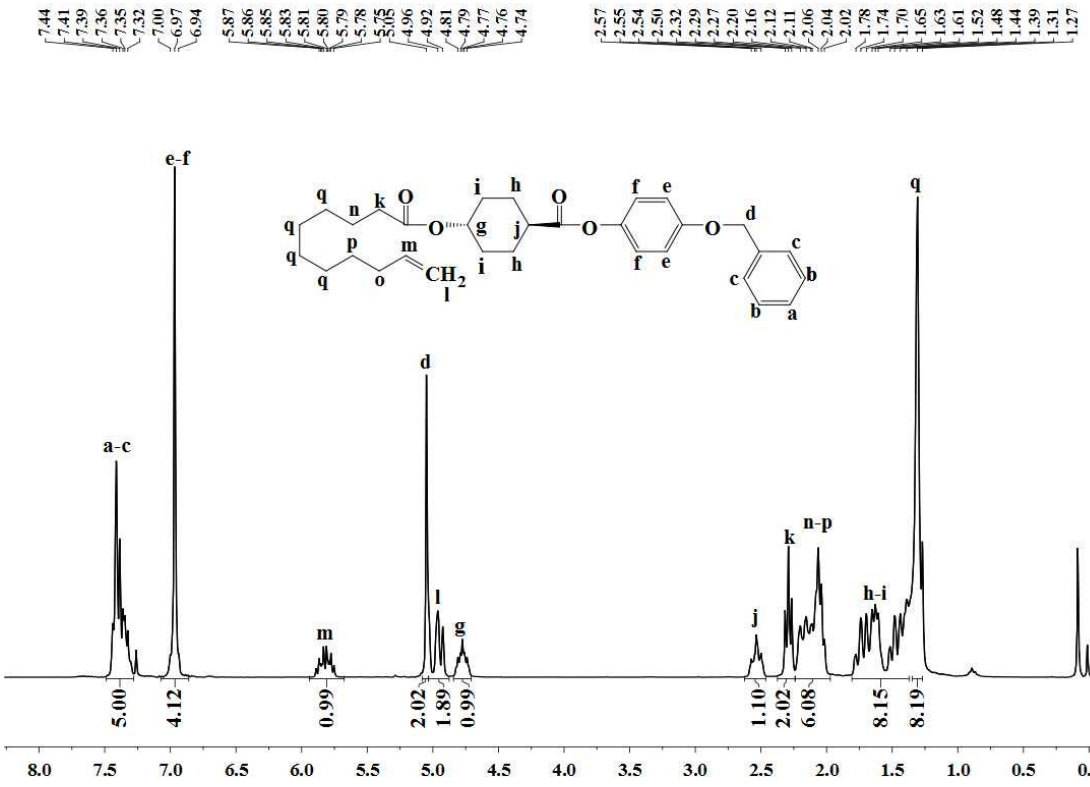
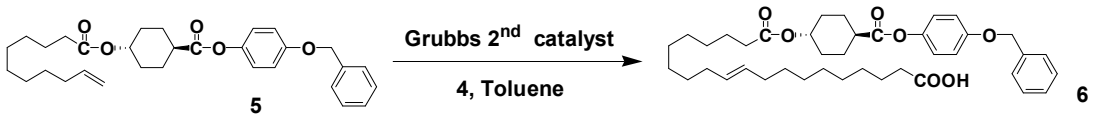


Figure S3. ^{1}H NMR spectrum of compound **5**.



Icos-10-enedioic acid mono[4-(4-benzyloxyphenoxycarbonyl)cyclohexyl]ester (6). Compound **5** (400 mg, 0.81 mmol), undec-10-enoic acid **4** (220 mg, 1.19 mmol) and Grubbs' catalyst 2nd generation (7.0 mg, 8.25×10^{-3} mmol) were dissolved in freshly distilled toluene (15 mL) in a Schlenk flask (50 mL) under nitrogen. The resulting mixture was degassed with nitrogen for 30 min at room temperature and then heated to 40 ℃. After 24 h of stirring, the solution was quenched with excess ethylvinyl ether (0.08 mL). The solution was stirred for another 1 h and then concentrated under vacuum. The resulting mixture was purified by flash chromatography (hexane/EtOAc 30:1) to get the desired product **6** as a white solid (216 mg, Yield: 41%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 5H), 6.96 (s, 4H), 5.38 (s, 2H), 5.05 (s, 2H), 4.83 – 4.67 (m, 1H), 2.53 (m, 1H), 2.37 – 2.26 (m, 4H), 2.20 – 1.91 (m, 8H), 1.79 – 1.44 (m, 8H), 1.38 – 1.14 (m, 20H).

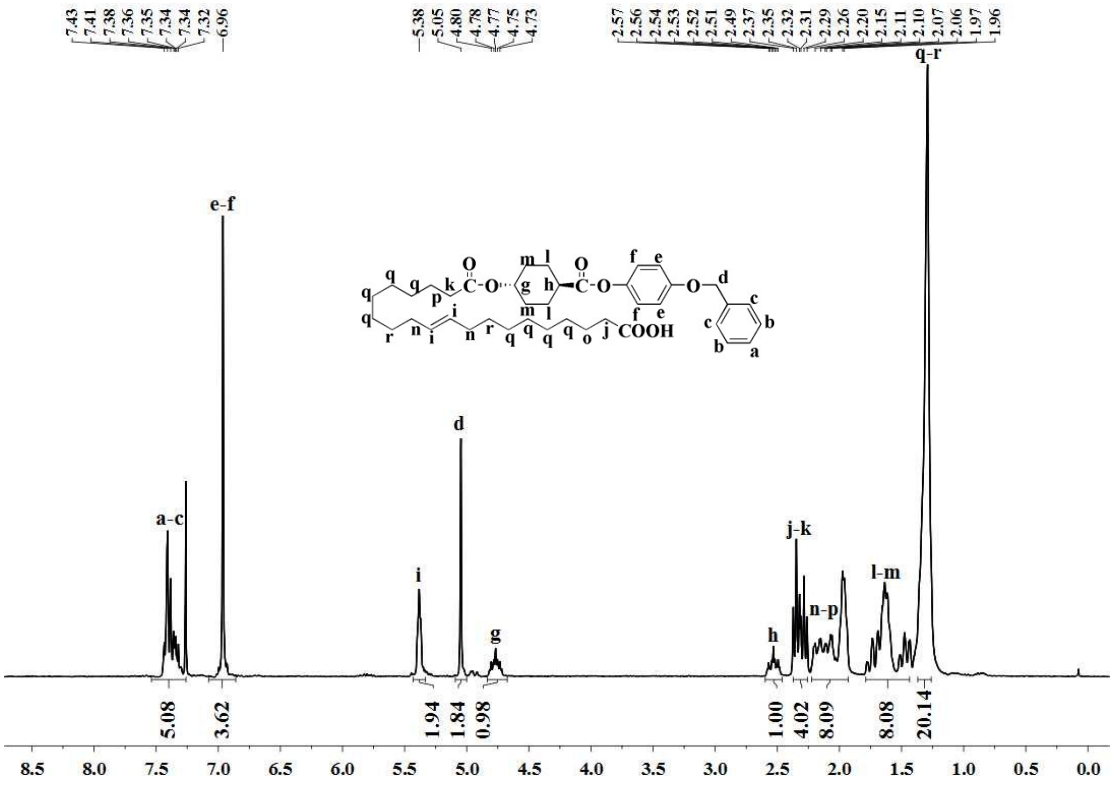
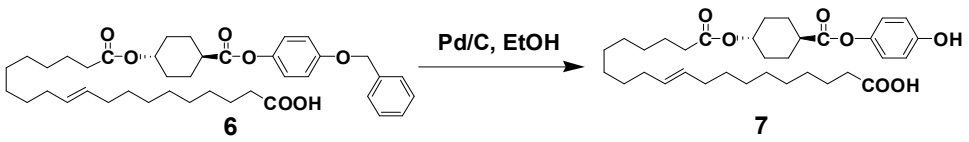


Figure S4. ^{1}H NMR spectrum of compound **6**.



