—— Electronic Supplementary Information ——

Synthesis of Polymeric Ladders by Topochemical Polymerization

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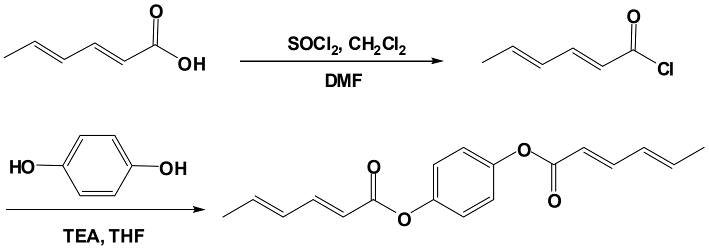
Material and Method

All starting materials were obtained commercially and used as received. Analytical TLC was performed on silica G TLC plate w/UV254 (Sorbent Technologies). ^{1}H NMR and ^{13}C NMR data were collected on a Brüker Advance 500 spectrometer, and processed with its self-bond software. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak ($CDCl_3$ signal as reference, $^{1}H = 7.27$ ppm, $^{13}C = 77.0$ ppm). Electrospray Ionization Mass Spectra (ESI-MS) were obtained using 10 mM ammonium acetate as the matrix on a Time-of-Flight MS G1969A Series 6200 spectrometer (Agilent Technologies Co. Ltd.) with Fragmentor 250V and ESI 5000V. The X-ray data were collected by a Brüker D8 single crystal X-ray diffractometer (Apex II). IR spectra were acquired on a Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. Melting points of compounds were detected by Melting Point Apparatus SMP10 (Bibby Scientific Ltd., UK) without correction. X-ray powder diffraction spectra were recorded on a X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 KW copper tube X-ray generator of $\lambda = 0.1541$ nm under 40 mA and 45 KV. Spectra were collected at room temperature in a 2θ range of 3°~35° at a scanning rate of 3°/min. Calorimetric curves were recorded on a Perkin Elmer Jade DSC at a ramping rate 10 ^{o}C/min. Heat flow was recorded from both the first heating and cooling curve.

Synthesis of compound I

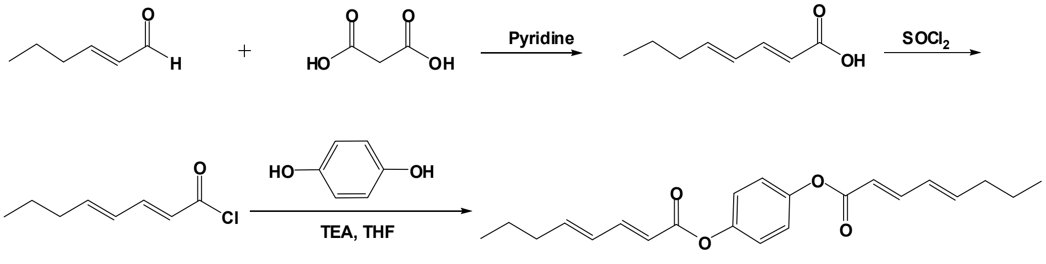


I

Scheme S1. Synthesis of monomer **I**

In a dried 100 mL round bottom flask, hydroquinone (0.55 g, 5 mmol) and triethylamine (1.1 g, 11 mmol) were dissolved in 20 mL THF while stirring in an ice bath. Freshly synthesized sorbic chloride (1.43 g, 11 mmol) in 10 mL THF was added to the above solution dropwisely within 20 min. After finishing dropping, the mixture was stirred for another 15 min at r.t, and then was poured into 150 mL ice-water. The yellow precipitate was collected by filtration and recrystallized in acetone to afford colorless crystals as the titled product with yield over 90% with m.p.178~180 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 1.90(d, 6H), 5.94-5.97 (d, 2H), 6.24-6.28 (m, 4H), 7.14 (s, 4H), 7.41-7.46(m, 2H); ^{13}C NMR($CDCl_3$, δ, ppm): 19.22, 118.25, 122.85, 130.14, 141.30, 147.52, 148.50, 165.98.

Synthesis of compound II



II

Scheme S2. Synthesis of monomer **II**

Synthesis of (2*E*,4*E*)-octa-2,4-dienoic acid

A 250 mL round-bottom flask was charged with malonic acid (20.8 g, 0.2 mol) and pyridine (20 mL) as solvent, and the mixture was heated under stirring until a clear solution was obtained. To the solution was added hexenal (9.8g, 0.1mol) and kept refulxing for 1 h, more hexenal (9.8 g, 0.1 mol) was added and continued to reflux for 2~4 h until the spot of hexenal disappeared on TLC plate. The mixture was poured into about 100 mL ice and acidified by concentrated sulfuric acid. An oil phase was formed on the top of the mixture. The mixture was then put in the freezer overnight for the product to crystallize out. The titled compound as colorless crystals was collected by filtration with yield 60%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.89(t, 6H), 1.38-1.46(m, 4H), 2.11-2.15(m, 4H), 5.78-5.81(d, 2H), 6.18-6.29(m, 4H), 7.13-7.18(m, 2H); ^{13}C NMR($CDCl_3$, δ, ppm):13.89, 21.78, 34.70, 120.49, 128.37, 144.28, 144.93, 168.06.

The compound **II** was synthesized by a similar procedure for the synthesis of compound **I** in which the acid was first transferred to acyl chloride and then esterified with hydroquinone. The obtained crude product was further purified by recrystallization in acetone to afford colorless crystals as compound **II** with overall yield 70%. ^{1}H NMR ($CDCl_3$, δ, ppm): 0.92(t, 6H), 1.47-1.48(m, 4H), 2.17-2.18(m, 4H), 5.94-5.97(d, 2H), 6.23(m, 4H), 7.12(s, 4H), 7.40-7.45(m, 2H); ^{13}C NMR($CDCl_3$, δ, ppm): 14.10, 22.29, 35.51, 118.0, 122.8, 128.8, 146.3, 146.5, 147.7, 147.8, 148.4, 166.0.

Recrystallization Procedures

In a 20 mL vial with screw lid, a certain amount of powder was dissolved in a pure solvent to obtain a supersaturated solution by heating. The solution was then put at ambient temperature to allow the solution to cool down and/or slowly evaporate by gently loosing the lid until single crystals grow.

