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## **Linear Polyester Synthesized from Furfural-based Monomer by Photoreaction in Sunlight**

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## 1. Experimental Section

**General Methods:** All the reagents were purchased from Alfa Aesar, Sigma-Aldrich and used without further purification. The light sources used for the photopolymerization were sunlight and a Hanovia medium pressure mercury lamp (PC 451050, 450 W). The optical filter used for the photoreaction with mercury lamp was ZRR0340 Red Rejection UV Filter from Asahi Spectra USA Inc. The solution phase nuclear magnetic resonance spectra (NMR) were recorded with Bruker ADVANCE ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz). All spectra were obtained in deuterium dimethyl sulfoxide (DMSO- $d_6$ ). Single crystal X-ray data were recorded on Bruker Kappa Apex II Duo X-Ray Diffractometer with Mo  $K\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) or Cu  $K\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ). Melting points were measured on a MEL-TEMP device without correction. Infrared spectroscopy (IR) was recorded on Thermo Scientific Nicolet iS5 FT-IR spectrometer. The mass spectrometric analyses were performed using a high-resolution time of flight G1969A with electrospray (atmospheric pressure chemical) ionization (Agilent, Santa Clara, CA, USA) and reported as  $m/z$  (relative intensity). X-ray Powder Diffraction (XRD) was performed on a X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 KW copper tube X-ray generator of  $\lambda = 0.1541 \text{ nm}$  under 40 mA and 45 KV. Spectra were collected at room temperature in a  $2\theta$  range of  $3^\circ \sim 35^\circ$  at a scanning rate of  $3^\circ/\text{min}$ .

**Synthesis of 2-Furanacrylic Acid:** Furfural (1.2 g, 12.5 mmol), Malonic acid (1.6 g, 15.0 mmol) and pyridine (2.0 g, 25 mmol) were added to 20 mL of 2-MeTHF.<sup>1</sup> The mixture was stirred at reflux for 16 h. After the reaction the mixture was adjusted to  $\text{pH} \approx 2$  with concentrated HCl and washed with brine (20 mL  $\times$  3). The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give 2-furanacrylic acid (1.5 g, 87%, yellow solid) as a photoreactive building block.<sup>2</sup>  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  12.41 (s, 1H), 7.84 (s, 1H), 7.38 (d,  $J = 16 \text{ Hz}$ , 1H),

6.93 (d,  $J = 3.5$  Hz, 1H), 6.62 ppm (t,  $J = 3.5$  Hz, 1H), 6.15 (d,  $J = 16$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  167.7, 150.7, 146.1, 131.2, 116.3, 115.9, 113.1.

**Synthesis of Monomer I:** The 2-furanacrylic acid (1.4 g, 10.5 mmol) was dissolved in 10 mL of thionylchloride and the mixture was stirred at reflux for 2 h. Then the reaction mixture was concentrated and the residue was diluted with THF (10 mL).<sup>3</sup> Another solution of 1,5-pentanediol (0.5 g, 4.8 mmol) and triethylamine (1.6 g, 15.9 mmol) in THF (10 mL)<sup>4</sup> was added dropwise to the above diluted residue. The mixture was stirred at room temperature for 16 h and then was poured into 200 mL of water. The precipitate was filtered to give monomer **I** (1.3 g, 79%) as a gray solid. mp: 66-67 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  7.85 (s, 2H), 7.45 (d,  $J = 15.5$  Hz, 2H), 6.97 (d,  $J = 3.5$  Hz, 2H), 6.63 (t,  $J = 3.5$  Hz, 1H), 6.21 (d,  $J = 15.5$  Hz, 2H), 4.13-4.15 (m, 4H), 1.65-1.70 (m, 4H), 1.41-1.44 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  166.4, 150.5, 146.4, 131.5, 116.4, 115.1, 113.1, 64.2, 28.2, 22.3; IR: 1701, 1635, 1556, 963  $\text{cm}^{-1}$ ; UV/Vis:  $\lambda_{\text{max}}$  302 nm; HRMS (m/z):  $[\text{M}+\text{Na}]^+$  calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_6\text{Na}$ , 367.1157; found 367.1119.