Icos-10-enedioic acid mono[4-(4-hydroxyphenoxycarbonyl)cyclohexyl] ester (7). Compound **6** (300 mg, 0.46 mmol) and Pd/C (150 mg, 50% w/w) were dissolved in ethanol (30 mL) in a Schlenk flask (50 mL). After exclusion of oxygen, the reaction mixture was stirred under H_2 atmosphere (1 atm) at 20 ºC for 12 h. After 24 h of stirring, the dark Pd/C powder was filtered off and the residue was concentrated to get the desired product **7** as a white solid (227 mg, Yield: 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 5.36 (s, 2H), 4.65 (m, 1H), 2.56 (m, 1H), 2.34 – 2.23 (m, 4H), 2.11 – 1.78 (m, 8H), 1.68 – 1.34 (m, 8H), 1.33 – 1.10 (m, 20H).

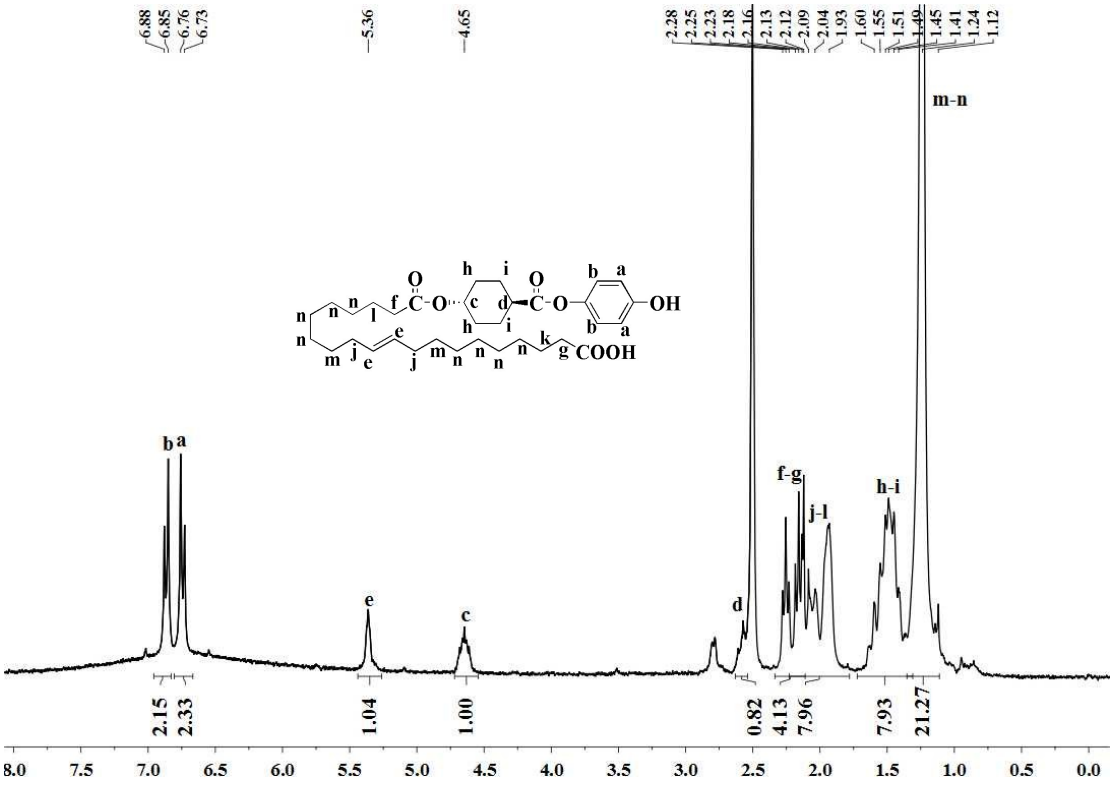
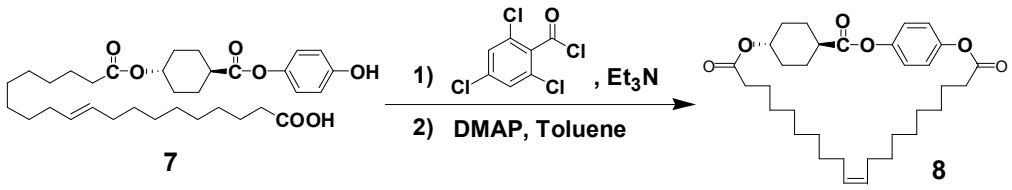


Figure S5. ^{1}H NMR spectrum of compound **7**



Macrocyclic monomer (8)

To an ice-cooled solution of seco-acid **7** (200 mg, 0.36 mmol) in THF (10 ml) was added Et_3N (40 mg, 0.40 mmol), followed by 2,4,6-trichlorobenzoyl chloride (58 μL, 0.36 mmol). The mixture was stirred at 0 °C for 30 min and was then allowed to be warmed to room temperature, after which the mixture was stirred for 2 h. Triethylamine hydrochloride solid was filtered off and the filtrate was diluted with toluene (170 mL). This diluted solution was slowly added into a refluxing toluene (35 mL) solution containing DMAP (220 mg, 1.80 mmol) in a period of 8 h. Upon completion, stirring was maintained for an additional 2 h. The resulting mixture was concentrated and purified by flash chromatography (hexane/EtOAc 50:1) to give the desired product **8** as a white solid (30 mg, Yield: 15%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 4H), 5.43 – 5.29 (m, 2H), 4.84 – 4.69 (m, 1H), 2.53 (m, 3H), 2.28 (t, J = 7.2 Hz, 2H), 2.21 – 1.91 (m, 8H), 1.80 – 1.47 (m, 8H), 1.41 – 1.23 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.37, 173.18, 172.04, 148.08, 130.37, 122.37, 122.20, 77.26, 77.00, 76.75, 71.42, 41.98, 34.61, 34.31, 32.40, 30.43, 29.16, 28.78, 26.62, 24.92. Phase transitions: Crys – 162 ºC – Iso (on heating, determined by POM), Iso – 148 ºC – Crys (on cooling, determined by POM).