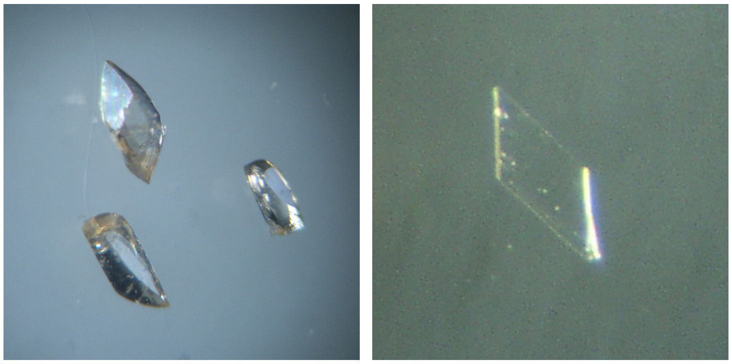


Figure S1. Photographs of crystals: monomer **I** (left) and **II** (right) obtained by slowly evaporating their acetone solutions.

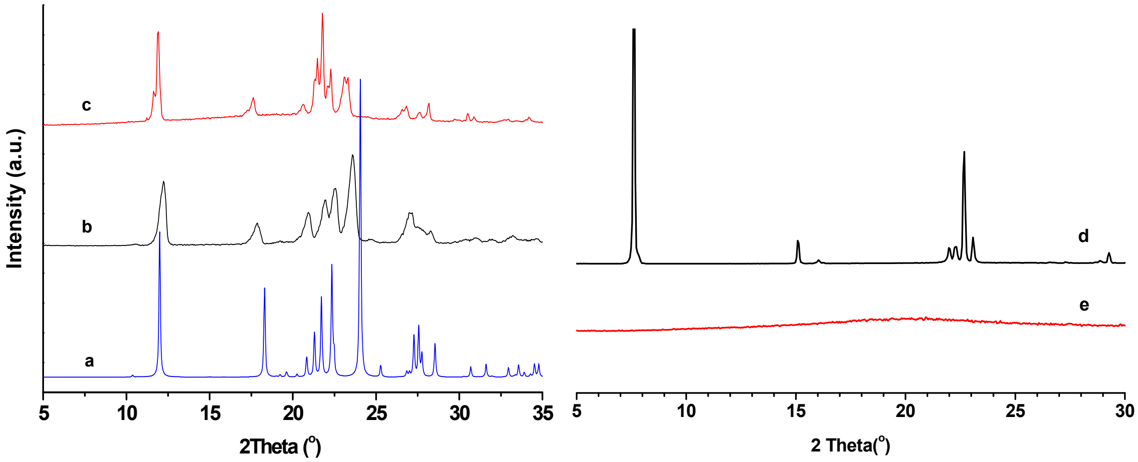


Figure S2. Powder XRD spectra of the two monomers and their polymers: (a) calculated based on its single crystal structure of **I** collected at 150 K; (b) powder sample of monomer **I**; (c) polymer **I** by UV at 120 °C for 8 h; (d) ground crystals sample of monomer **II**; (e) polymer **II** obtained by UV at 70 °C for 64 h.

Table S1. Crystal Data of the Two Monomer Monomers **I** and **II**.

Crystals	Monomer **I**	Monomer **II**
CCDC #	957993	957994
Formula	$C_{18}H_{18}O_4$	$C_{22}H_{26}O_4$
FW	298.32	354.43
Cryst. Size [mm]	0.15, 0.15, 0.65	0.25, 0.50, 1.0
Space Group, Z	$P2_1/c$	P-1
a (Å)	5.6003(3)	5.4869(3)
b (Å)	8.1769(4)	8.0395(4)
c (Å)	17.0907(9)	12.2631(8)
α (°)	90.00	71.633(4)
β (°)	94.409(3)	89.640(3)
γ (°)	90.00	74.810(3)
V ($Å^3$)	780.32(7)	493.73(5)
Temp. (K)	150(2)	150(2)
ρcalc [g/cm^3]	1.270	1.192
μ [mm^{-1}]	0.089	0.081
Radiation Type	Mo	Mo
F(000)	316	190
No of measured refl.	12403	4904
No of independent refl.	2252	2800
No of refl. ($I \geq 2\sigma$)	1727	2423
R1/wR2 ($I \geq 2\sigma$) [%]	4.10/10.19	4.30/12.58
R1/wR2 (all data) [%]	5.90/11.49	5.18/14.27

Photopolymerization Procedures

Photoirradiation was carried out using a high-pressure Hg lamp (450 W, ACE Glass Inc.) at a distance of about 10 cm. The inside wall of the reaction chamber was a mirror to enhance the irradiation. The reaction temperature was regulated by a cooling fan and a lid attached to the reaction chamber. The polymer yield was gravimetrically determined after removing any unreacted monomer with chloroform.

Table S2. Thermal and UV Polymerization of Monomer **I**.

Samples	Method	Temp. (°C)	Time (h)	Yield[a] (%)
Compound **I**	Heating	150	7 days	96
	UV [b]	70	2	20
	UV	70	24	50
	UV	70	72	83
	UV	120	2	46
	UV	120	6	84
	UV	120	16	99

[a] Isolated yield after washing with $CHCl_3$. [b] A high pressure 450 W Hg lamp was used. The samples were kept for about 10 cm away from the lamp and the reaction chamber was cooled by a fan.

Polymer Hydrolysis Procedures

The monomer **I** was polymerized by UV irradiation at 120 °C for 16 h. The obtained polymeric ladder was added into 2M KOH aqueous solution. The mixture was stirring for 1 h at ambient temperature until it forms two phases, the upper layer of a black aqueous phase and the lower layer of some brown insoluble solid. The black soluble phase was used for NMR measurement with deuterated methanol as solvent (See page S14-15). As shown in the NMR sprectra, hydrolysis of the polymeric product of **I** yielded hydroquinone salt and no unreacted monomer was observed. The insoluble solid has poor solubility in all common organic solvents.