**Crystallization:** The crystals of **I** were obtained in  $\text{DMSO}/\text{H}_2\text{O}$  (3:1) at room temperature. Monomer **I** (20 mg) was added to solvent  $\text{DMSO}/\text{H}_2\text{O}$  (20 mL). The vial of the suspended mixture was put in ultrasonic cleaner (Bransonic® Models 1200) for a half hour. The mixture was filtered into a 20 mL vial with filter paper. The vial with clear solution was allowed to stay without a cover until the crystals were formed. Crystallographic data for monomer **I** and intermediate **Ia**, are available in Cambridge Crystallographic Data Centre (CCDC# 1406681, and 1408218).

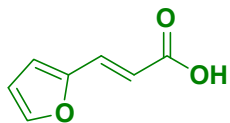
**Photoreaction:** Crystals were irradiated in sunlight on a slide glass. 10 mg of monomer **I** was scattered on a slide glass and the sample was placed outdoors for photoreaction. The process of photoreaction was monitored by FT-IR. The photoreaction of monomer **I** was carried out in 3 days with 8 h of solar irradiation per day.

During the UV photoreaction, 10 mg of monomer **I** crystal powder was scattered on a glass plate and covered by a ZRR0340 Red Rejection UV Filter. The combined plates with the monomer **I** were put in a photoreactor equipped with Hanovia medium pressure mercury lamp (PC 451050, 450 W). Due to its low melting point of monomer **I** (66-67 °C), the photoreaction was further cooled with a fan besides the immersion cooling well and the polymerization was carried out near ambient temperature. The polymerization was accomplished in 24 h.

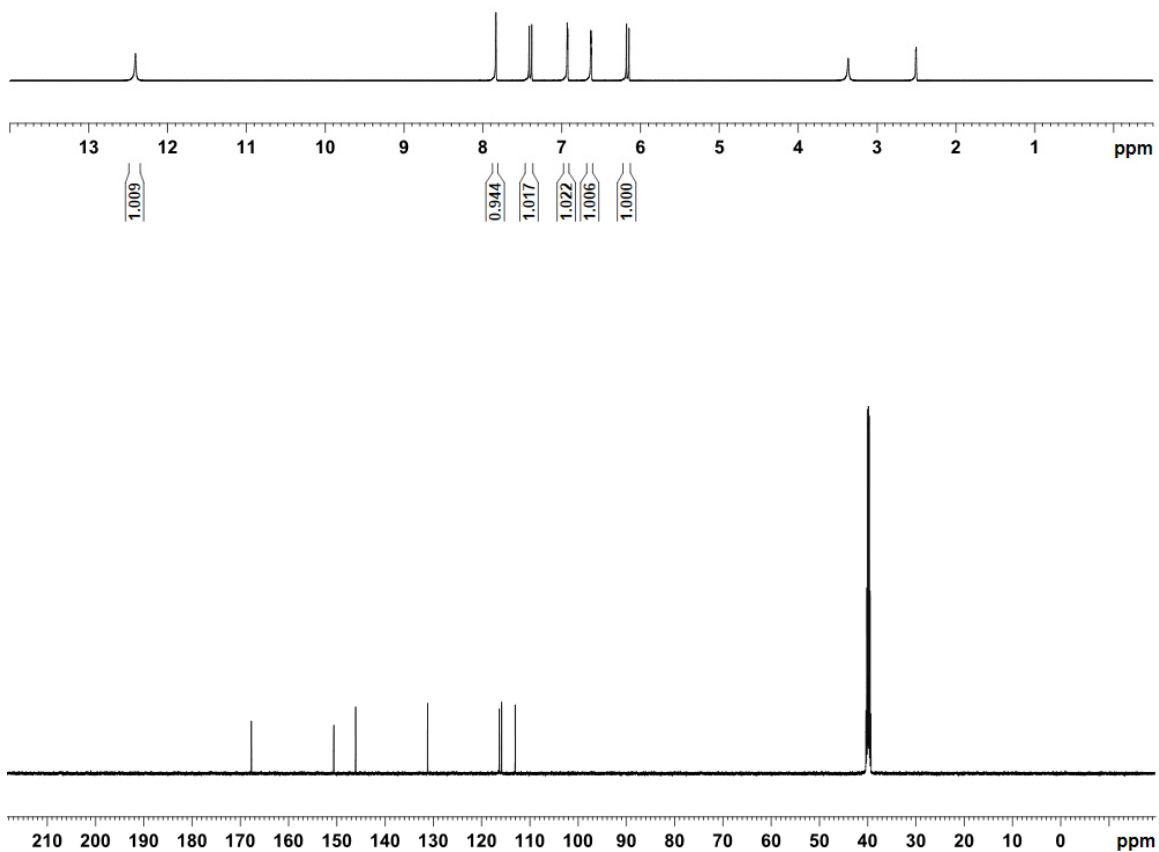
In a gram-scale test, 1.0 g of monomer **I** powder was scattered on a 5" × 5" glass plate and covered by ZRR0340 Red Rejection UV Filter. The combined plates with monomer **I** were put in the photoreactor and the powder was stirred every 2 h until the reaction completed in 24 h at room temperature.<sup>4</sup>