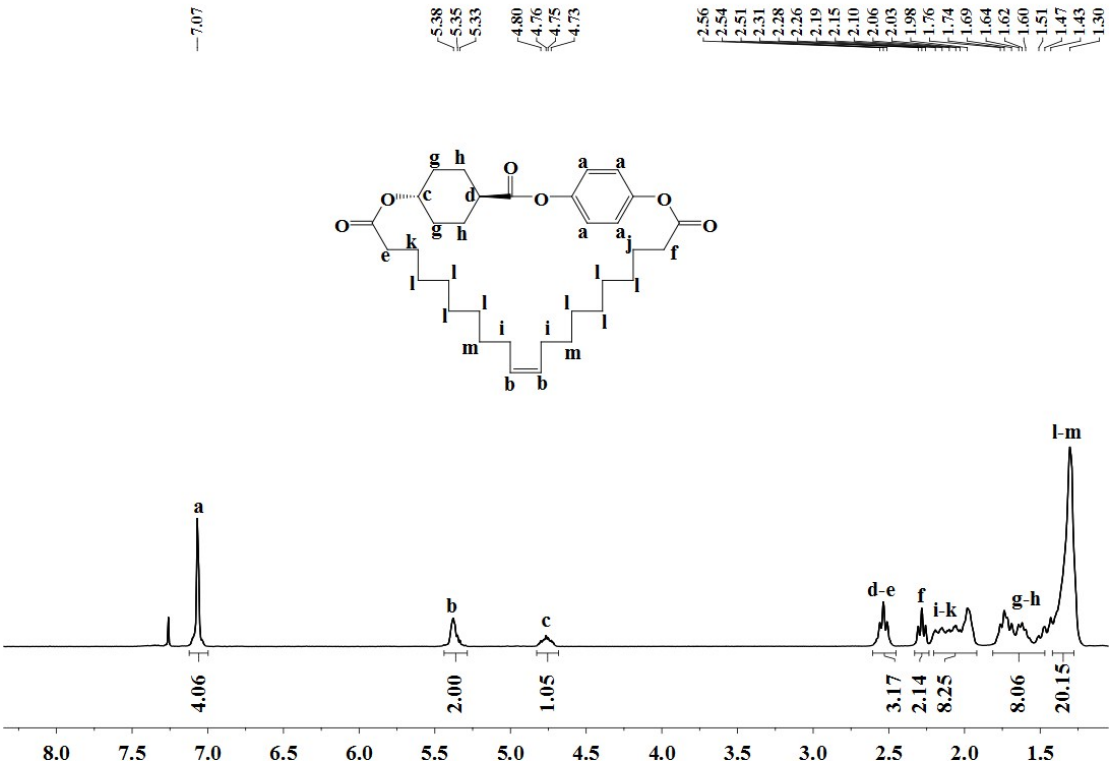


Figure S6. ^{1}H NMR spectrum of compound **8**

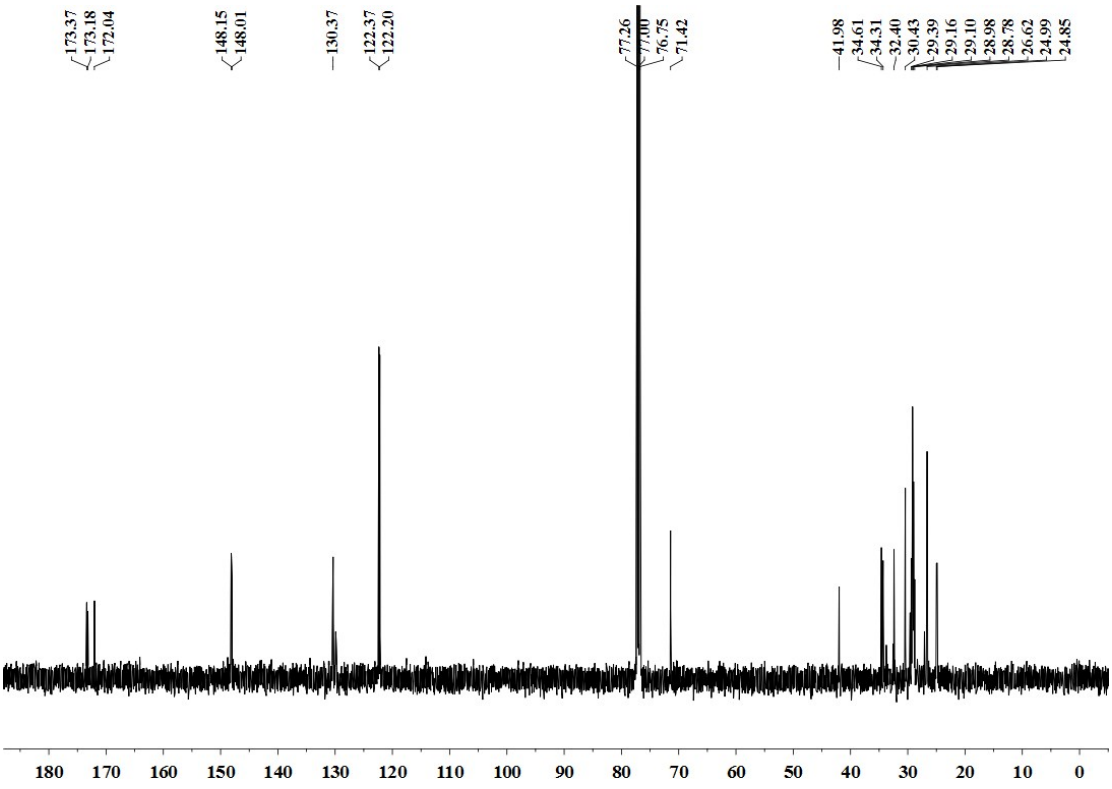
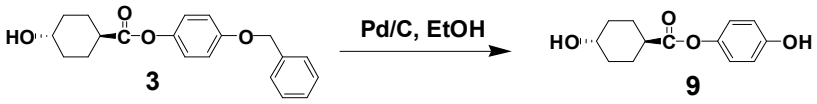


Figure S7. ^{13}C NMR spectrum of compound **8**

Synthesis of macrocyclic monomer by RCM



4-Hydroxy-cyclohexanecarboxylic acid 4-hydroxy-phenyl ester (9)

Compound **3** (500 mg, 1.53 mmol) and Pd/C (165 mg, 33% w/w) were dissolved in ethanol (30 mL) in a Schlenk flask (50 mL). After exclusion of oxygen, the reaction mixture was stirred under H_2 atmosphere (1 atm) at 20 ºC for 6 h. After 6 h of stirring, the dark Pd/C powder was filtered off and the residue was concentrated to give the desired product **9** as a white solid (322 mg, Yield: 89%). ^{1}H NMR (300 MHz, DMSO) δ 9.42 (s, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.74 (d, J = 8.7 Hz, 2H), 4.59 (s, 1H), 3.47 – 3.35 (m, 1H), 2.42 (m, 1H), 2.00 (m, 2H), 1.84 (m, 2H), 1.55 – 1.36 (m, 2H), 1.31 – 1.12 (m, 2H).

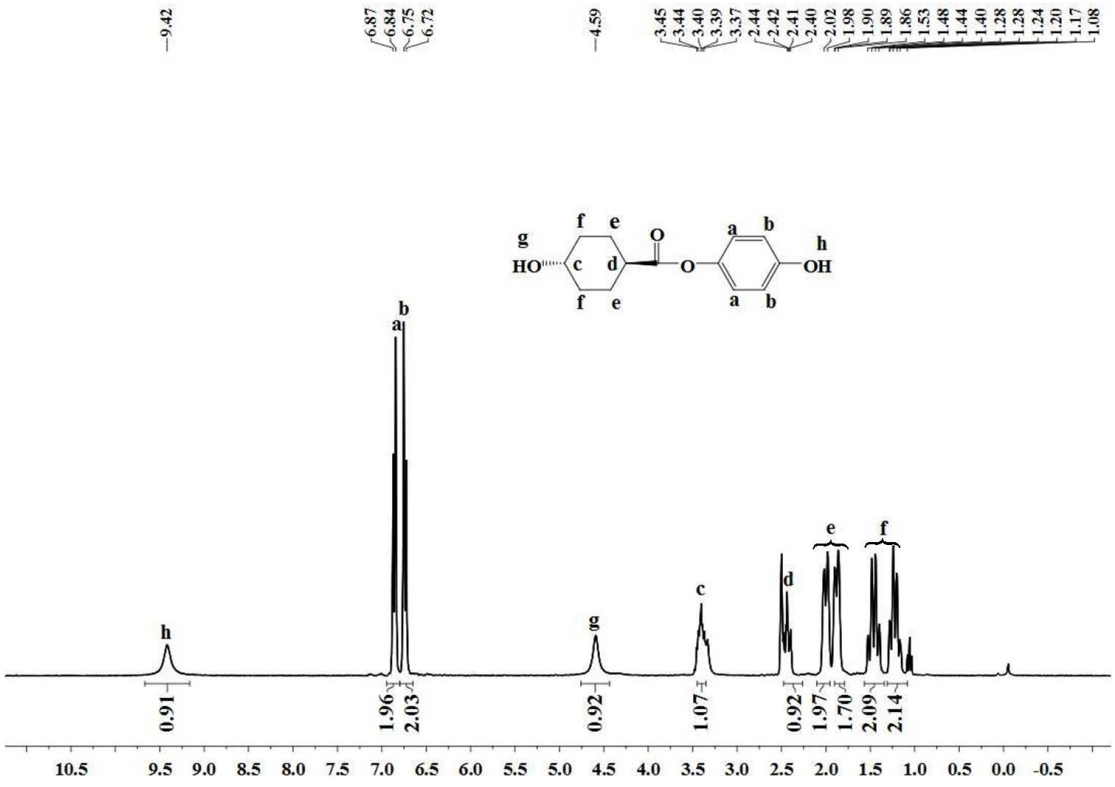
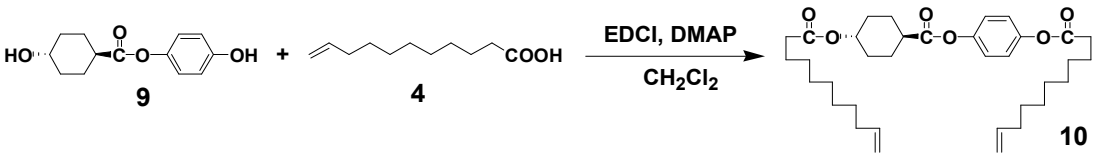


Figure S8. ^{1}H NMR spectrum of compound **9**.