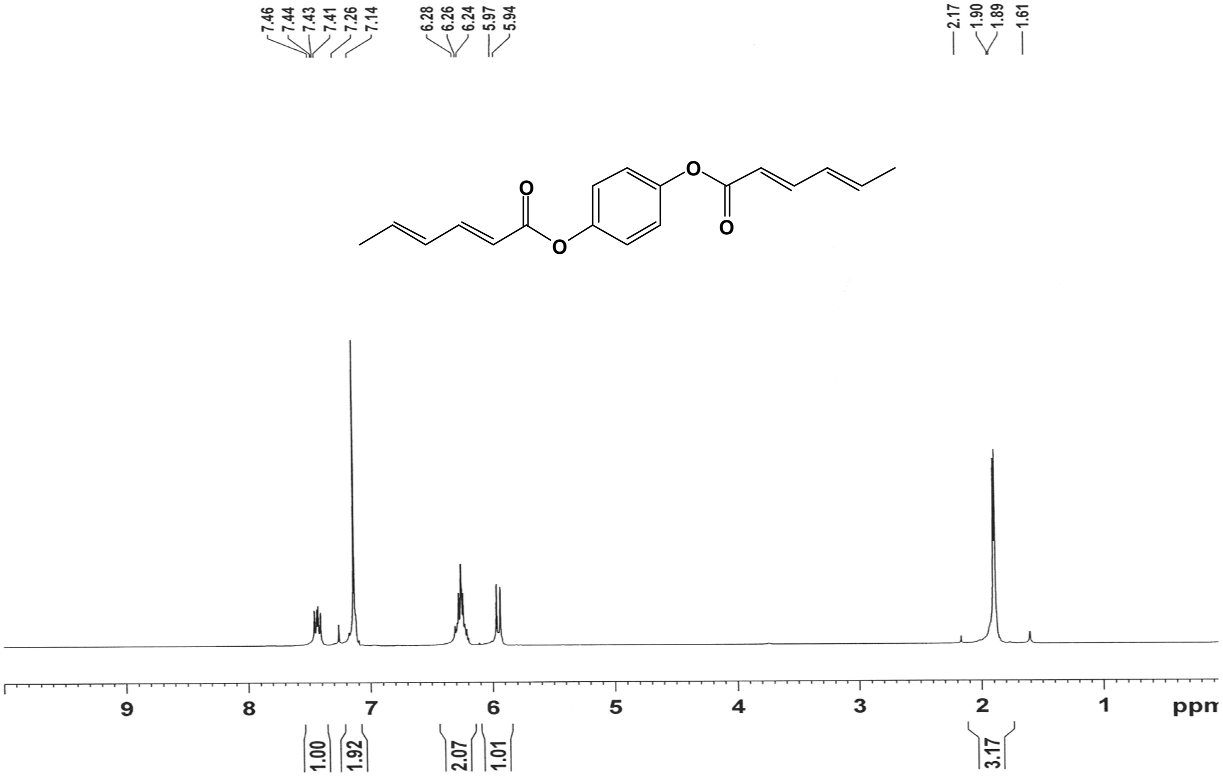


Figure S3. ^{1}H NMR spectrum of compound **I**

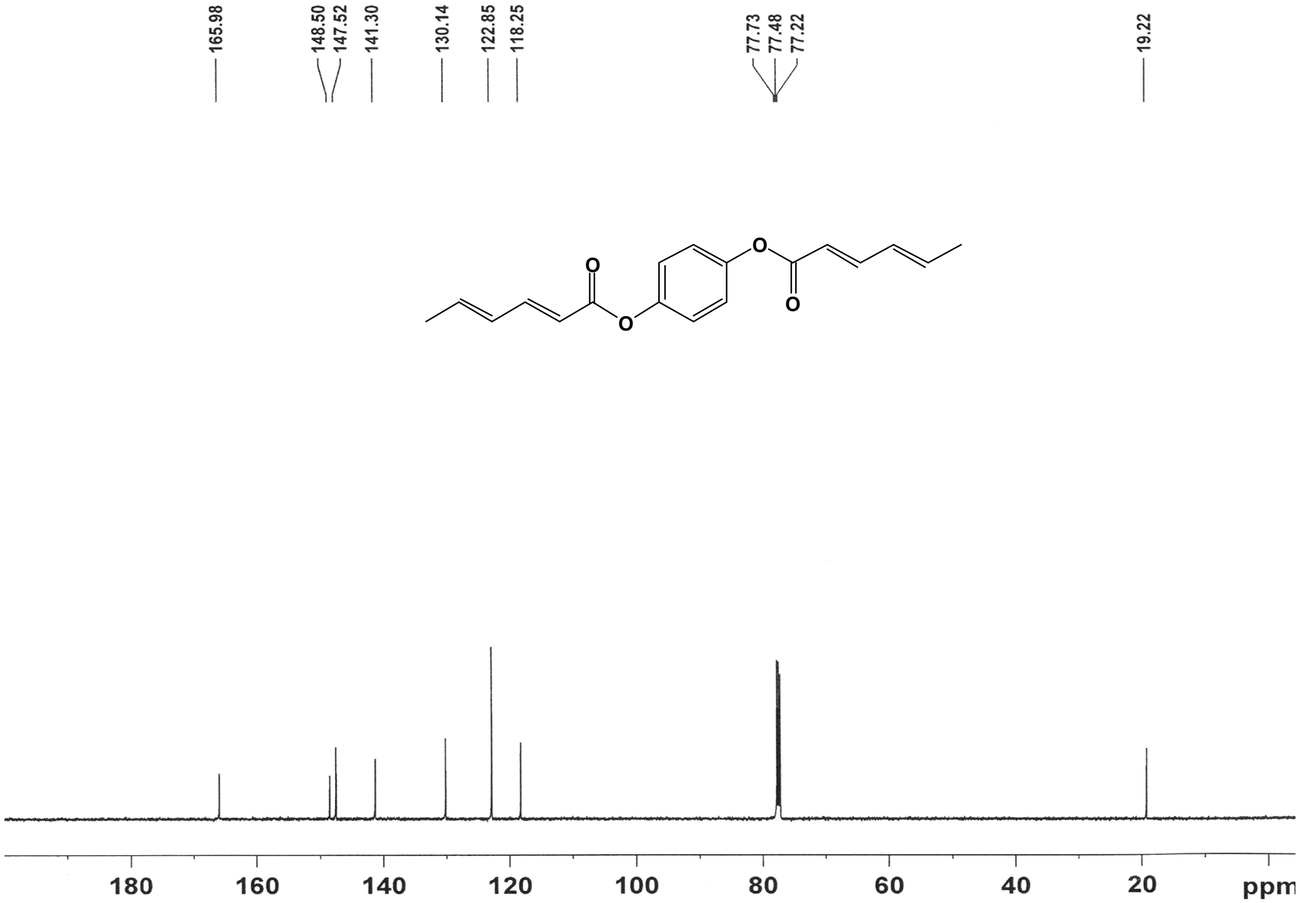


Figure S4. ^{13}C NMR spectrum of compound **I**

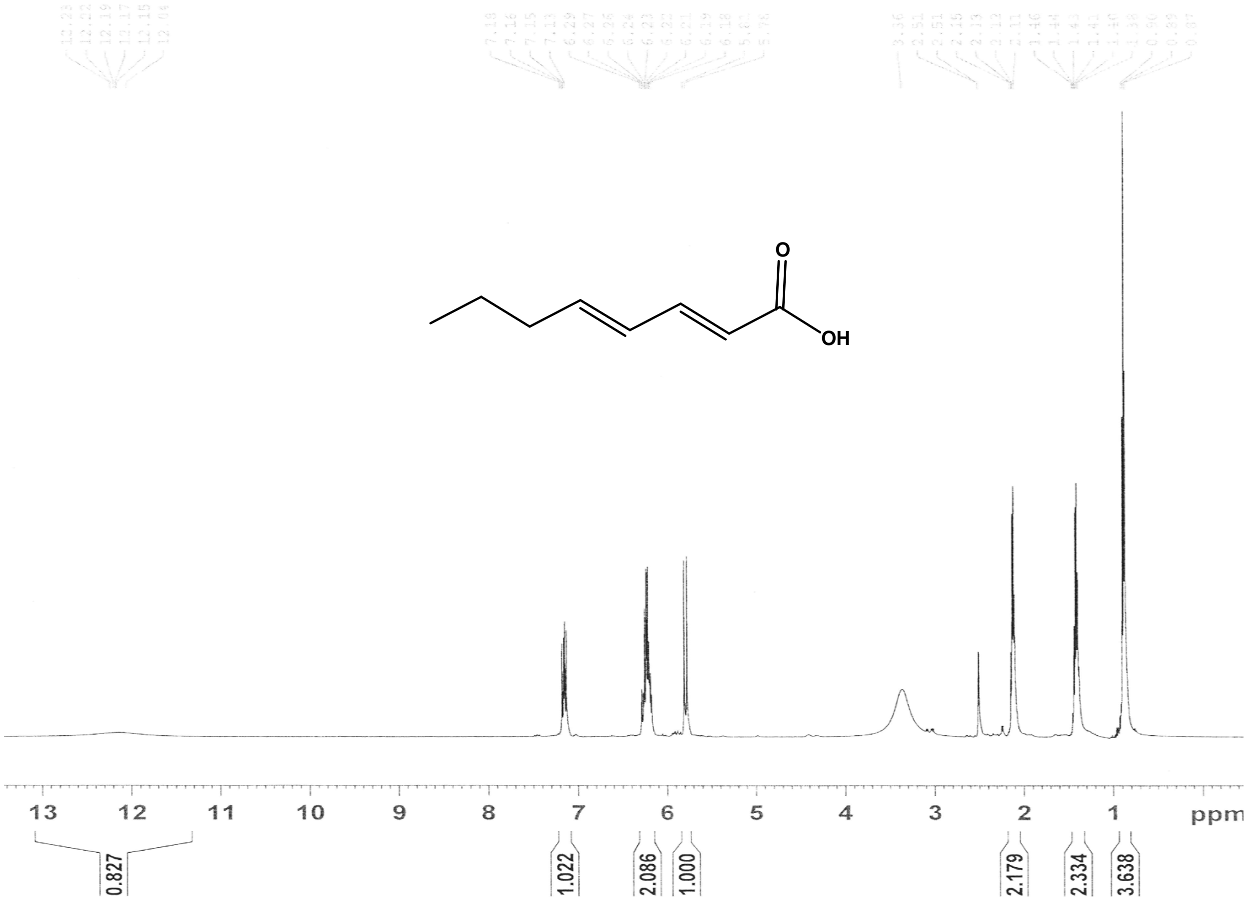