For the partial single-crystal-to-single-crystal (SCSC) transformation, 4 mg of single crystals were used instead of the monomer powder **I** in the photopolymerization. The intermediate crystal **Ia** was obtained after 2 days of the UV irradiation.<sup>5</sup>

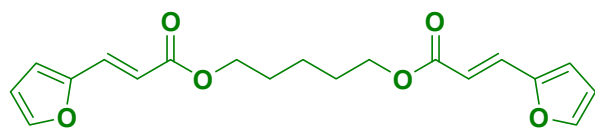
## 2. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



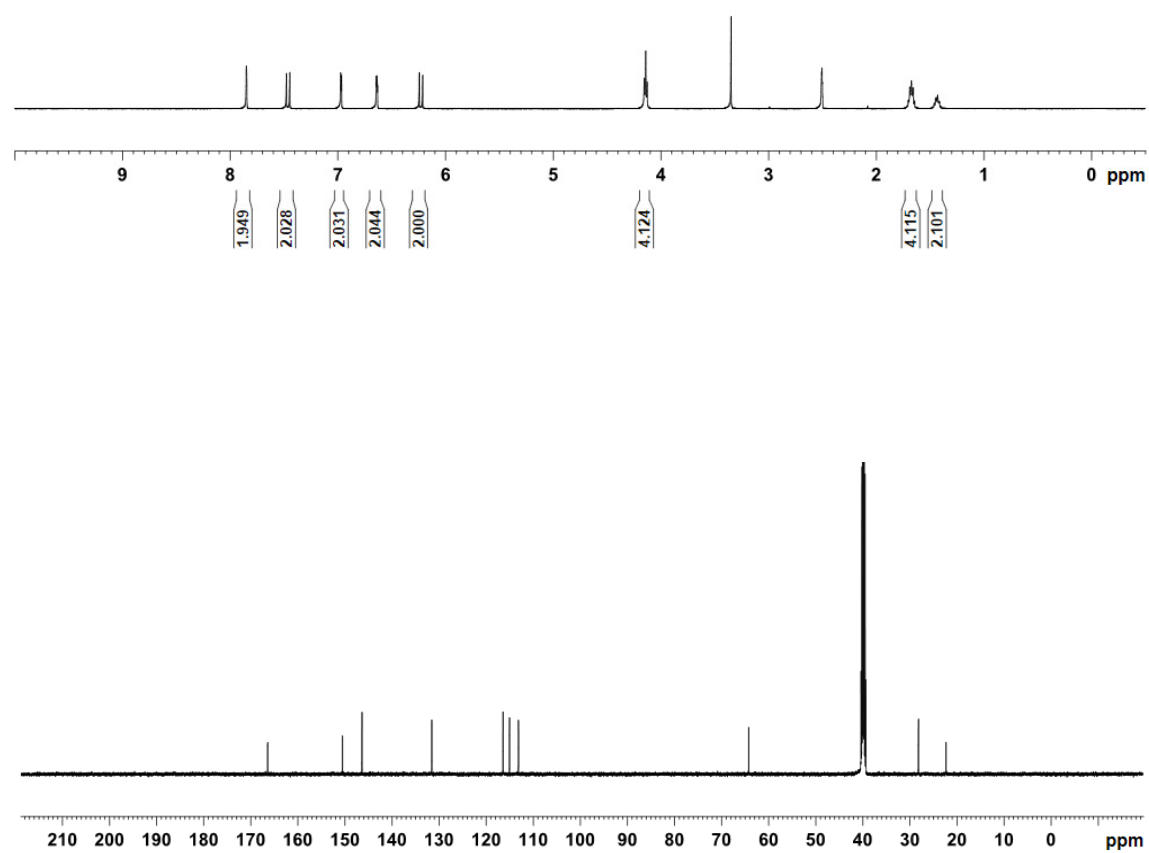
Photoreactive Building Block for the Monomers



**Figure S1.**  $^1\text{H}$ - (a) and  $^{13}\text{C}$ - (b) NMR spectra of the photoreactive building block of the monomer in  $\text{DMSO}-d_6$  at room temperature.