4-Undec-10-enoyloxy-cyclohexanecarboxylic acid 4-undec-10-enoyloxy-phenyl ester (10).

Compound **9** (300 mg, 1.18 mmol), dimethylaminopyridine (80 mg, 0.65 mmol) and undec-10-enoic acid **4** (700 mg, 3.80 mmol) were dissolved in freshly distilled dichloromethane (30 mL) under nitrogen. After cooled it down to -20 ºC, a mixture of triethylamine (740 mg, 7.32 mmol) and EDCI (1.40 g, 7.32 mmol) in freshly distilled dichloromethane (20 mL) were added slowly into the above mixture. The reaction mixture was stirred at -20 ºC for 15 min and then stirred at room temperature for another 20 h. The resulting solution was washed with water and brine solution (3×30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude compound was purified by flash chromatography (hexane/EtOAc 30:1) to afford the desired diene **10** as a white solid (607 mg, Yield: 84%).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 – 6.96 (m, 4H), 5.90 – 5.70 (m, 2H), 4.97 – 4.87 (m, 4H), 4.86 – 4.66 (m, 1H), 2.54 (m, 3H), 2.28 (t, J = 7.4 Hz, 2H), 2.24 – 1.96 (m, 8H), 1.84 – 1.45 (m, 8H), 1.43 – 1.20 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30, 172.07, 148.07, 139.13, 122.30, 114.14, 77.43, 77.00, 76.58, 71.44, 42.00, 34.62, 34.32, 33.75, 30.45, 29.26, 29.16, 29.07, 29.05, 29.02, 28.87, 26.65, 24.95. ESI-MS m/z: 591.4 $[m+Na]^+$. Phase transitions: Crys – 70 ºC – SmA – 86 ºC –Iso (on heating, determined by POM), Iso – 85 ºC – SmA – 50 ºC – Crys (on cooling, determined by POM).

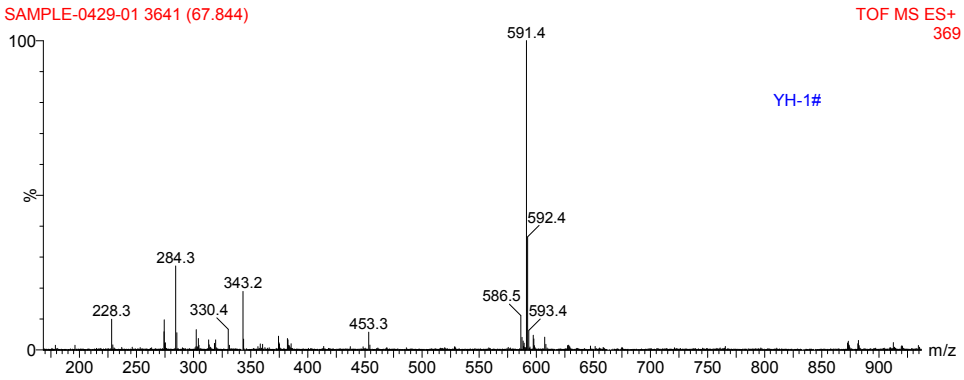


Figure S9. ESI-MS spectrum of compound **10**.

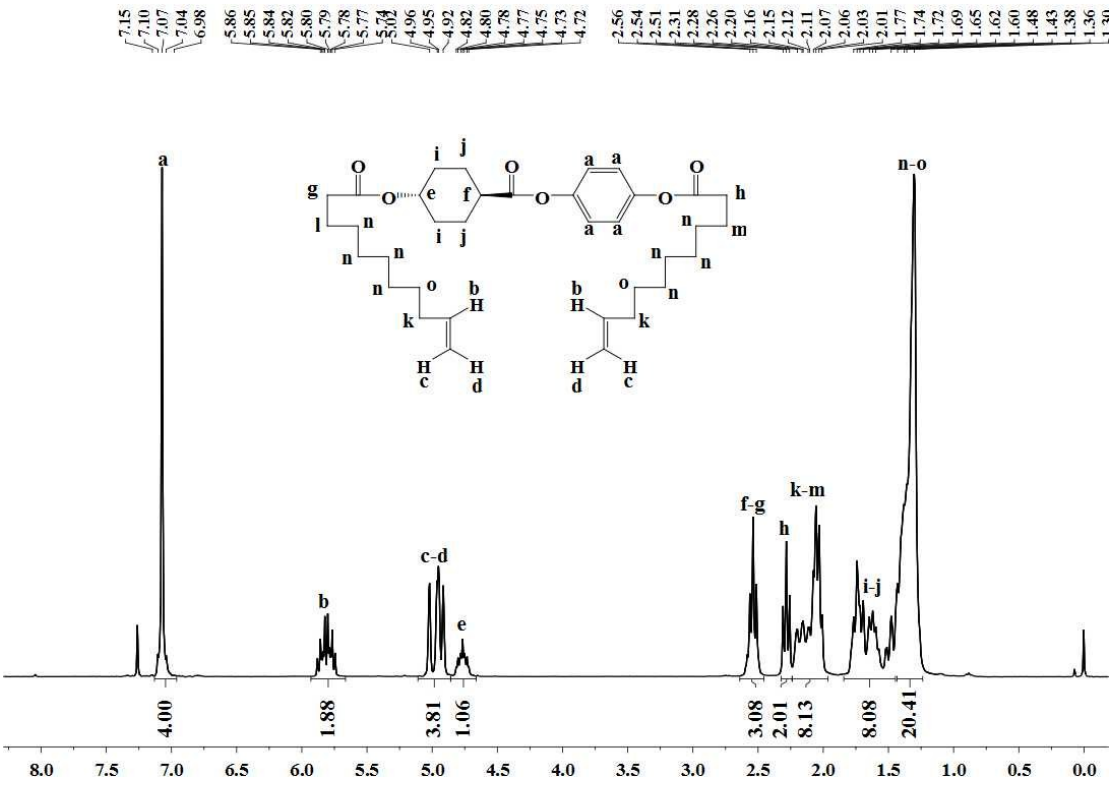


Figure S10. ^{1}H NMR spectrum of compound **10**.

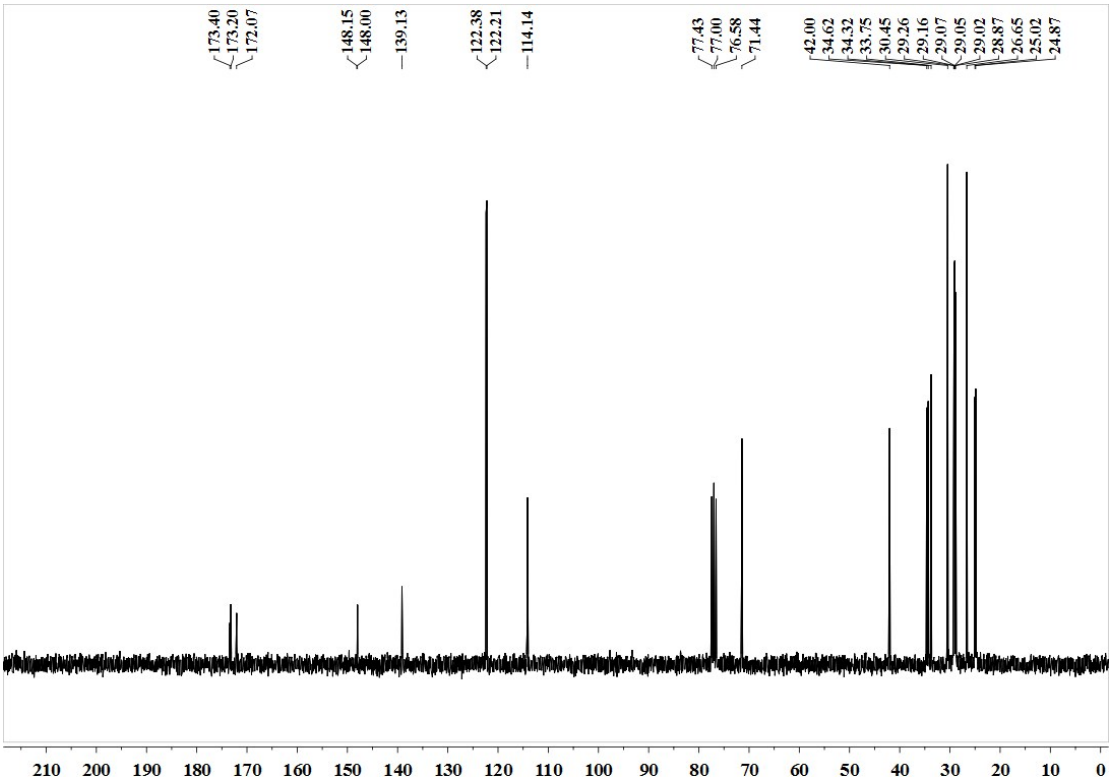
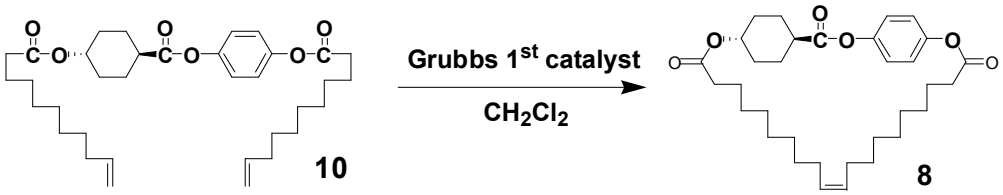