Figure S5. ^{1}H NMR spectrum of (2*E*, 4*E*)-octa-2, 4-dienoic acid.

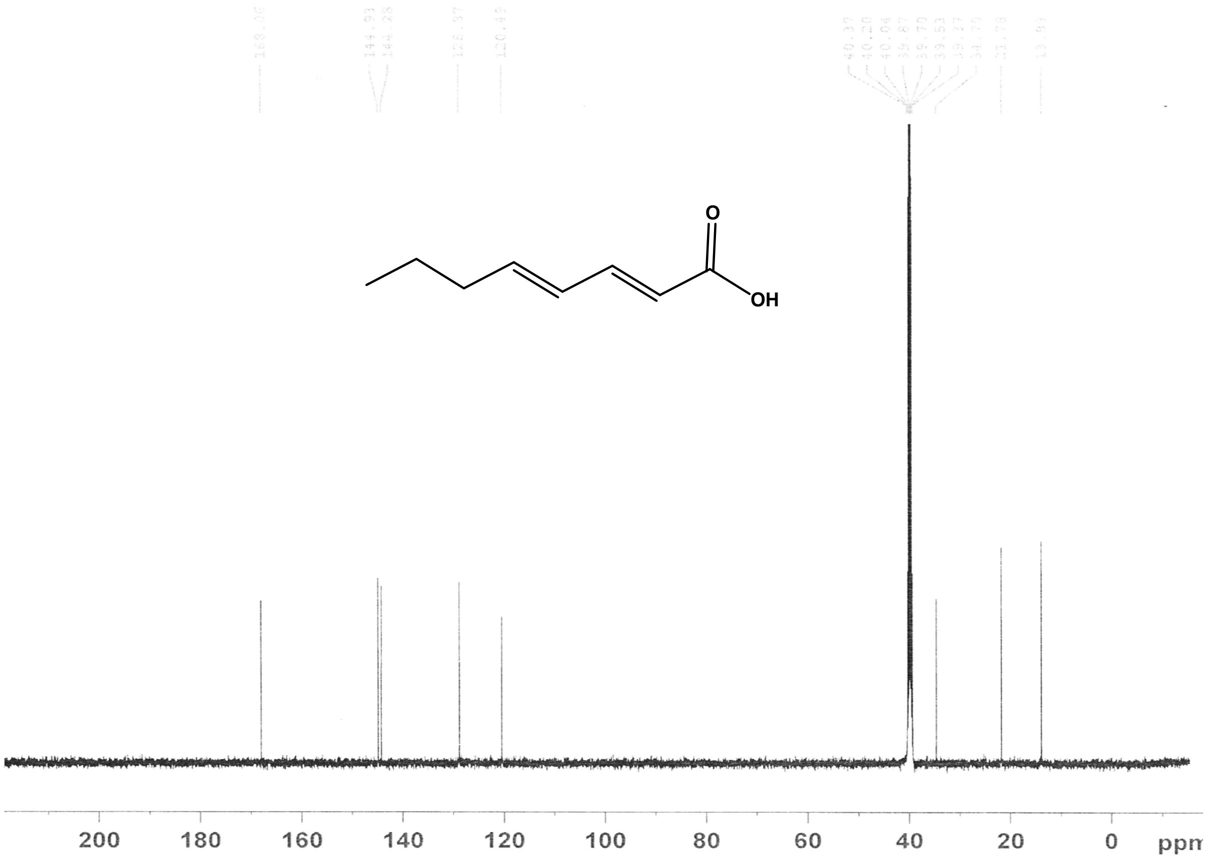


Figure S6. ^{13}C NMR spectrum of (2*E*, 4*E*)-octa-2, 4-dienoic acid.