Monomer I



**Figure S2.**  $^1\text{H}$ - (a) and  $^{13}\text{C}$ - (b) NMR spectra of monomer I in  $\text{DMSO-}d_6$  at room temperature.

### 3. Crystal Images and Data of Monomer I & Intermediate Ia

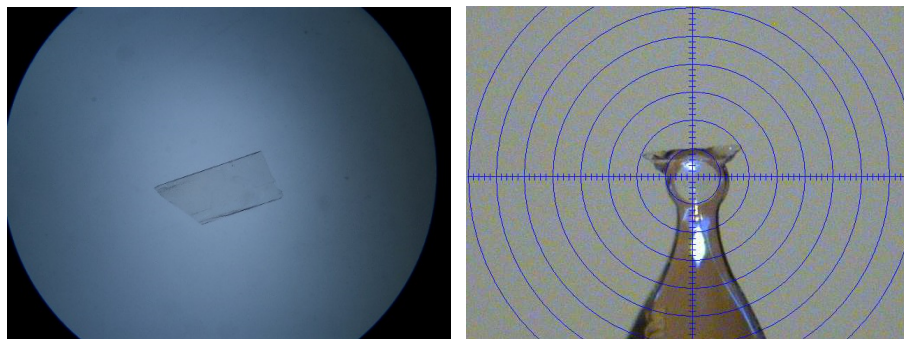
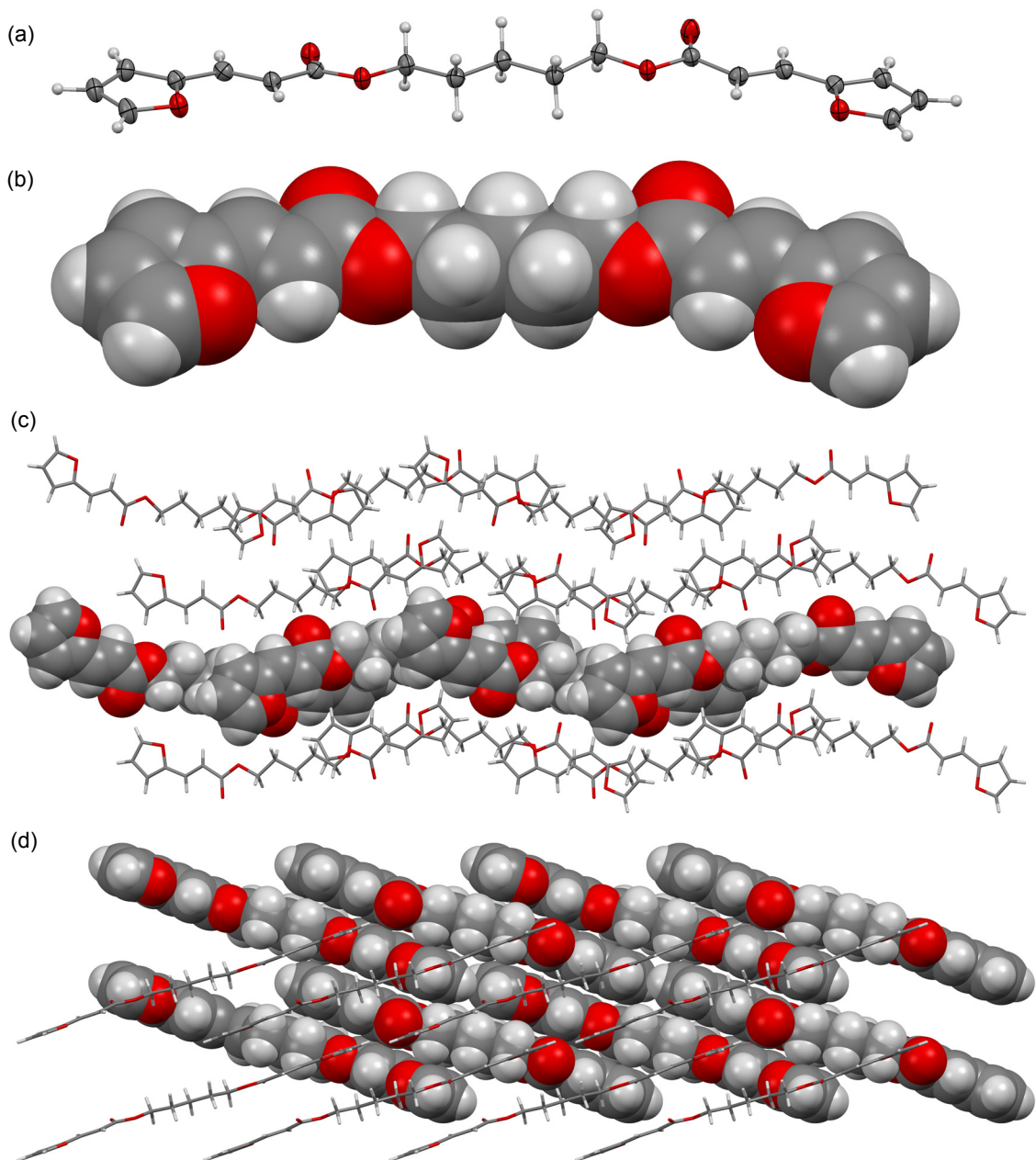