Figure S11. ^{13}C NMR spectrum of compound **10**.



Macrocyclic monomer (8)

Compound **10** (110 mg, 0.19 mmol) and Grubbs catalyst 1st generation (8.0 mg, 9.72×10^{-3} mmol) were dissolved in freshly distilled dichloromethane (250 mL) under nitrogen in a round-bottom flask (3-neck, 500 mL). The resulting mixture was degassed with nitrogen for 30 min at room temperature and then heated to 40 ℃. After 24 h of stirring, the solution was quenched with excess ethylvinyl ether (0.08 mL). The solution was stirred for another 1 h and then concentrated under vacuum. The crude solid was washed with a solution of hexane/dichloromethane (v/v 50/1, 51 mL) twice to give the desired macrocyclic monomer **8** as a white solid (74 mg, Yield: 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 4H), 5.43 – 5.29 (m, 2H), 4.84 – 4.69 (m, 1H), 2.53 (m, 3H), 2.28 (t, J = 7.2 Hz, 2H), 2.21 – 1.91 (m, 8H), 1.80 – 1.47 (m, 8H), 1.41 – 1.23 (m, 20H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.37, 173.18, 172.04, 148.08, 130.37, 122.37, 122.20, 77.26, 77.00, 76.75, 71.42, 41.98, 34.61, 34.31, 32.40, 30.43, 29.16, 28.78, 26.62, 24.92. ESI-MS m/z: 540.8 $[M + H]^+$. Phase transitions: Crys – 162 ℃ – Iso (on heating, determined by POM), Iso – 148 ℃ – Crys (on cooling, determined by POM).

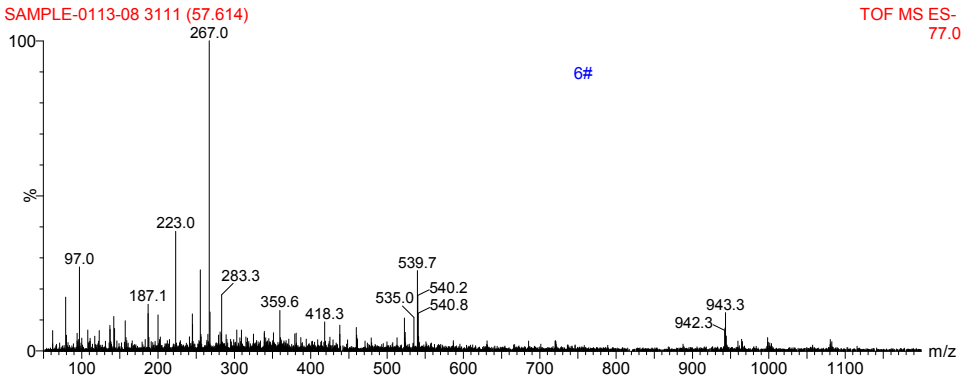


Figure S12. ESI-MS spectrum of compound **8**.