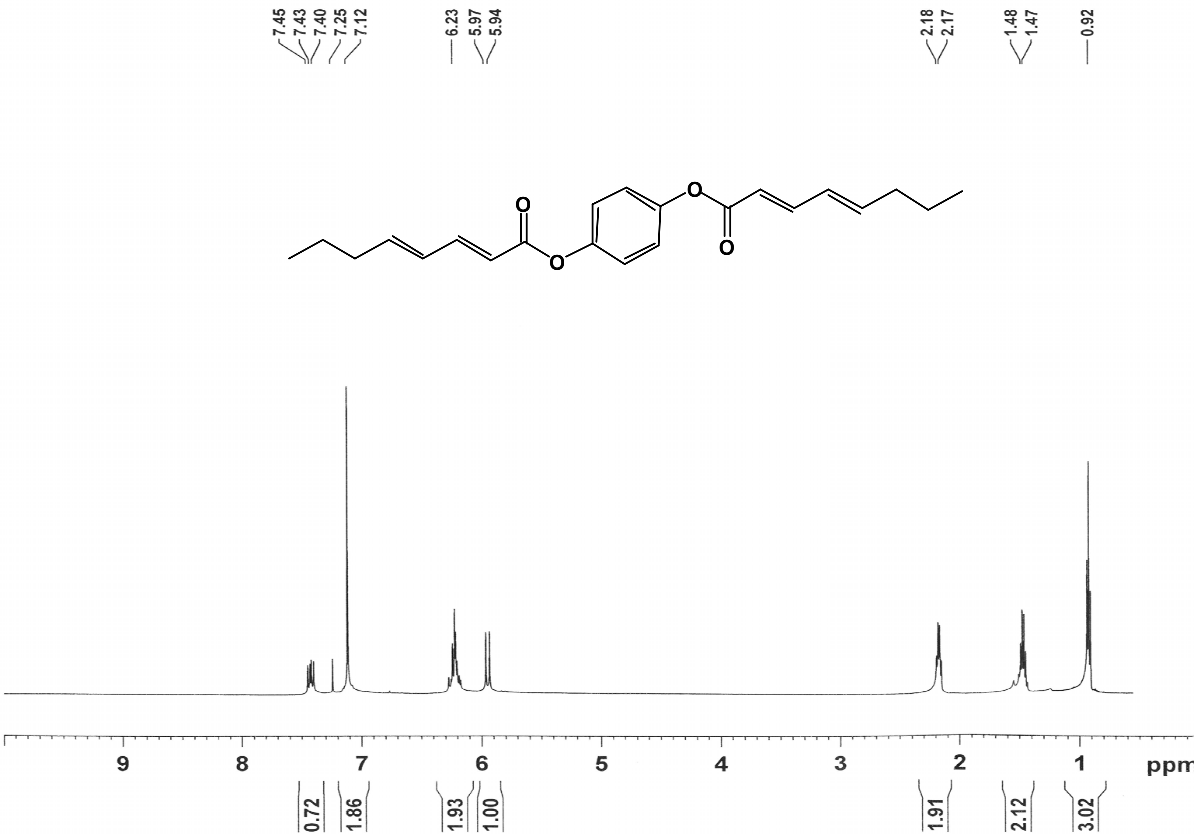


Figure S7. ^{1}H NMR spectrum of compound **II**

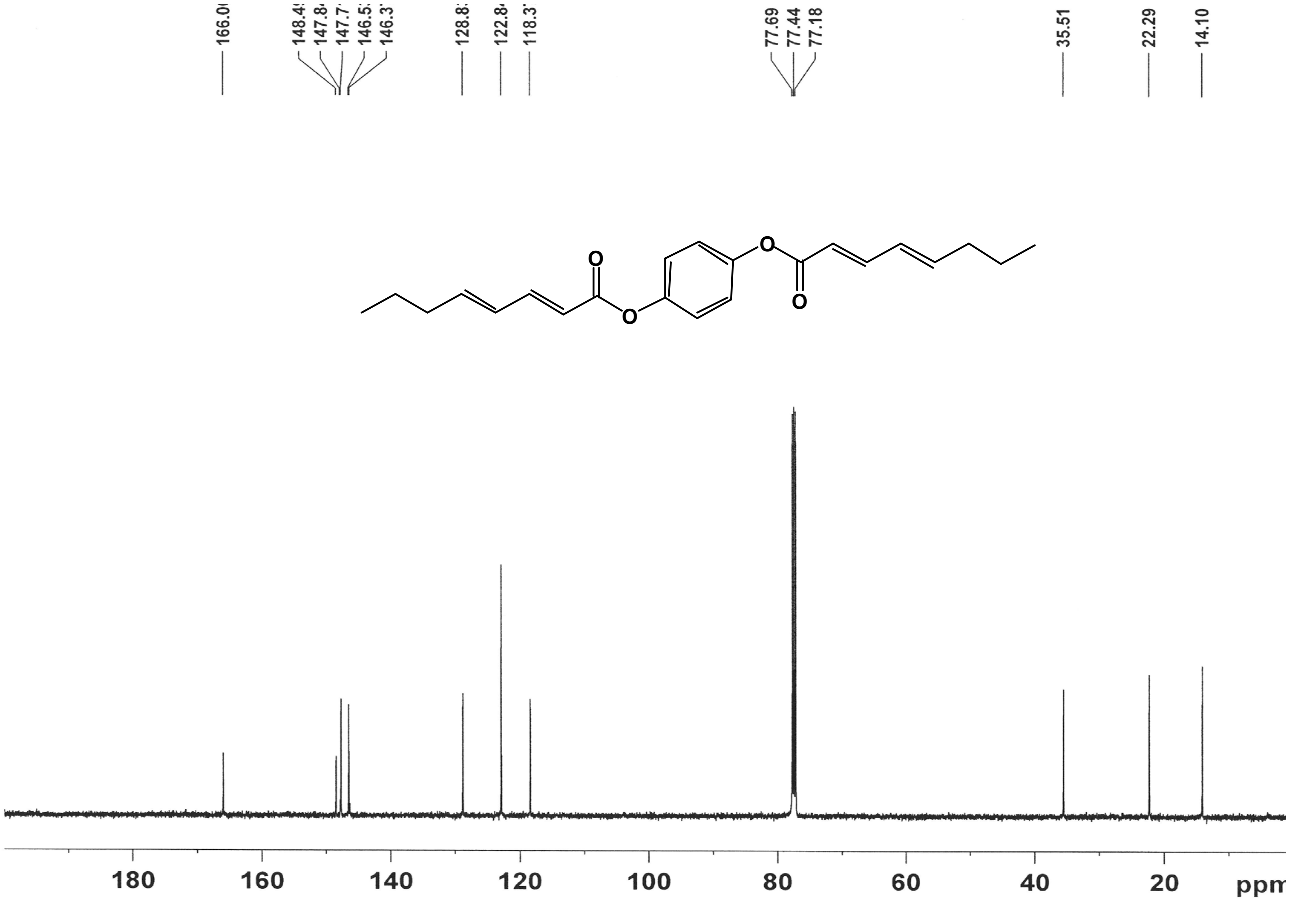


Figure S8. ^{13}C NMR spectrum of compound **II**

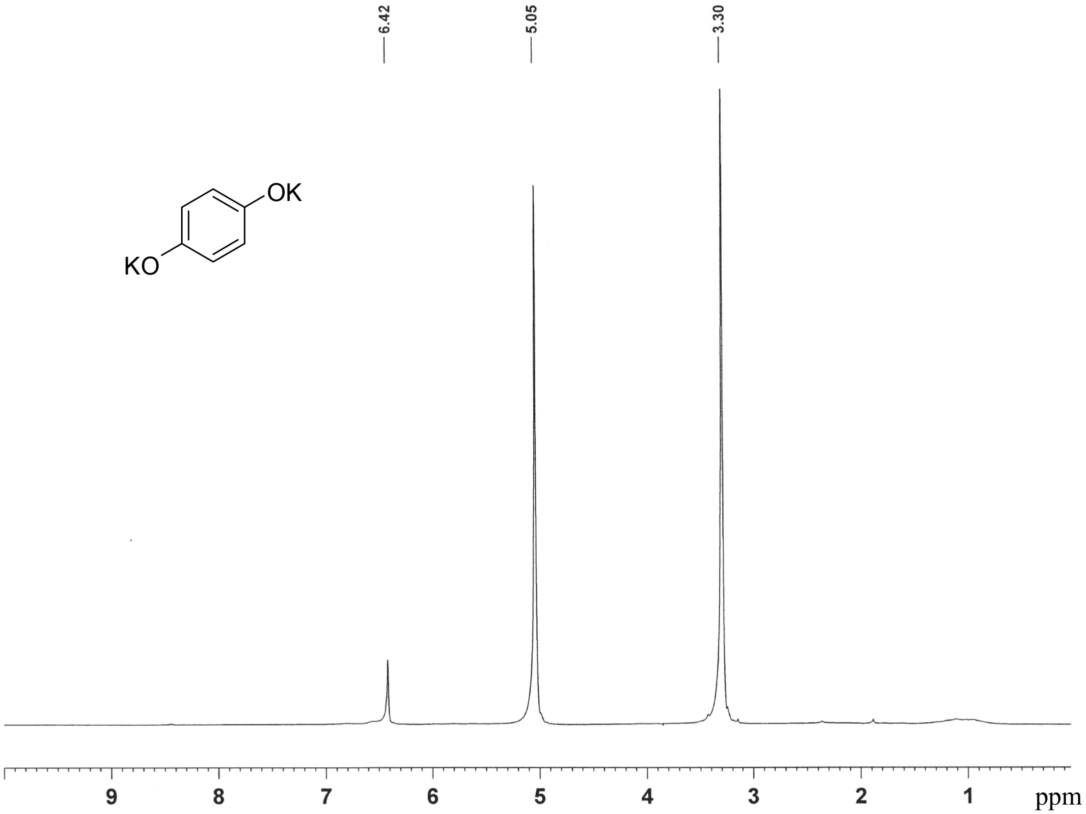


Figure S9. ^{1}H NMR of potassium benzene-1,4-bis(olate) from hydrolysis of polymer **I**