Figure S3. Images of a monomer I crystals.

Table S1. Crystal Data of the Monomer I & Intermediate Ia.

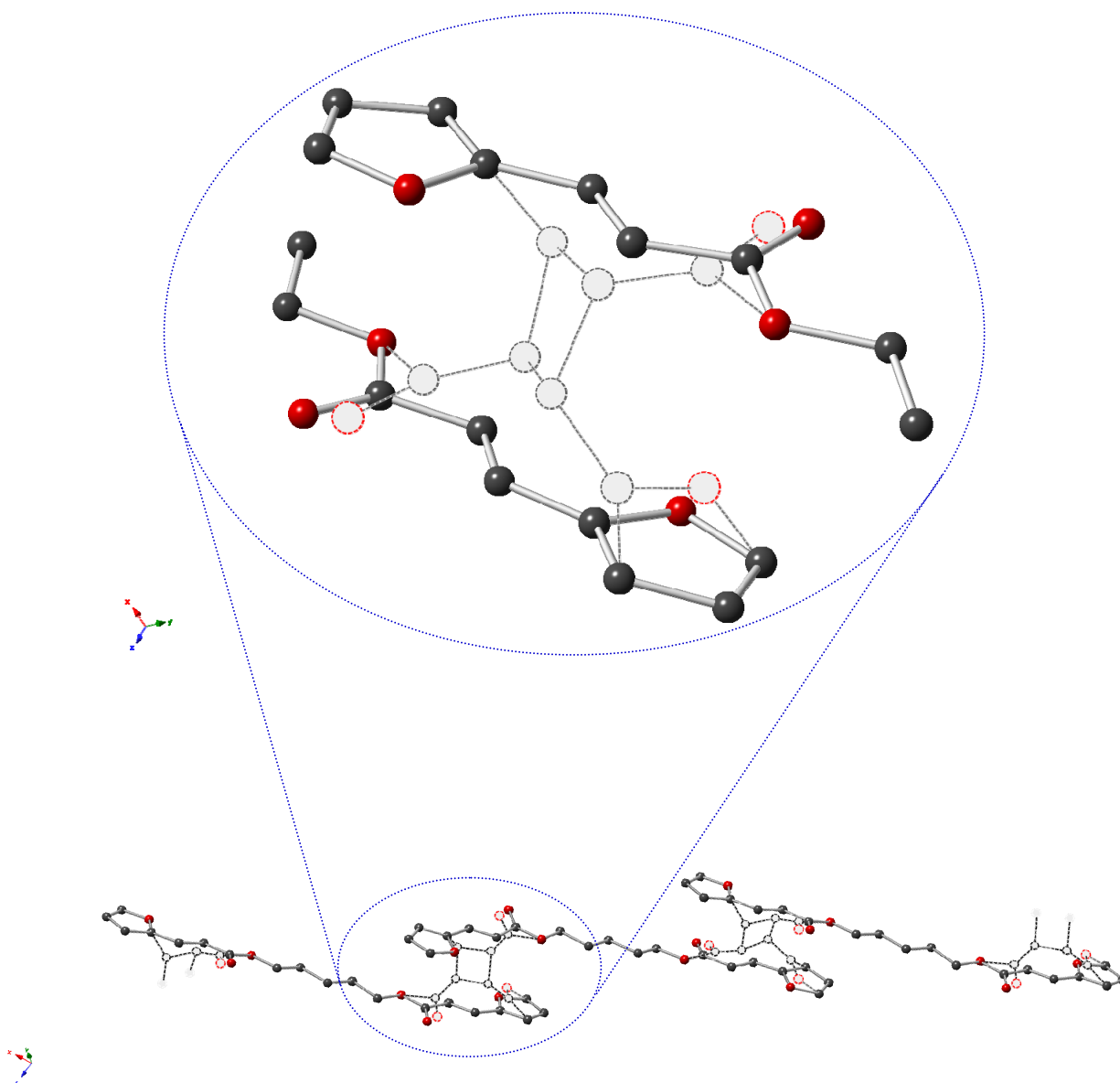
Crystals	Monomer I	Intermediate Ia
CCDC #	1406681	1408218
Formula	C <sub>19</sub> H <sub>20</sub> O <sub>6</sub>	C <sub>19</sub> H <sub>20</sub> O <sub>6</sub>
FW	344.35	344.35
Cryst. Size [mm]	0.33, 0.16, 0.05	0.51, 0.45, 0.22
Space Group, Z	P na2(1)	P na2(1)
a (Å)	23.0884(7)	22.9356(9)
b (Å)	10.4956(4)	10.4908(4)
c (Å)	7.3329(2)	7.3765(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å <sup>3</sup> )	1776.96(10)	1774.88(12)
Temp. (K)	100(2)	100(2)
ρ <sub>calc</sub> [g/cm <sup>3</sup> ]	1.287	1.289
μ [mm <sup>-1</sup> ]	0.798	0.096
Radiation Type	Cu	Mo
F(000)	728.0	728.0
No of measured refl.	9555	10826
No of independent refl.	3093	3498
No of refl. (I ≥ 2σ)	2832	2804
R1/wR2 (I ≥ 2σ) [%]	3.15/3.66	5.35/7.18
R1/wR2 (all data) [%]	7.91/8.18	11.51/12.29