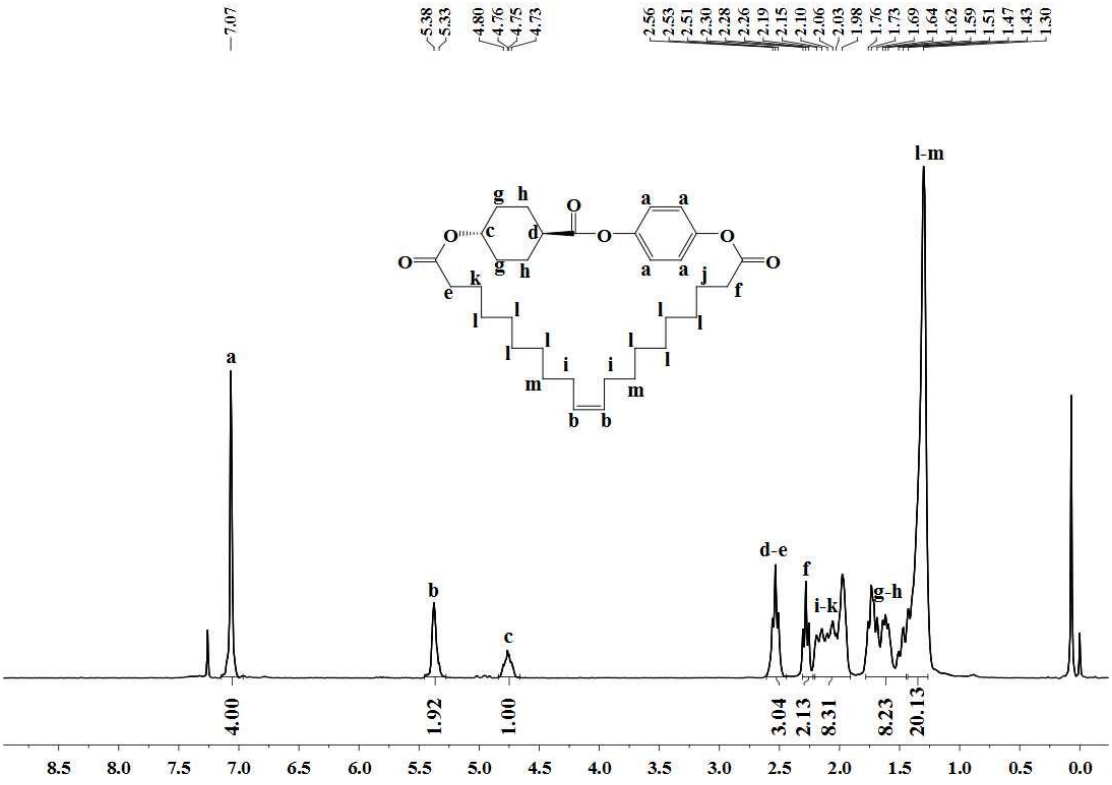


Figure S13. ^{1}H NMR spectrum of compound **8**

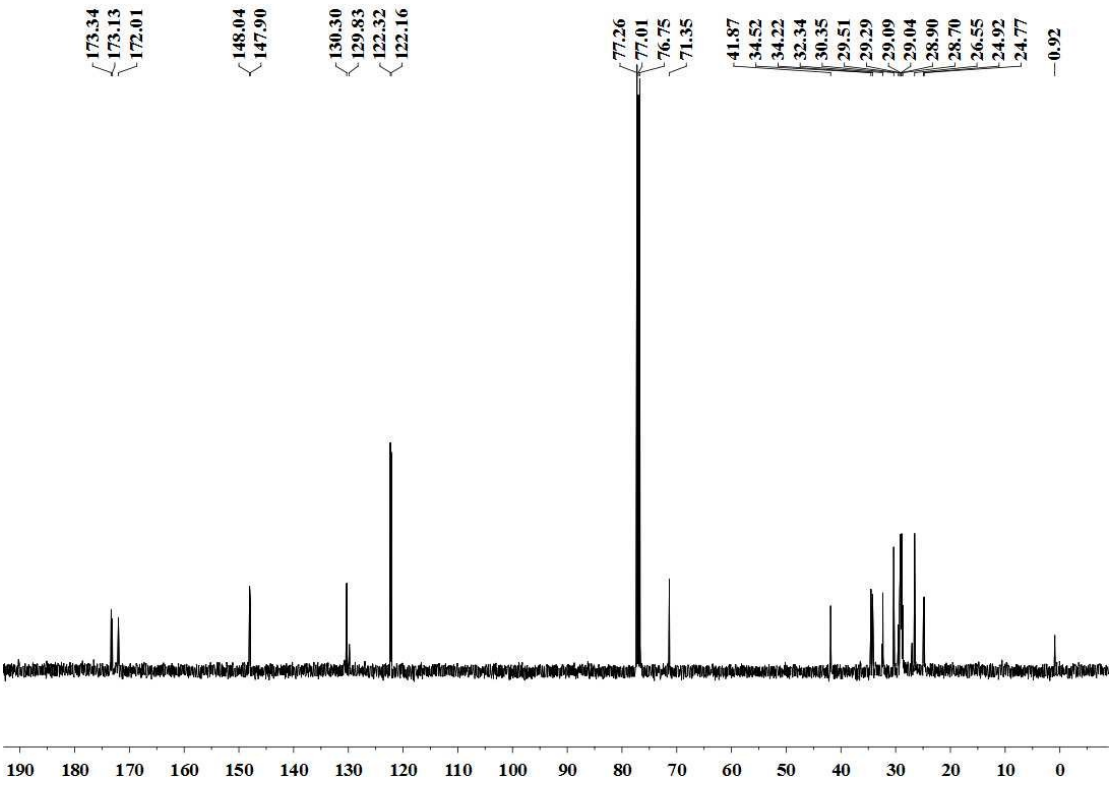
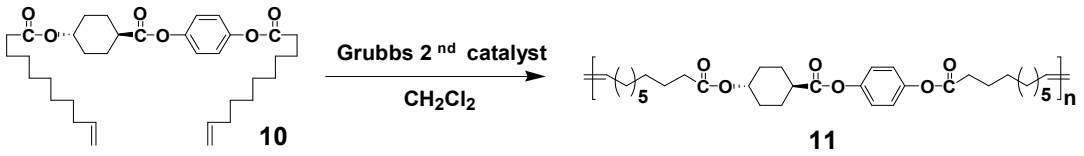


Figure S14. ^{13}C NMR spectrum of compound **8**

2. Synthesis of MCLCPs by ADMET



In a 10 mL Schlenk tube, monomer **10** (56 mg, 0.10 mmol) and Grubbs 2nd generation catalyst (2.0 mg, 2.36×10^{-3} mmol) were dissolved in degassed and freshly distilled dichloromethane (0.1 mL) under nitrogen. Vacuum was applied to remove ethylene periodically. After 24 h of stirring at 20 ℃, the solution was quenched with excess ethylvinyl ether (0.02 mL) and was then stirred for another 5 min. The resulting solution was diluted with dichloromethane (1 mL), dispersed in methanol (50 mL) and centrifuged to provide the polymer precipitate. The above process was repeated two more times. The polymer product was dried under vacuum to give the desired polymer **11** as a white solid (39 mg, Yield: 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 – 7.01 (m, 4H), 5.51 – 5.22 (m, 2H), 5.05 – 4.87 (m, 1H), 4.84 – 4.67 (m, 1H), 2.54 (t, J = 7.4 Hz, 3H), 2.28 (m, 2H), 2.24 – 1.86 (m, 8H), 1.83 – 1.45 (m, 8H), 1.43 – 1.18 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30, 172.08, 148.07, 130.33, 122.30, 77.43, 77.01, 76.58, 71.44, 42.00, 34.63, 34.33, 32.56, 30.45, 29.60, 29.30, 29.21, 29.08, 27.20, 26.65, 24.96.