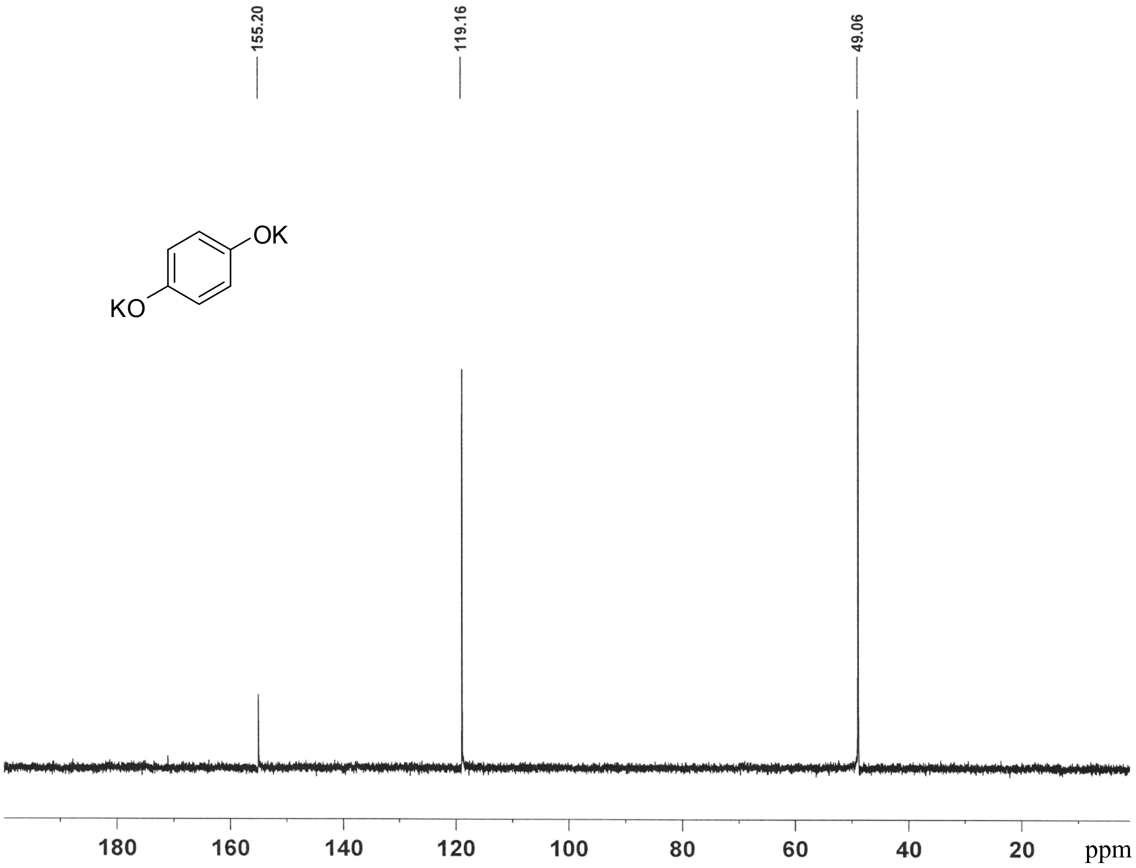


Figure S10. ^{13}C NMR of potassium benzene-1,4-bis(olate) from hydrolysis of polymer **I**