#### 4. Crystal Structure Images of I and Ia



**Figure S4.** The crystal structure of monomer I: a) Oak Ridge Thermal Ellipsoid Plot (ORTEP) perspective at 50% electron density of the monomer I crystal structure. b) The monomer I crystal structure shown in space filling style. c) A top view of four layers of  $\pi$ - $\pi$  stacked assemblies. Three layers shown in capped sticks style and one in space filling style. d) A side view of two neighboring layers of  $\pi$ - $\pi$  stacked assemblies. The front layers shown in capped sticks style and the back layer shown in space filling style.

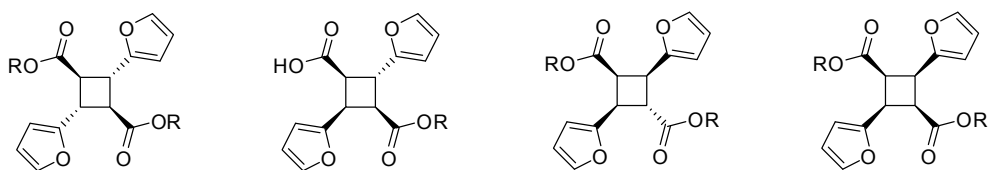
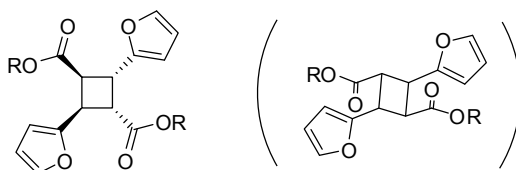




**Figure S5.** The X-ray single crystal structure of intermediate **Ia** showing the stereoregularity of the polymerization. (The 15% of polymer is shown in grey and only part of the monomer/polymer is shown for simplicity)

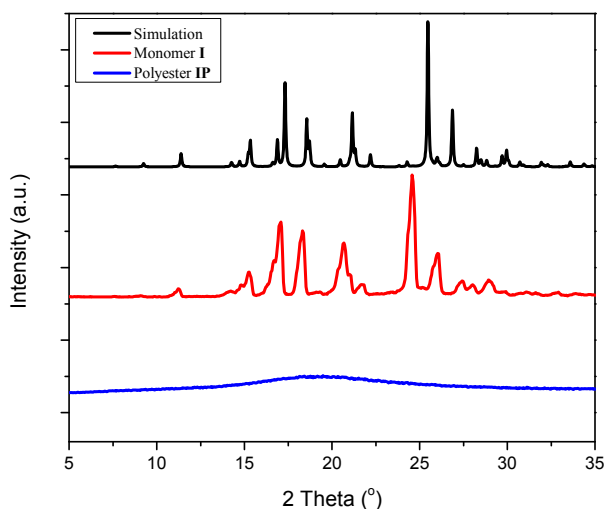
## 5. Cyclobutane Observed and its Four Possible Stereoisomers