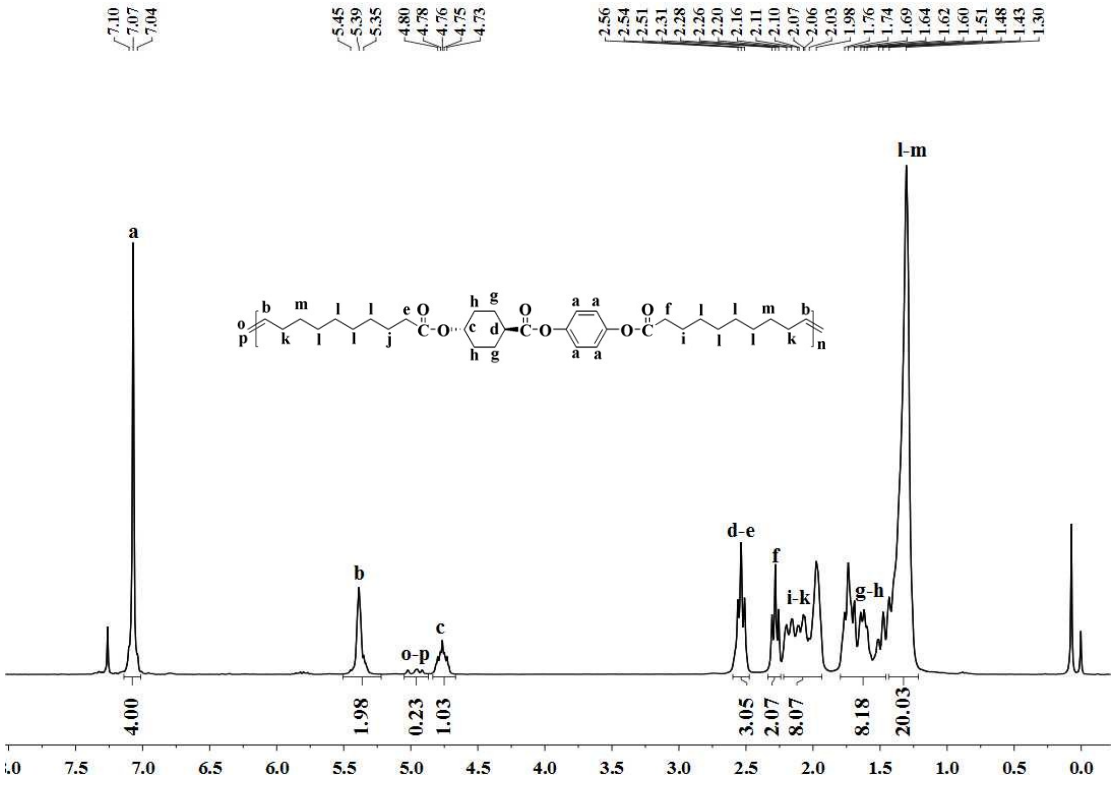


Figure S15. ^{1}H NMR spectrum of polymer **11** from ADMET

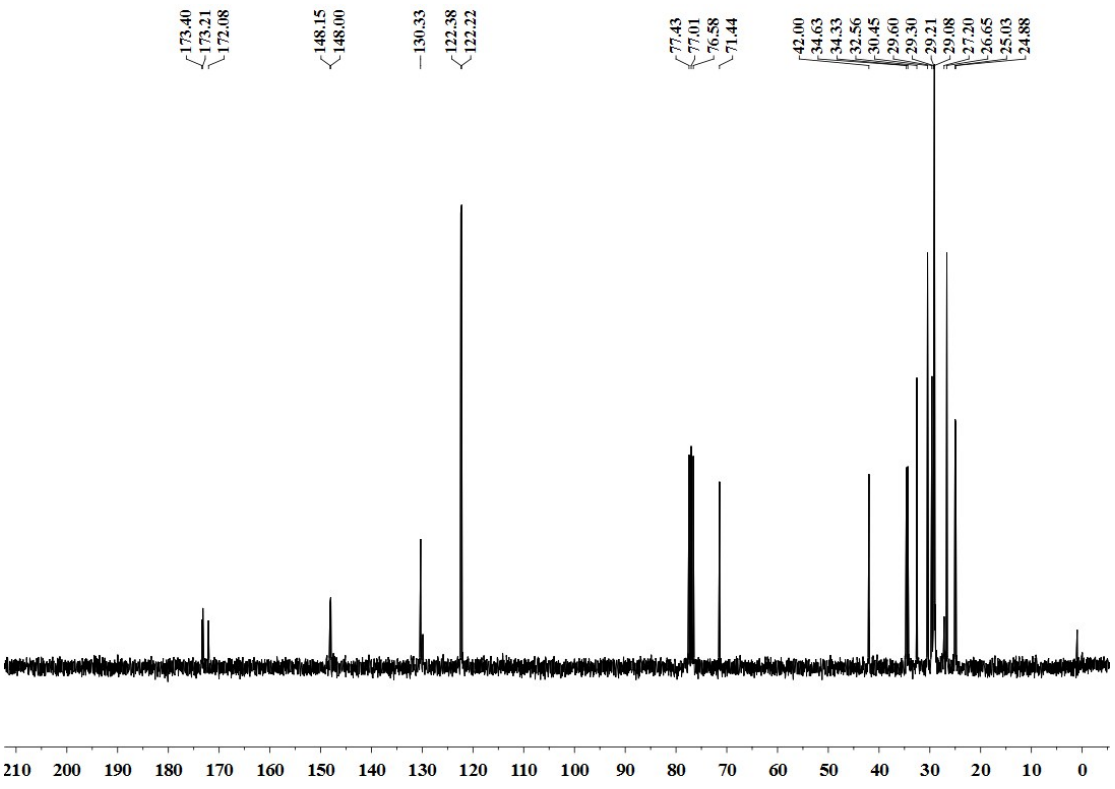
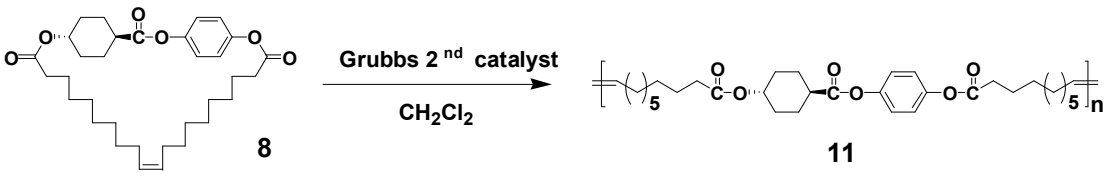


Figure S16. ^{13}C NMR spectrum of polymer **11** from ADMET

3. Synthesis of MCLCPs by ED-ROMP



In a 10 mL Schlenk tube, macrocyclic monomer **8** (54 mg, 0.10 mmol) and Grubbs 2nd generation catalyst (2.0 mg, 2.36×10^{-3} mmol) were dissolved in degassed and freshly distilled dichloromethane (0.1 mL) under nitrogen. After 3 h of stirring at 20 ℃, the mixture became viscous and dark brown oil appeared. The solution was quenched with excess ethylvinyl ether (0.02 mL) and was then stirred for another 5 min. The resulting solution was diluted with dichloromethane (1 mL), dispersed in methanol (50 mL) and centrifuged to provide the polymer precipitate. The above process was repeated two more times. The polymer product was dried under vacuum to give the desired polymer **11** as a white solid (48 mg, Yield: 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (s, 4H), 5.46 – 5.29 (m, 2H), 4.85 – 4.69 (m, 1H), 2.54 (m, 3H), 2.28 (m, 2H), 2.22 – 1.93 (m, 8H), 1.87 – 1.48 (m, 8H), 1.44 – 1.17 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30, 148.07, 130.33, 129.86, 122.30, 77.44, 77.01, 76.59, 71.44, 42.00, 34.63, 34.33, 32.56, 30.45, 29.66, 29.30, 29.21, 29.08, 27.20, 26.65, 24.96.

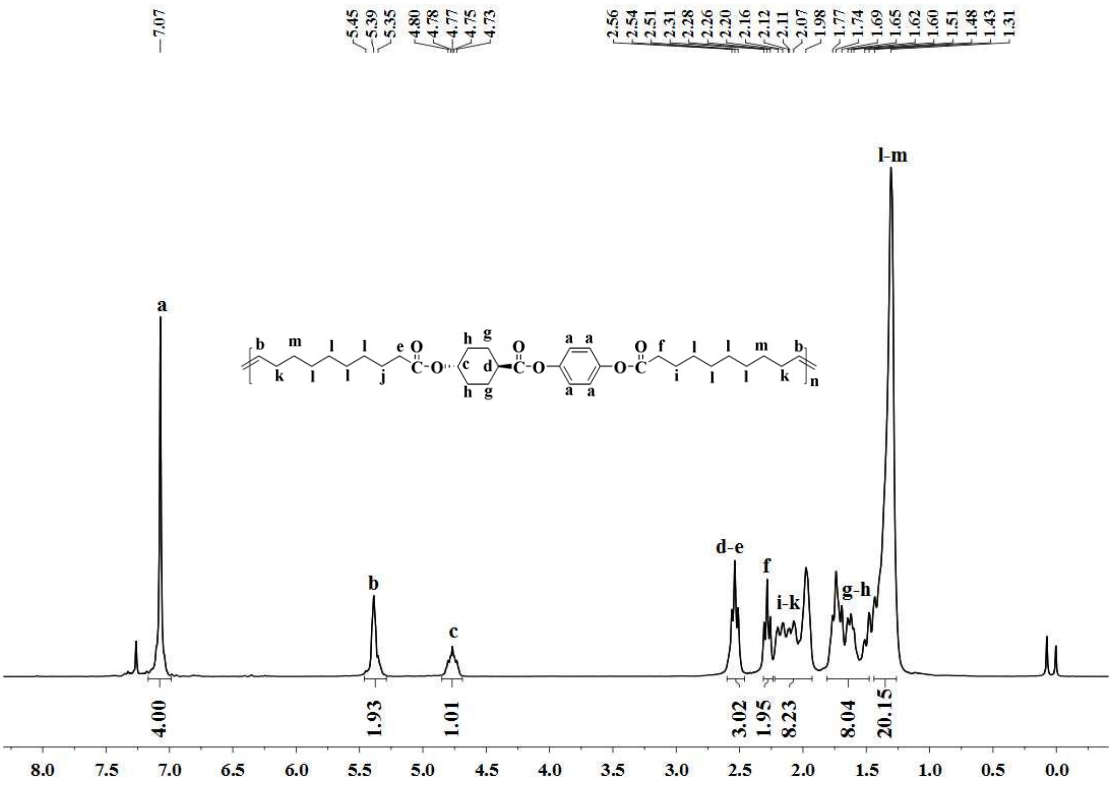


Figure S17. ^{1}H NMR spectrum of polymer **11** from ED-ROMP

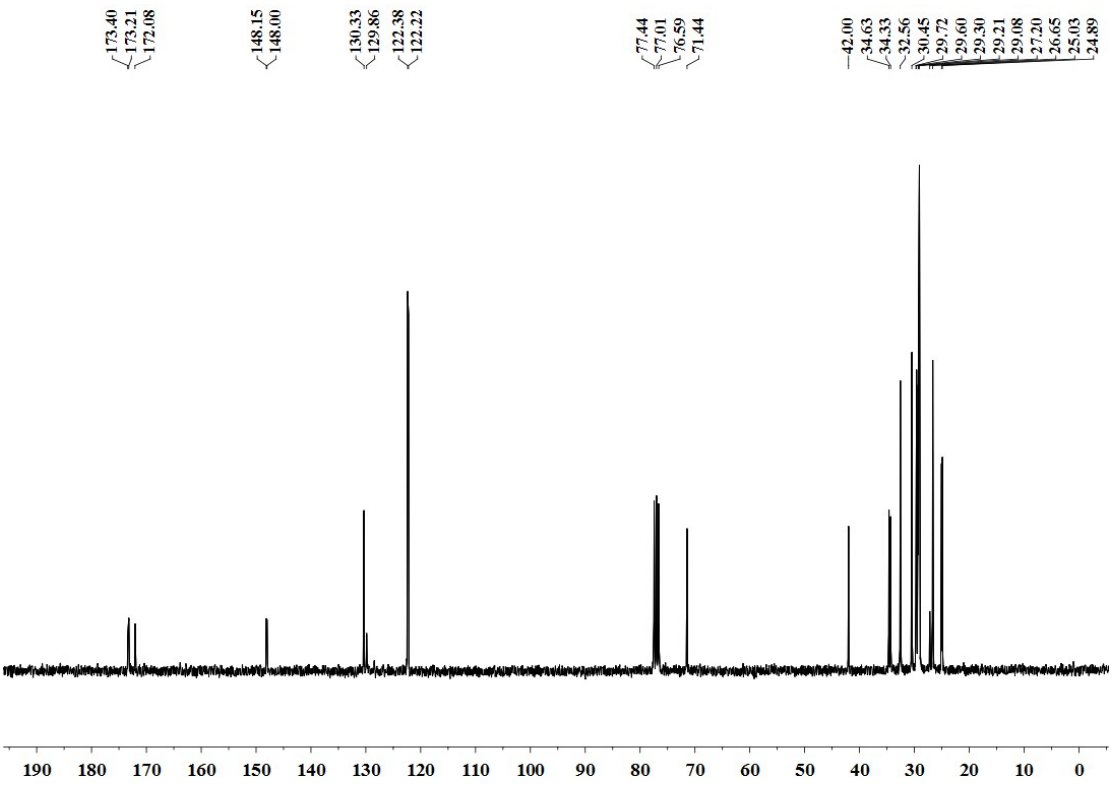


Figure S18. ^{13}C NMR spectrum of polymer **11** from ED-ROMP

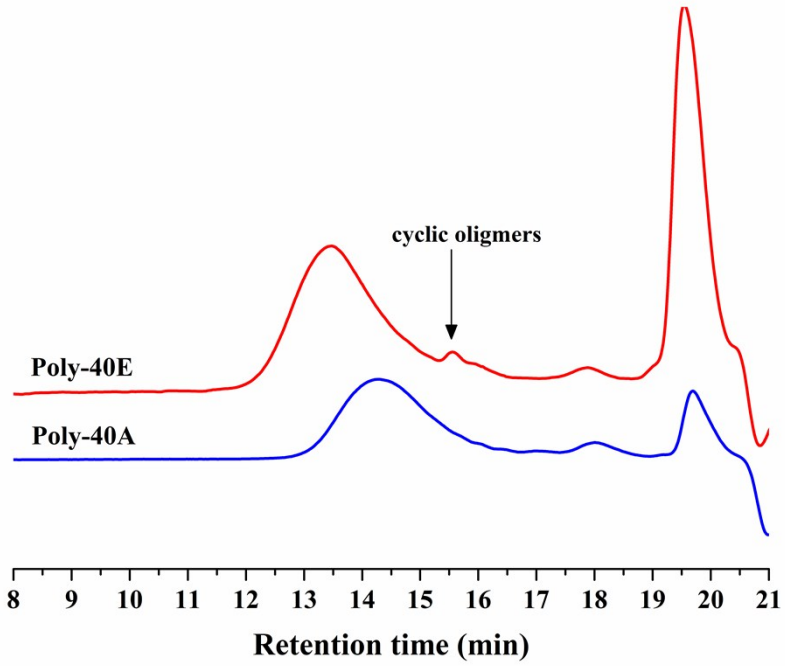


Figure S19. GPC curves of Poly-20E and Poly-20A.

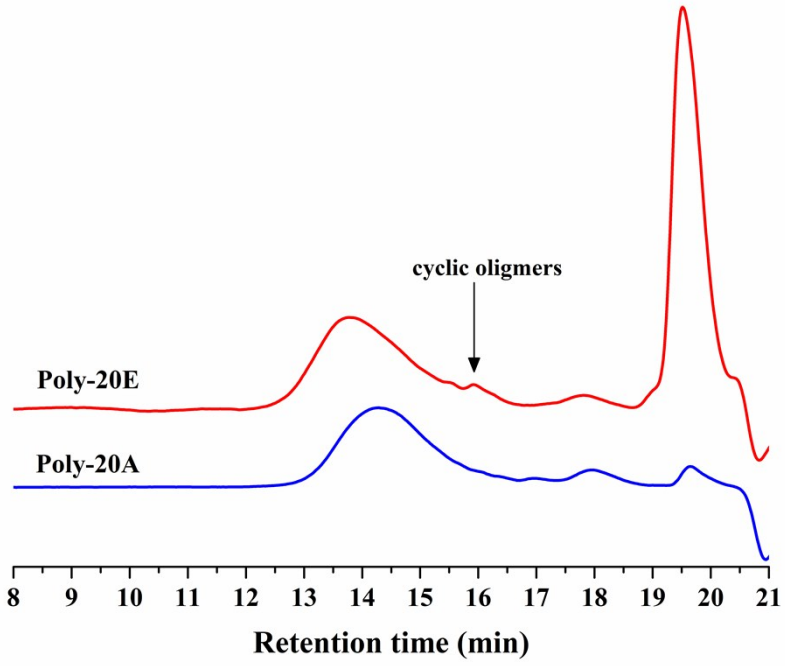


Figure S20. GPC curves of Poly-40E and Poly-40A.

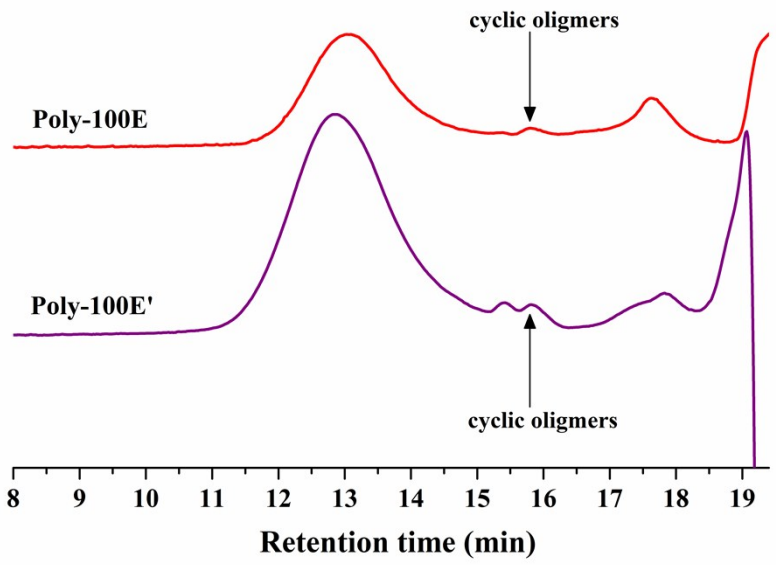


Figure S21. GPC curves of Poly-60A, Poly-60E and Poly-60E'.

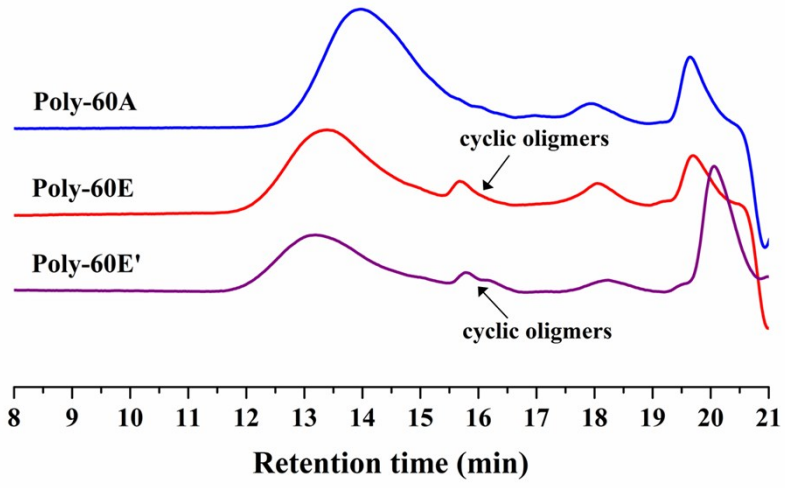


Figure S22. GPC trace of Poly-100E and Poly-100 E'.

Table S1. Phase Behavior of Polymers prepared by ED-ROMP[a]

Compound	Transition temperature (°C) [enthalpies, J/g]
Poly-20E	Heat: SmX 156.3 [3.6] Iso Cool: SmX 140.3 [2.1] Iso
Poly-60E	Heat: SmX 157.1 [4.1] Iso Cool: SmX 140.3 [2.9] Iso
Poly-100E	Heat: SmX 158.6 [5.6] Iso Cool: SmX 140.7 [4.1] Iso

[a] Temperatures taken from the second heating and fist cooling cycles determined by DSC (10 °C/min). SmX: unidentified smectic phase, Iso: isotropic phase.