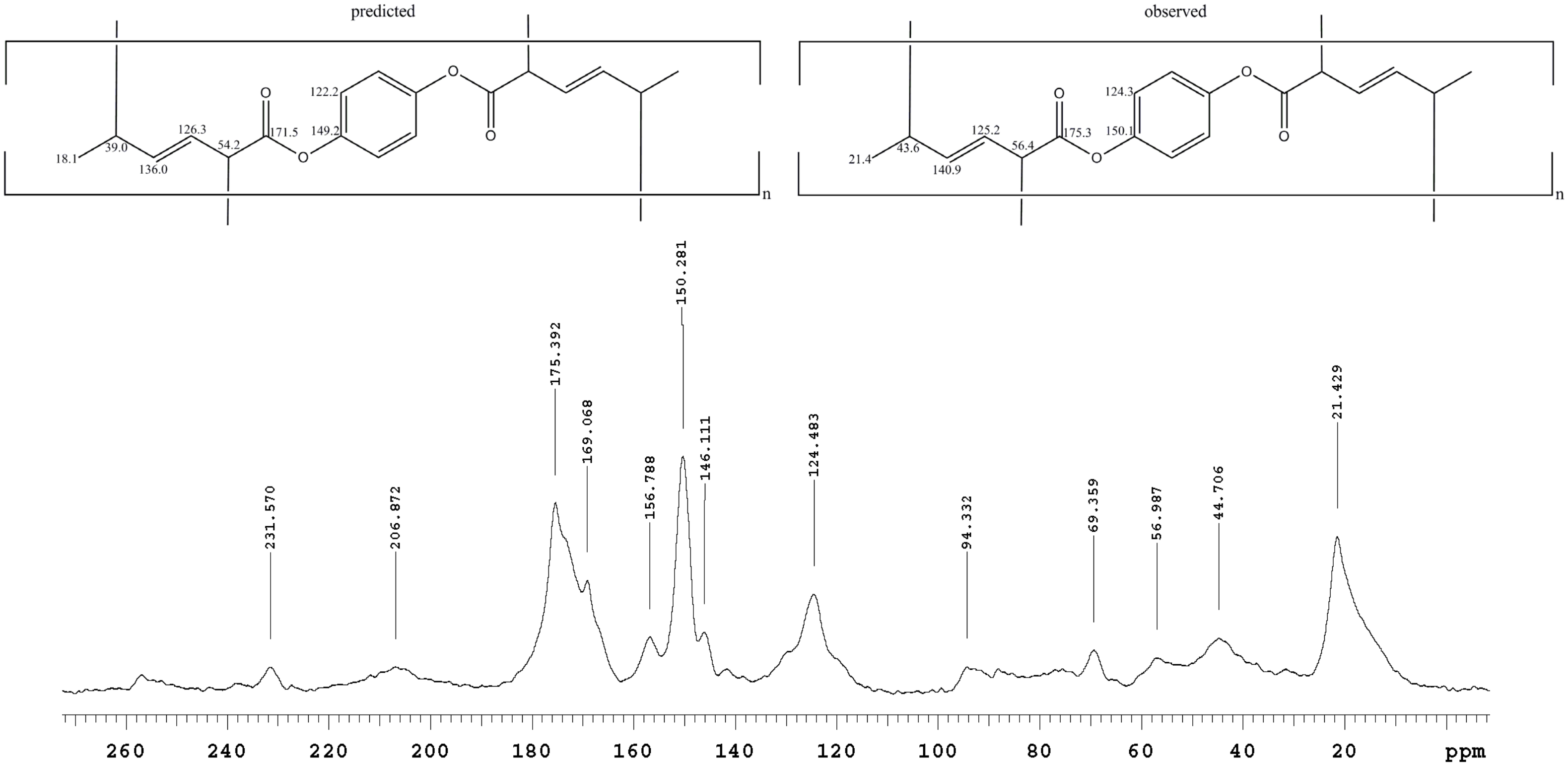


Figure S11. Solid State ^{13}C NMR spectrum of polymer **I**

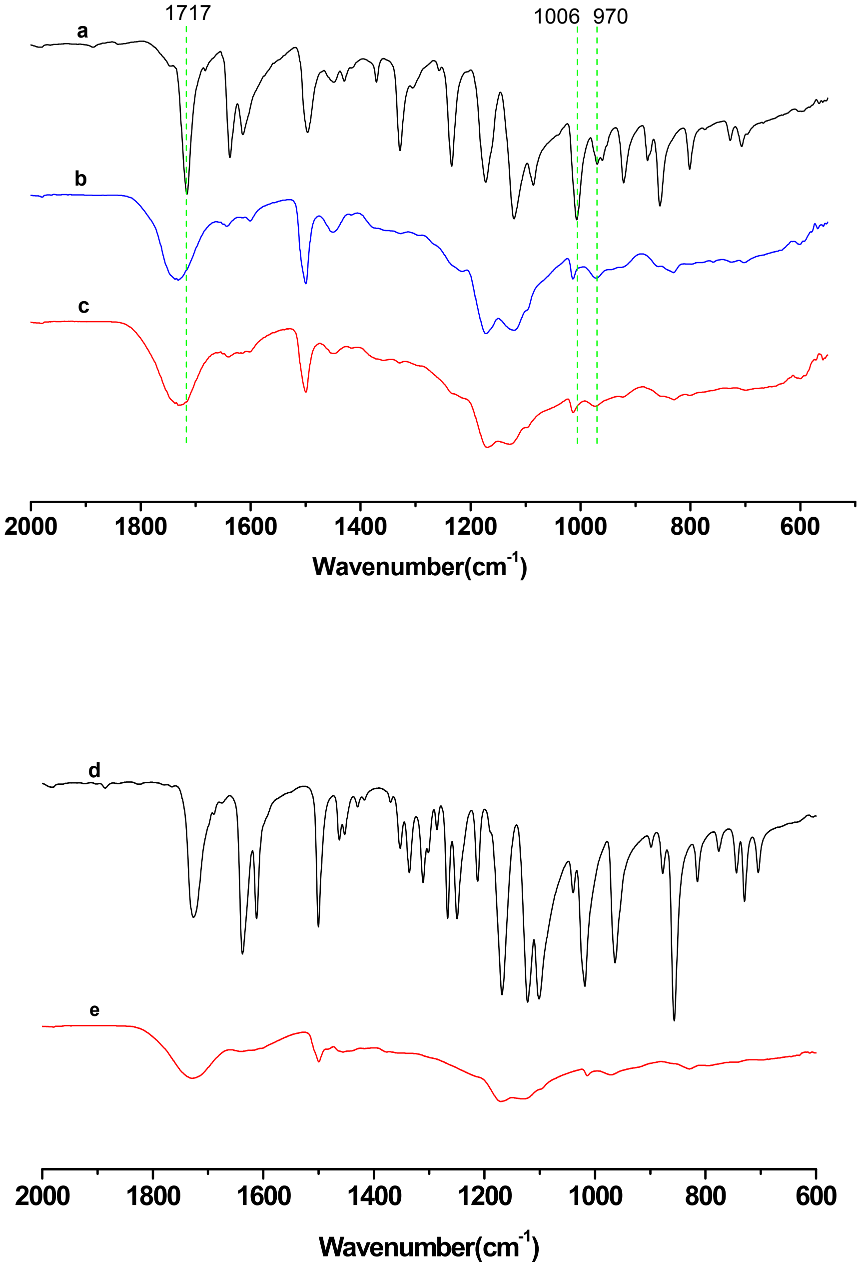


Figure S12. FT-IR spectra of the two monomers and their polymers: (a) monomer **I**, (b) polymer **I** obtained by reaction at 150 °C for 7 days, (c) Polymer **I** obtained by UV at 120 °C for 8 h; (d) monomer **II**; (e) polymer **II** obtained by UV at 70 °C for 64 h.

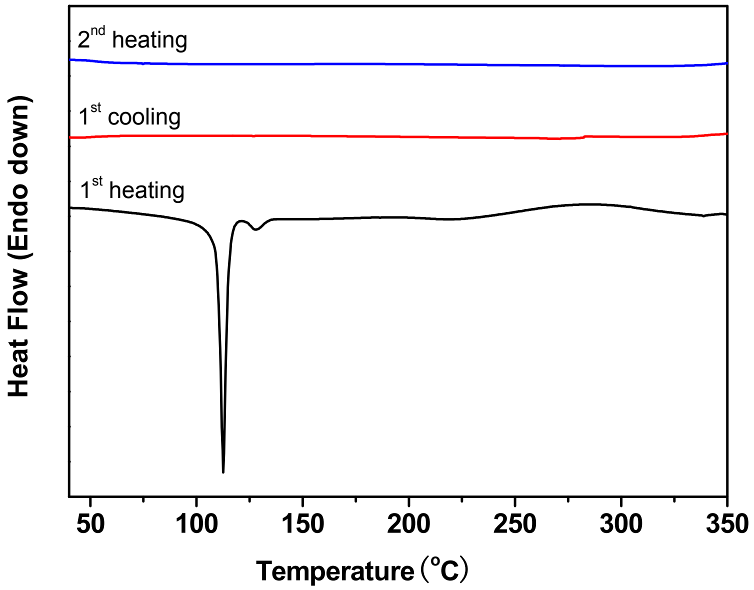