The stereospecific  
cyclobutane observed  
in the linear polymer:



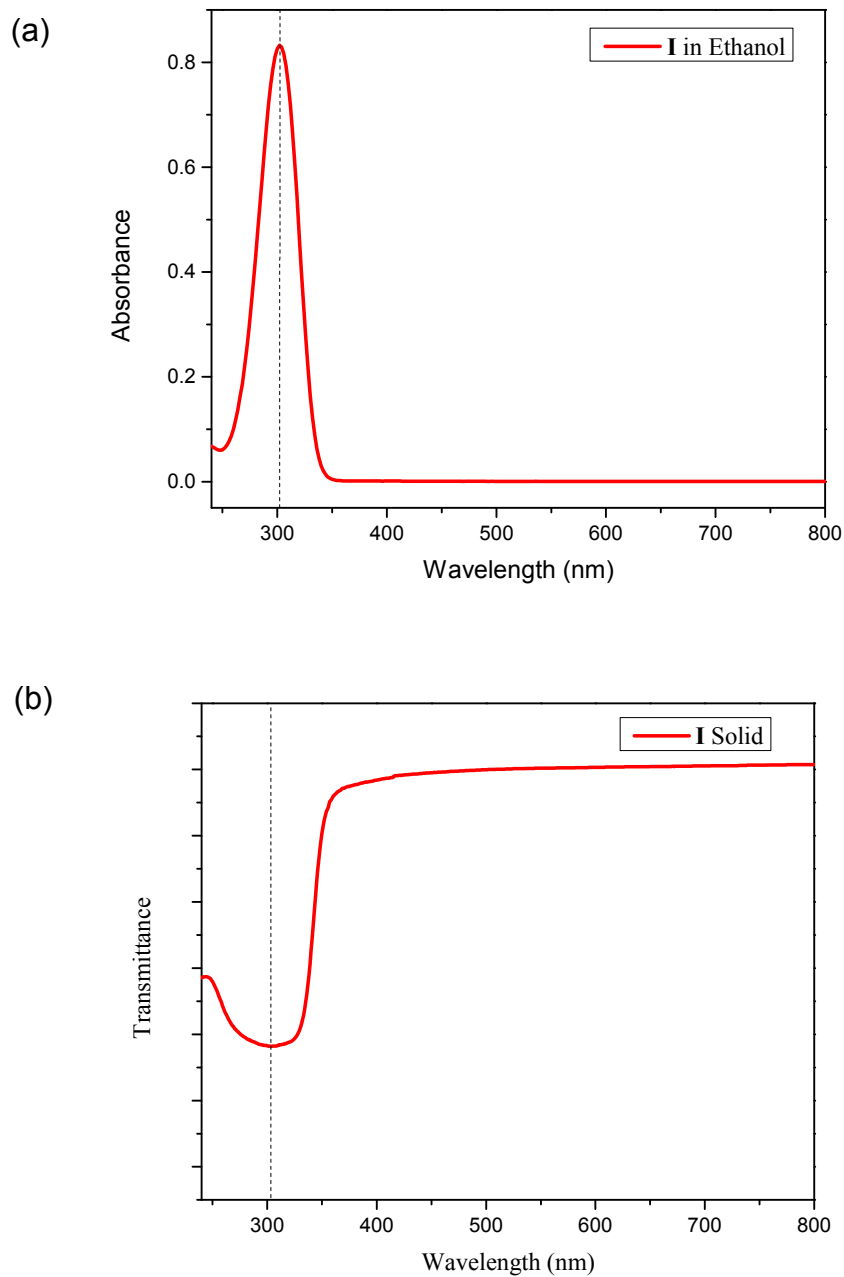
**Scheme S1.** Chemical structures of the stereospecific cyclobutane observed in the linear polyester and the other four possible head-to-tail stereoisomers that were not observed.

## 6. X-ray Powder Diffraction (XRD)



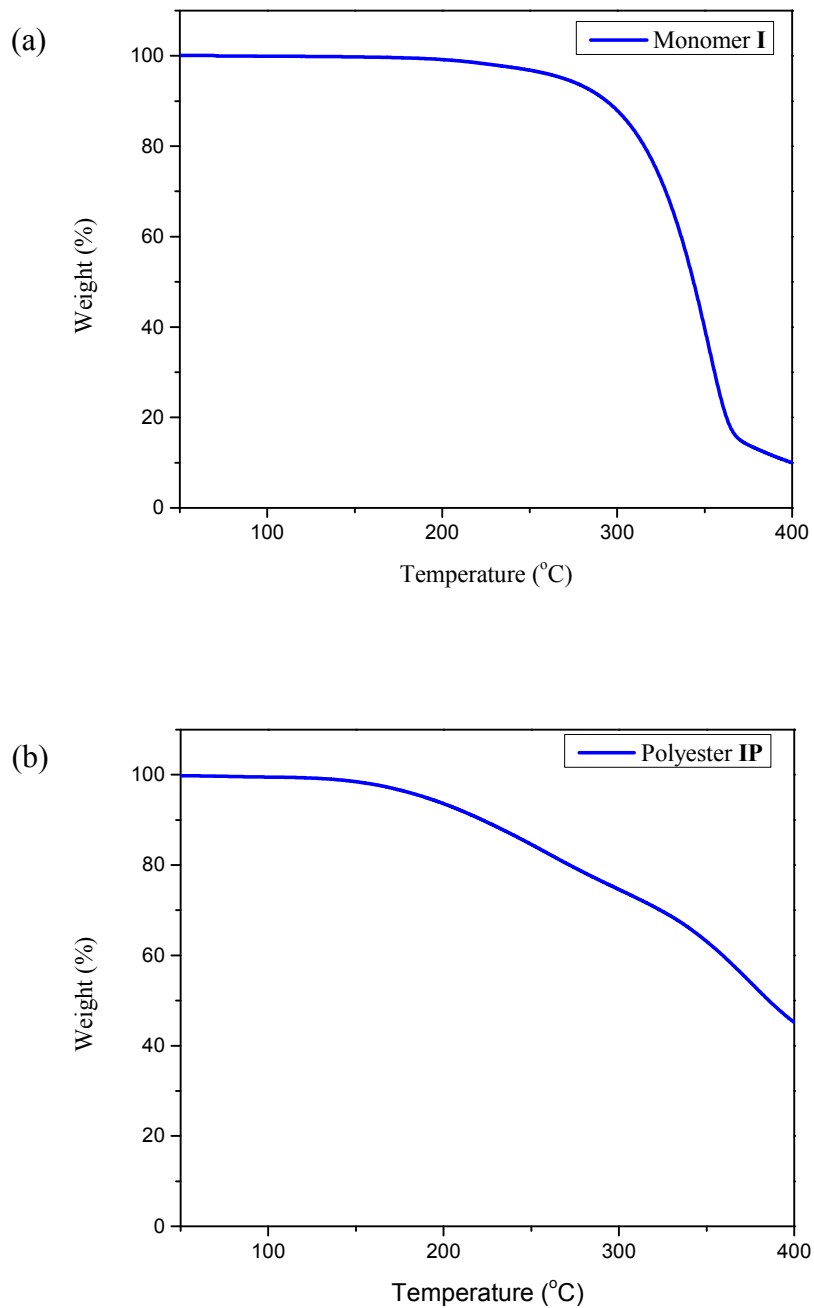
**Figure S6.** X-ray Powder Diffraction: a) the calculated pattern based on the crystal structure of monomer **I** (top, black); the pattern of monomer **I** powder directly from synthesis (middle, red); Polymer **IP** powder after photoreaction (bottom, black).

## 7. Ultraviolet (UV) Absorption



**Figure S7.** a) The ultraviolet (UV) absorbance of monomer **I** in ethanol. b) The UV transmittance of monomer **I** in the solid state.

## 8. Thermogravimetric Analysis (TGA)



**Figure S8.** TGA curves of (a) monomer **I** and (b) polymer **IP** operated under nitrogen (50.0 ml/min) with rate 20 °C/min.

## 9. References

1. Pyridine can also be used as a solvent if 2-MeTHF is not available.
2. Synonym: 3-(2-Furyl)acrylic acid, which is commercially available.
3. 2-MeTHF can be used as an alternative green solvent in this reaction.
4. The reaction was carried out 12 h per day for two days.
5. The speed of the photoreaction depended on the surface area (or size) of the crystals. Because the single-crystal-to-single-crystal (SCSC) experiments used crystals with larger size than that of the particles in the above powder (microcrystals) photopolymerization experiments, the SCSC reaction needed longer time accordingly.