Figure S13. DSC curves of monomer **II**: The melting of the compound **II** starts at 105 °C and reaches its peak at 112°C. Continuing heating triggers the polymerization that starts at 225 °C, reaches its peak at 285 °C and finishes at 345 °C. The featureless curves of the first cooling and the second heating confirmed the completion of polymerization of compound **II**.

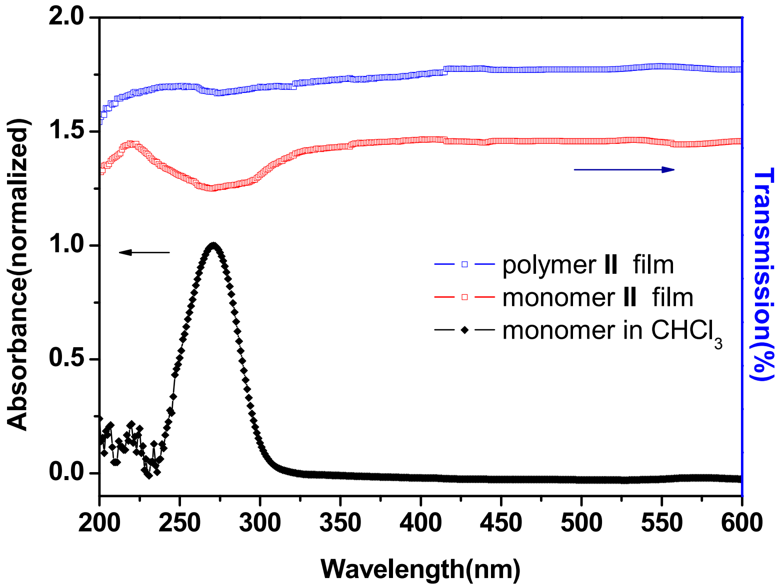


Figure S14. UV-vis spectra of monomer **II** and its polymer: