



Supporting Information

Selenium Dioxide Catalyzed Polymerization of N-doped Poly(benzodifurandione) (n-PBDF) and Its Derivatives

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Selenium Dioxide Catalyzed Polymerization of n-Doped Poly(benzodifurandione) (n-PBDF) and its Derivatives

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1. General procedures and experimental details

Materials. All reagents and solvents for the synthesis and analysis were purchased from Sigma-Aldrich, Alfa Aesar, Thermo Fisher, and TCI and were used without further purification, unless otherwise mentioned. 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (BDF) monomer was synthesized according to previous report.^[1] All air and water sensitive reactions were performed under a nitrogen atmosphere.

Characterizations. ¹H and ¹³C NMR spectra were recorded on Bruker ARX-400 (400 MHz). All chemical shifts were reported in parts per million (ppm). ¹H NMR chemical shifts were referenced to DMSO-*d*₆ (2.50 ppm) and ¹³C NMR chemical shifts were referenced to DMSO-*d*₆ (39.52 ppm). High resolution mass spectra (HRMS) were recorded on an AB Sciex-5800 MALDI-TOF mass spectrometer and a Bruker Solarix XR mass spectrometer. UV–Vis–NIR absorption spectra were measured on an Agilent Cary 5000 UV–Vis spectrometer. Fourier-transformed infrared (FTIR) spectra were measured on Thermo Nicolet 6700 FTIR Spectrophotometer. Dynamic Light Scattering (DLS) was measured on Wyatt DynaPro NanoStar II instrument. X-ray photoelectron spectroscopy (XPS) was recorded on Omicron surface analysis cluster. Inductively coupled plasma mass spectrometry (ICP-MS) was measured by Thermo Scientific Element II ICP-MS. The electrical conductivity was characterized by Keithley 4200 SCS semiconductor characterization system. The sheet resistance for conductivity mapping of the large-area transparent n-PBDF conductive thin film was measured by Filmetrics R50 Resistance Mapper. Film thickness was measured by Bruker DektakXT profilometer. The transmittance of the large-area transparent n-PBDF conductive film was measured by Filmetrics F10-RT thin film analyzer. The molecular weights of PBDF-C12 polymers were measured by TOSOH HLC-8321GPC/HT in 1,2,4-trichlorobenzene at 150 °C.

Substrate and Film Preparation. Glass substrate (19 × 19 mm) was cleaned by consecutive sonication in soap, DI water, acetone, and isopropanol for 15 min each. After drying the substrates

with nitrogen, the substrates were exposed to UV-Ozone treatment (HELIOS-500 Ultraviolet-Ozone Cleaner) for 20 min to remove any organic residues and to increase surface hydrophilicity. We used the Van der Pauw (VDP) configuration to measure the conductivity of thin-film samples. Chromium (5 nm) was first deposited on the glass substrate at a slow deposition rate of 0.1 Å/s and gold (40 nm) was then deposited with a rate of 0.3 Å/s under a high vacuum (10^{-6} mbar). Polymer thin films were coated on the substrates with patterned electrodes. To obtain uniform thin-film samples, the polymer solutions were sonicated in an ultrasonic bath (Fisher Scientific) for 15 min and then stirred for 4 h. Before spin casting, all the polymer inks were treated by a vortex mixer (Fisher Scientific) for 5-10 min. n-PBDF thin films were prepared by the off-center spin coating method at various rates. The desired thicknesses are around 100 nm by controlling the number of layers. After coating, the film was dried in a vacuum oven (at 500 microns pressure at room temperature) for 1 to 2 h to remove residual solvent.

A 120 mm × 120 mm glass substrate was cleaned with ethanol and IPA solvent, then dried on a hot plate at 100°C for 10 minutes, followed by UV-Ozone treatment for 15 minutes. The concentration of the synthesized n-PBDF solution was diluted to 2 mg mL⁻¹ to prepare a 20 mL solution. Using a 120 kHz spray nozzle in an ultrasonic spray coating system (Sono-Tek, USA), the n-PBDF solution was uniformly sprayed in a single pass at room temperature and ambient air conditions. After spraying, the film was placed in a vacuum oven and dried under the same conditions as mentioned earlier. This process was repeated to achieve the desired film thickness.

2. Conductivity and Sheet Resistance Measurements

To investigate the impact of polymerization conditions on the polymer's electrical performance, we use the Van der Pauw (VDP) configuration to measure the conductivity of thin-film samples.^[2] Before the measurement, polymer thin films were scratched to form desired pattern suitable for VDP method. The current (I) with a range from -10.0 to 10.0 mA was sourced through two adjacent electrodes, and the potential difference (ΔV) was measured between the other two electrodes. The sheet resistance was calculated as the slope of the I - ΔV curve. To obtain an accurate estimation of conductivity, the sheet resistance was measured from four directions of the thin films by switching the source and sense electrodes. The sheet resistance was then calculated using the following equation:

$$R_s = \frac{\pi}{\ln 2} \times R_{ave} \approx 4.53 \times R_{ave}$$

where R_{ave} is the average resistance measured from four directions.

The conductivity of the films was then calculated by the equation below:

$$\sigma = \frac{1}{R_s t}$$

where t (film thickness) was measured by a profilometer.

3. SeO₂ mediated polymerization of n-PBDF

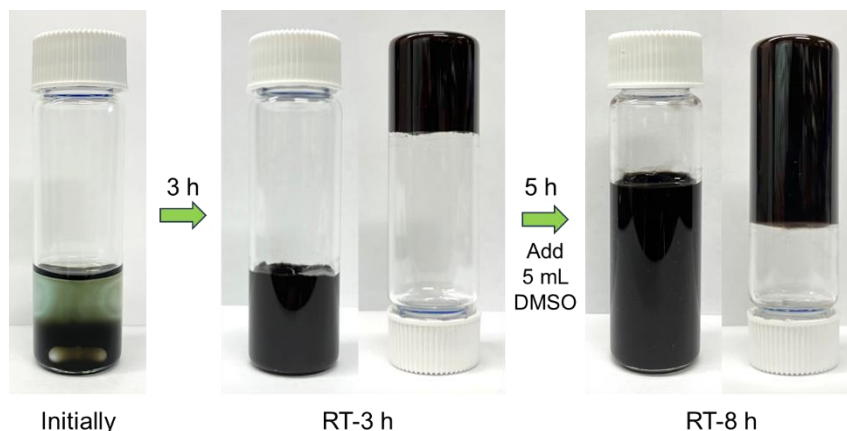


Figure S1 Schematic pictures of the polymerization of BDF (50 mg in 5 mL DMSO, 10 mg mL⁻¹) with SeO₂ (1 eq) at room temperature under a nitrogen atmosphere. A gel solution is formed after stirring at room temperature for 3 hours. Then another 5 mL DMSO was added to decrease the concentration of the mixture by half. The mixture formed gel again after further stirring for 5 hours. The corresponding conductivities of the polymers were increased from 560 S cm⁻¹ to 650 S cm⁻¹.

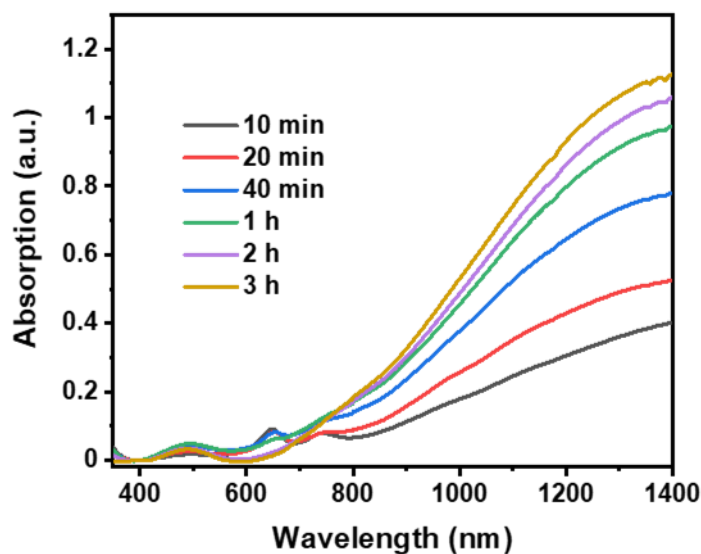


Figure S2 Time-dependent ultraviolet–visible–near infrared (UV-Vis-NIR) absorption spectroscopy of polymerization of BDF (50 mg in 5 mL DMSO, 10 mg mL⁻¹) with SeO₂ (1 eq) at room temperature under nitrogen atmosphere.

In situ NMR characterization of polymerization

To monitor the polymerization process, *in situ* ^1H -NMR spectra were recorded during the polymerization process. To quantitatively identify the monomer conversion and understand the degree of polymerization, an inert compound 1,2,4,5-Tetramethylbenzene (TMB) that does not affect polymerization was added as a standard. The mixtures of 50 mg BDF, TMB (1 equiv.) and SeO_2 (1 equiv.) were fully dissolved in 5 ml $\text{DMSO-}d_6$ and 0.6 ml of the mixture was charged into an NMR tube. The mixture was spinning at room temperature under a nitrogen atmosphere in the Bruker NMR instrument and ^1H -NMR signals for different reaction times were recorded. The results are shown in **Figure S3**. The NMR spectrums showed that the proton peaks of the monomer gradually decreased with the increased reaction time, which suggested the successful formation of n-PBDF since n-PBDF is in a doped state and has no obvious proton peak. The conversions of BDF monomer were calculated from the NMR integral by using TMB as reference, which shows an increasing trend over time. A high monomer conversion of 78% was achieved after 3 hours.

As for comparison, the same polymerization reactions were conducted at room temperature by using 2,3,5,6-Tetramethyl-1,4-benzoquinone (TMQ) and $\text{Cu}(\text{OAc})_2$ as oxidants. According to their optimal polymerization conditions, TMQ and $\text{Cu}(\text{OAc})_2$ mediated polymerization reactions were conducted under nitrogen and air atmosphere, respectively. BDF monomer could not be effectively oxidized to form n-PBDF polymer at room temperature when TMQ was used as an oxidizing agent. While a gel-solid mixture with poor solubility and processability was formed when $\text{Cu}(\text{OAc})_2$ was used as an oxidizing agent. **Figure S4** and **Figure S5** show the *in situ* ^1H -NMR spectra during the polymerization process. It can be seen that the monomer conversion in the SeO_2 system is higher than both TMQ and $\text{Cu}(\text{OAc})_2$ systems after 3 hours.

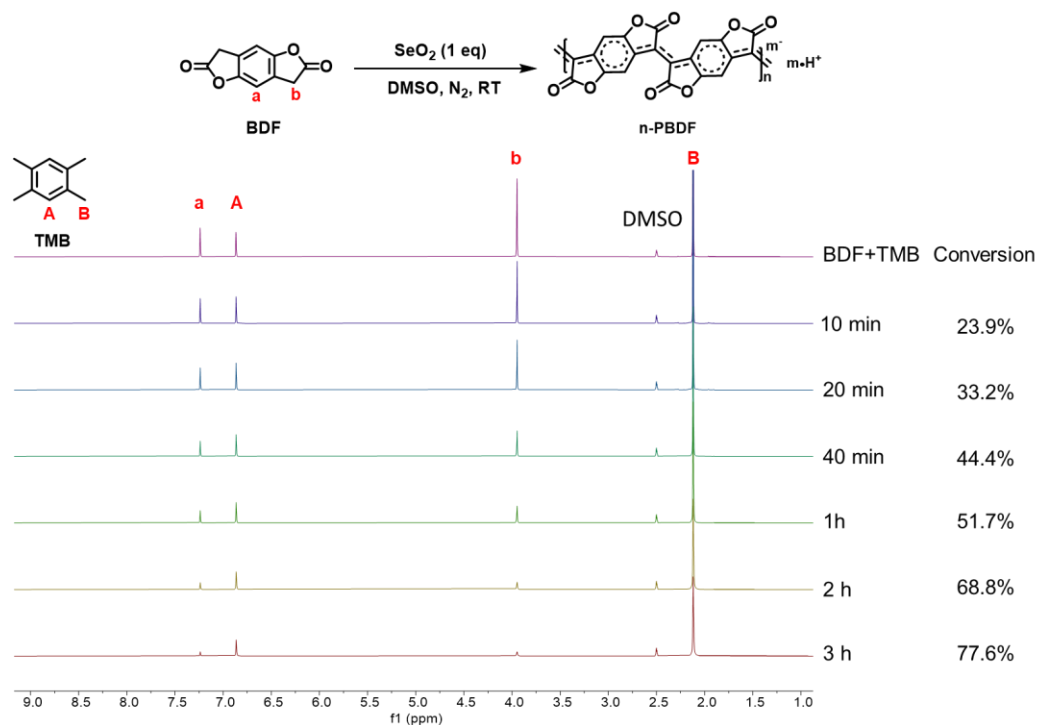


Figure S3 *In Situ* ^1H NMR spectrum of polymerization of BDF (10 mg mL^{-1}) with SeO_2 (1 eq) in $\text{DMSO}-d_6$ at room temperature under nitrogen. TMB was used as a reference.

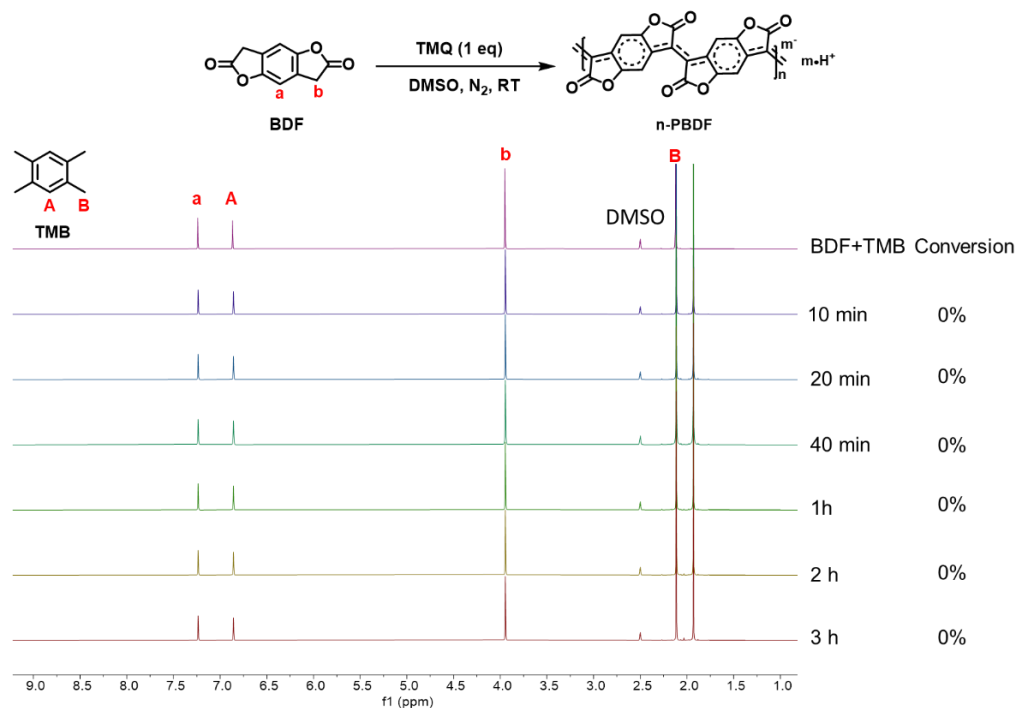


Figure S4 *In Situ* ^1H NMR spectrum of polymerization of BDF (10 mg mL^{-1}) with TMQ (1 eq) in $\text{DMSO}-d_6$ at room temperature under nitrogen. TMB was used as a reference.

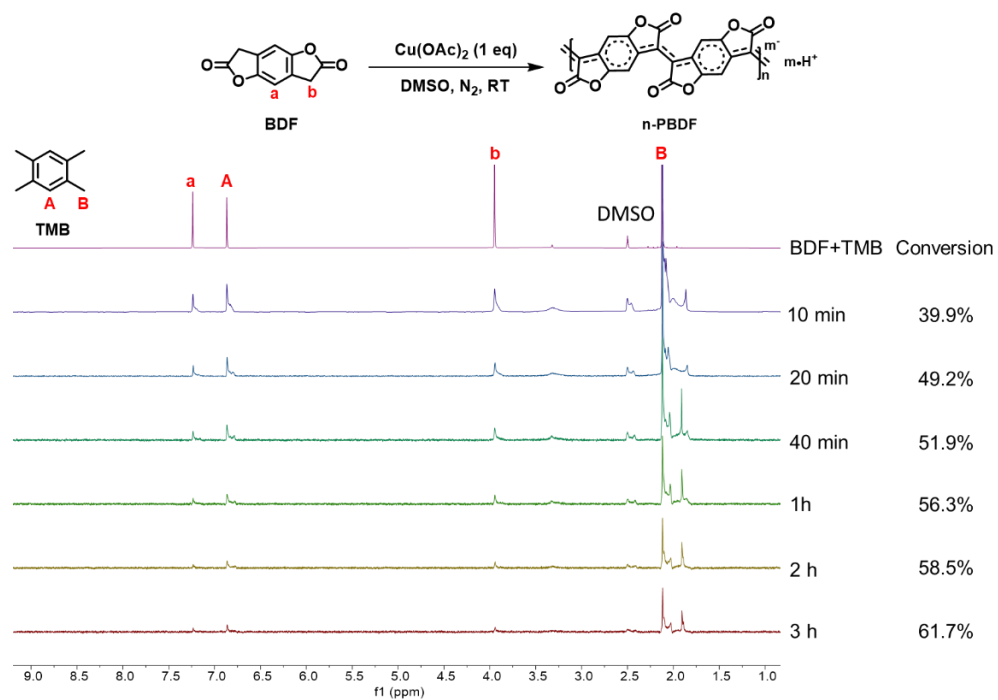


Figure S5 *In Situ* ^1H NMR spectrum of polymerization of BDF (10 mg mL^{-1}) with $\text{Cu}(\text{OAc})_2$ (1 eq) in $\text{DMSO}-d_6$ at room temperature under air. TMB was used as a reference.

4. Polymerization conditions optimization and kinetics study

General procedure for the polymerization of n-PBDF: The BDF monomer (from 5 mg mL⁻¹ to 25 mg mL⁻¹) and SeO₂ (from 0.01 equiv. to 1 equiv.) were dissolved in DMSO under a nitrogen atmosphere. The mixture was heated and stirred at various temperatures (from room temperature to 140 °C) for several hours. After the solution was cooled to room temperature, the mixture was dialyzed against DMSO using a dialysis bag with a cut-off molecular weight of 10 kDa (Viskase, USA) to remove low molecular weight fractions. The resulting solution was centrifuged and filtered to obtain a homogeneous and purified n-PBDF ink free of selenium. The polymerization condition investigation results are summarized in **Table S1**. The I-V characteristics of three batches of high conductivity samples (> 4000 S/cm) were summarized in **Figure S6**.

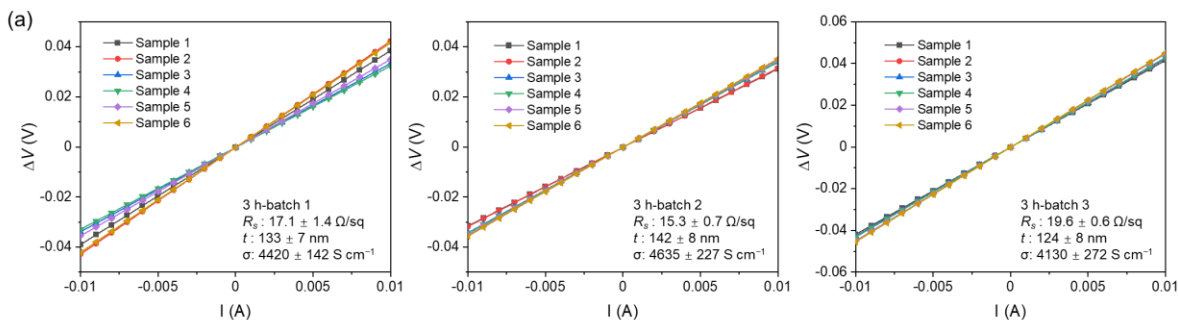
A detailed example of polymerization of n-PBDF: BDF monomer (75 mg, 0.3944 mol, 1 equiv.) and SeO₂ (4.4 mg, 0.0394 mmol, 0.1 equiv.) were dissolved in DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C with vigorous stirring for 24 hours. After the solution was cooled to room temperature, the mixture was dialyzed against DMSO using a dialysis bag with a cut-off molecular weight of 10 kDa (Viskase, USA) to remove low molecular weight fractions. The resulting solution was centrifuged to remove the insoluble solids (10000 rpm, 15 min) and then filtered through a 1 µm nylon filter to obtain a homogeneous and purified n-PBDF ink.

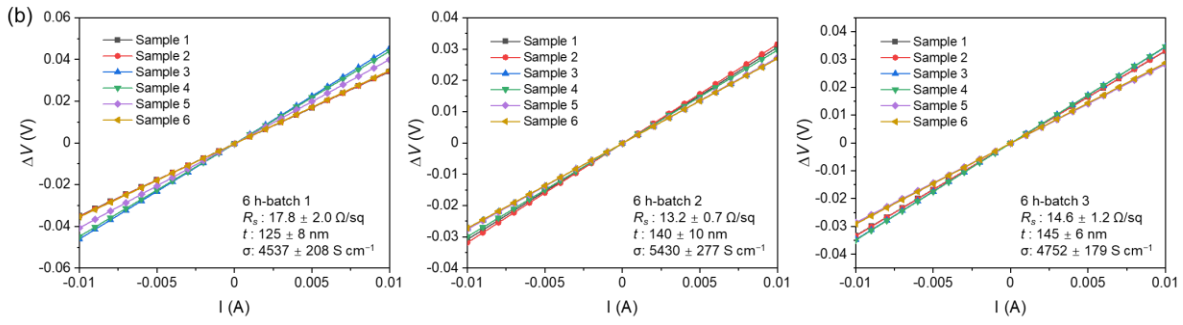
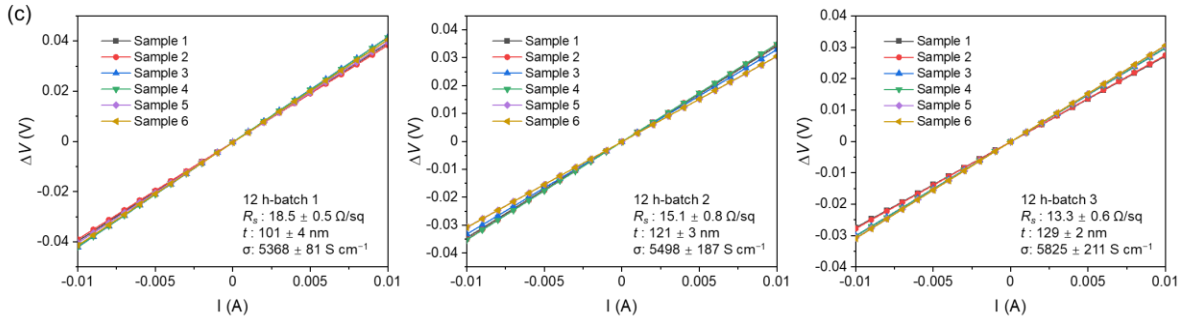
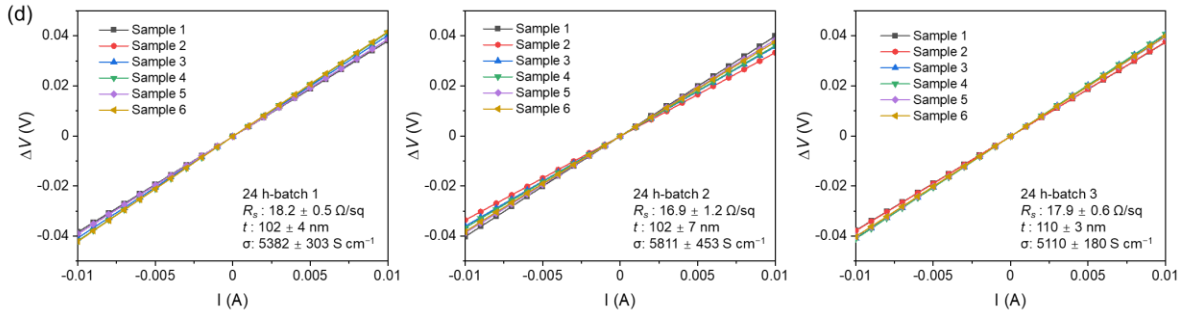
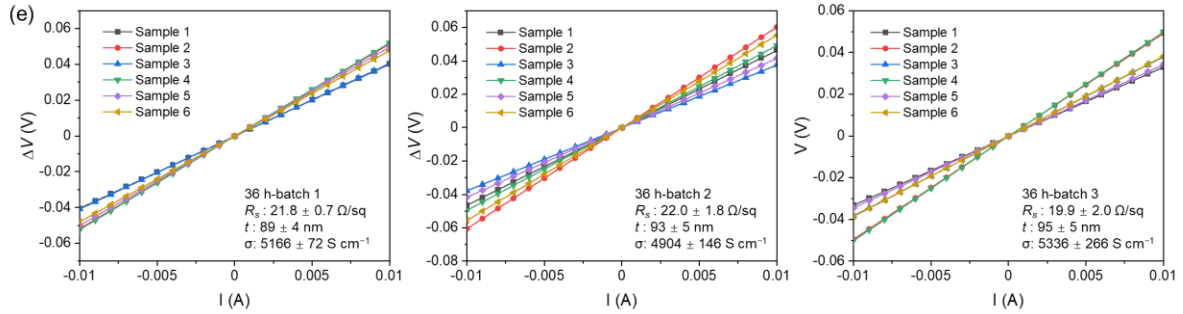
Table S1 Polymerization condition investigation

Entry	SeO ₂ (equiv.)	C _{BDF} (mg mL ⁻¹)	Temperature (°C)	Time (h)	monomer conversion (%) ^a	Appearance	Sheet resistance (Ω/sq)	Thickness (nm)	Conductivity (S cm ⁻¹)
1	1	15	RT	3	72.4	Gel	62.6 ± 2.5	122 ± 6	1304 ± 22
2	1	15	40	3	96.2	Gel	50.0 ± 1.6	119 ± 7	1678 ± 42
3	1	15	60	3	96.8	Gel	39.1 ± 2.3	102 ± 5	2501 ± 191
4	1	15	100	3	>99	Gel-Solid	28.3 ± 1.6	124 ± 4	2833 ± 88
5	1	15	140	3	>99	Gel-Solid	41.5 ± 3.0	113 ± 4	2195 ± 68

6	1	15	100	24	>99	Gel-Solid	38.6 ± 1.0	135 ± 5	1920 ± 55
7	0.5	15	100	24	>99	Gel-Solid	43.6 ± 5.7	109 ± 11	2110 ± 272
8	0.3	15	100	24	>99	Gel	26.4 ± 0.2	105 ± 2	3609 ± 91
9	0.1	15	100	24	66.8	Viscous Solution	17.7 ± 0.6	105 ± 4	5430 ± 263
10	0.05	15	100	24	44.0	Solution	25.4 ± 2.1	101 ± 3	3929 ± 292
11	0.01	15	100	24	13.3	Dilute Solution	803 ± 117	144 ± 12	88.0 ± 4.4
12	0.1	15	100	3	22.3	Dilute Solution	17.3 ± 1.8	133 ± 7	4394 ± 203
13	0.1	15	100	6	29.9	Dilute Solution	15.2 ± 1.9	137 ± 8	4904 ± 384
14	0.1	15	100	12	44.0	Solution	15.6 ± 2.2	117 ± 12	5565 ± 201
15	0.1	15	100	36	84.2	Viscous Solution	21.2 ± 0.9	93 ± 3	5176 ± 181
16	0.1	15	100	48	91.3	Viscous Solution	16.6 ± 1.3	118 ± 3	5165 ± 328
17	0.1	5	100	24	44.6	Dilute Solution	161 ± 15.8	112 ± 5	554 ± 35
18	0.1	10	100	24	50.0	Solution	24.6 ± 4.6	107 ± 9	3799 ± 152
19	0.1	20	100	24	69.0	Viscous Solution	19.1 ± 0.4	102 ± 5	5003 ± 272
20	0.1	25	100	24	75.0	Viscous Solution	33.0 ± 1.9	99 ± 7	3130 ± 166
21 ^b	0.1	15	100	24	>99	Viscous Solution	33.4 ± 2.4	110 ± 13	2738 ± 126

^aCalculated from NMR. ^bScale-up polymerization, purified by centrifugation and filtration. All other inks are purified by dialysis, centrifugation and filtration. All conductivities were measured by the Van der Pauw method. The conductivities were obtained from the average of three batches, and six Van der Pauw devices for each batch of samples were prepared for conductivities measurement, and six points in each film were chosen for film thickness measurements.





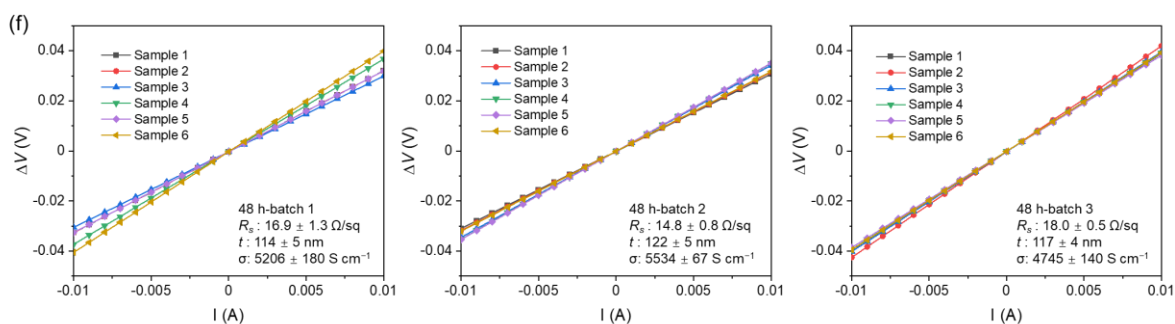


Figure S6 The I-V characteristics of three batches of polymer samples under 0.1 equivalents SeO_2 catalyzed polymerization at different time: (a) 3 h, (b) 6 h, (c) 12 h, (d) 24 h, (e) 36 h, (f) 48 h.

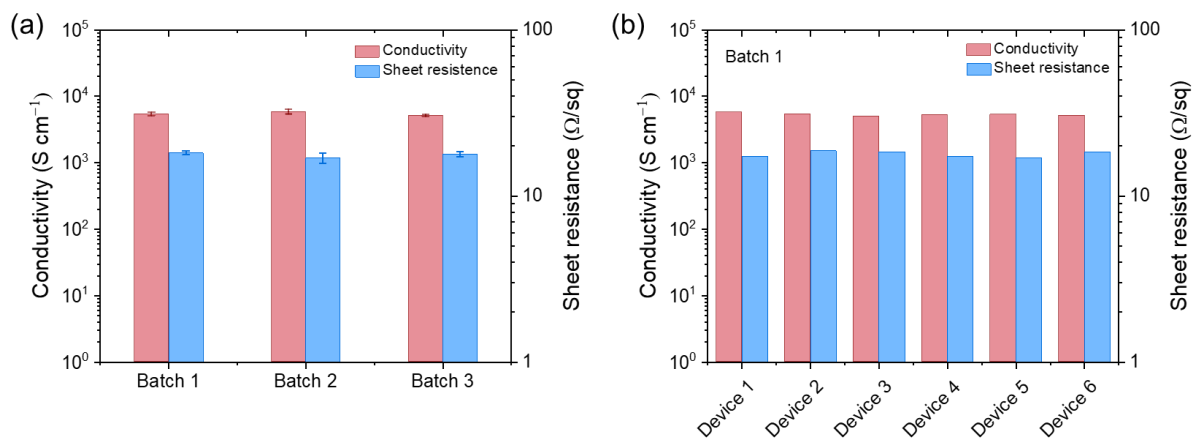


Figure S7 The conductivity and sheet resistance of (a) three batches of polymer samples and (b) six different Van der Pauw devices of batch 1 under 0.1 equivalents SeO_2 catalyzed polymerization for 24 h.

General procedure for ^1H NMR characterization of polymerization

The BDF monomer (from 5 mg mL^{-1} to 25 mg mL^{-1}), 1,2,4,5-Tetramethylbenzene (1 equiv.), and SeO_2 (from 0.01 equiv. to 1 equiv.) were fully dissolved in $\text{DMSO-}d_6$, and 0.6 ml of the mixture was charged into an NMR tube under nitrogen atmosphere. The mixture was then heated to various temperatures (from room temperature to $140\text{ }^\circ\text{C}$) for several hours, and ^1H -NMR signals of different polymerization conditions were recorded. The conversions of BDF monomer were calculated from NMR integral using TMB as reference. The results are shown in **Figures S8-S14**.

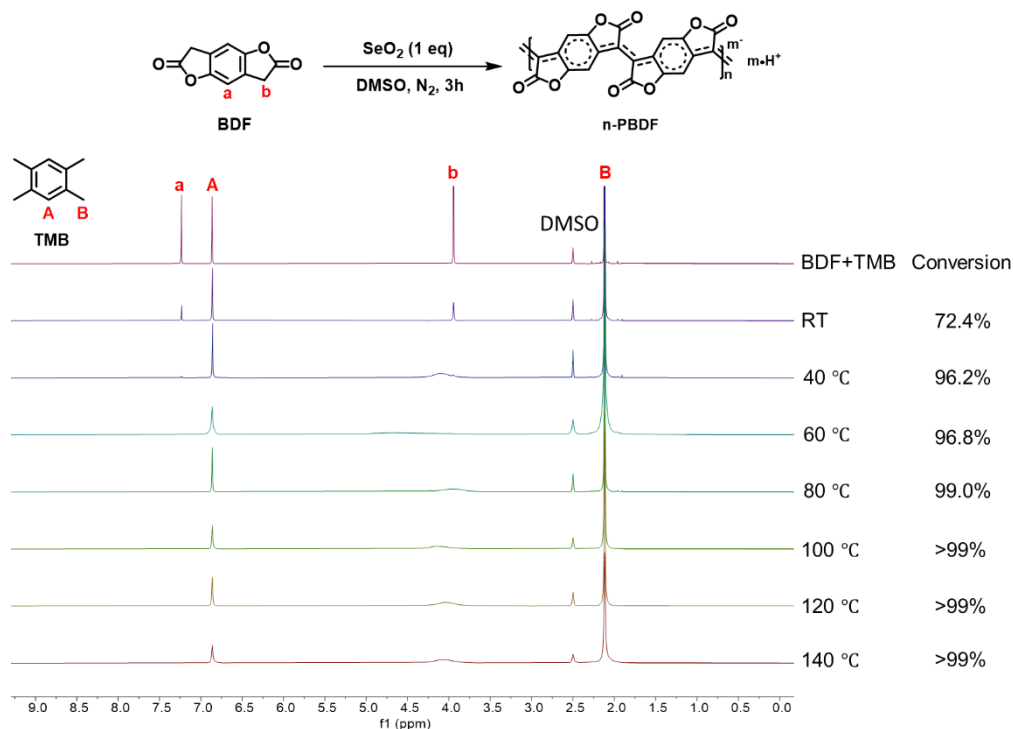


Figure S8 ^1H NMR spectrum of polymerization of BDF (15 mg mL^{-1}) with SeO_2 (1 eq) in $\text{DMSO-}d_6$ at different temperatures for 3 hours under nitrogen. TMB was used as a reference.

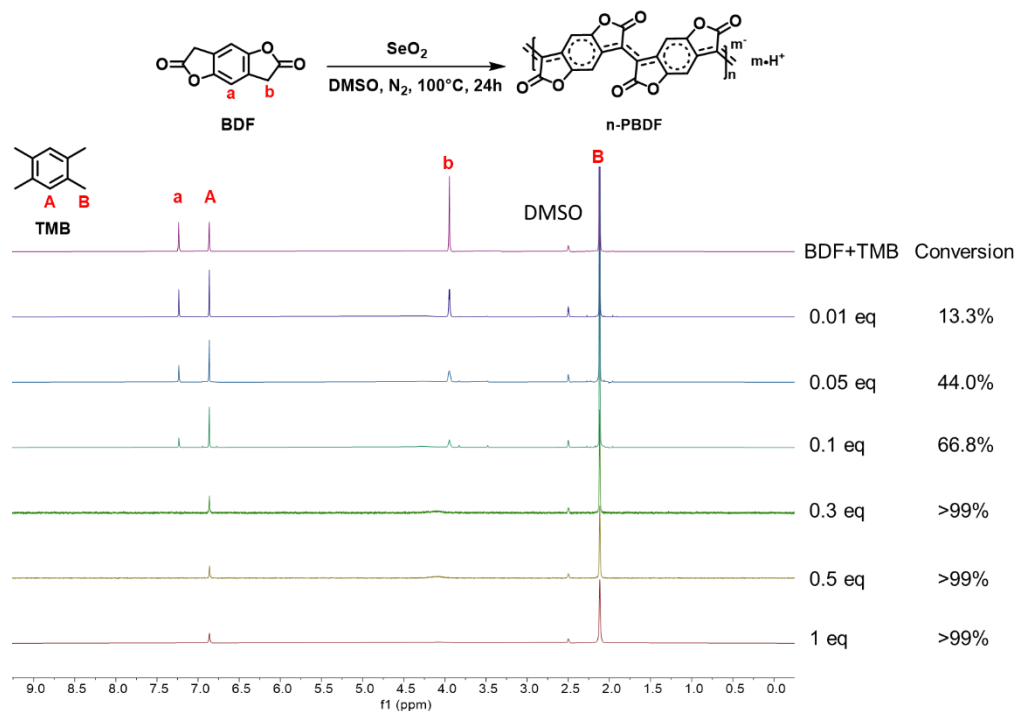


Figure S9 ^1H NMR spectrum of polymerization of BDF (15 mg mL^{-1}) with different equivalent SeO_2 in DMSO- d_6 at 100°C for 24 hours under nitrogen. TMB was used as a reference.

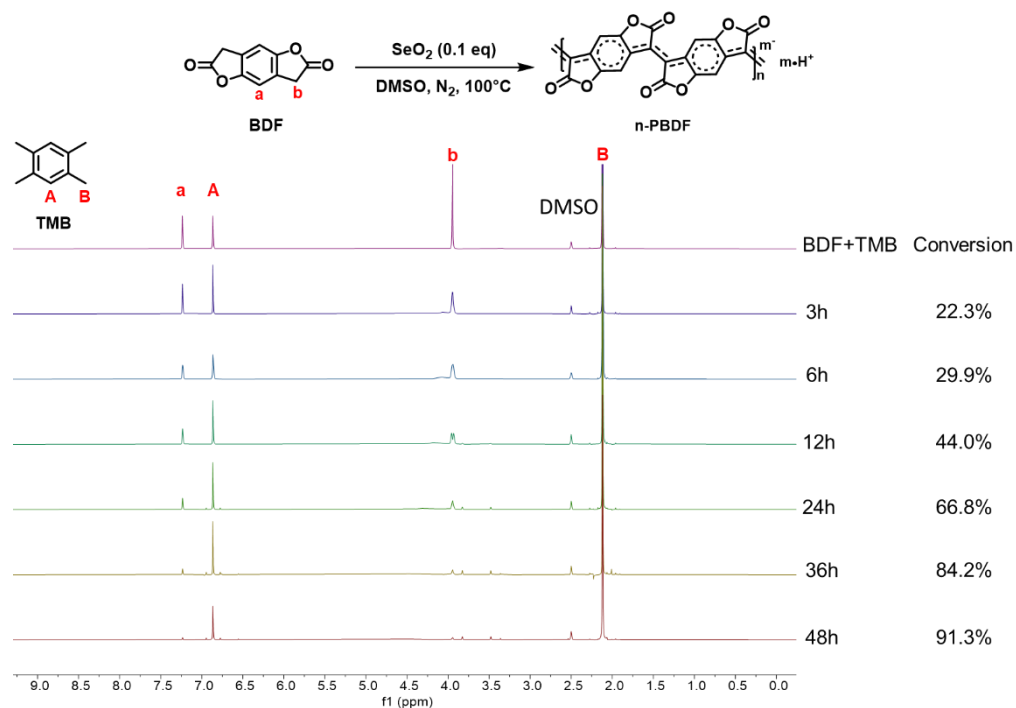


Figure S10 ^1H NMR spectrum of polymerization of BDF (15 mg mL^{-1}) with SeO_2 (0.1 eq) in DMSO- d_6 at 100°C for different time under nitrogen. TMB was used as a reference.

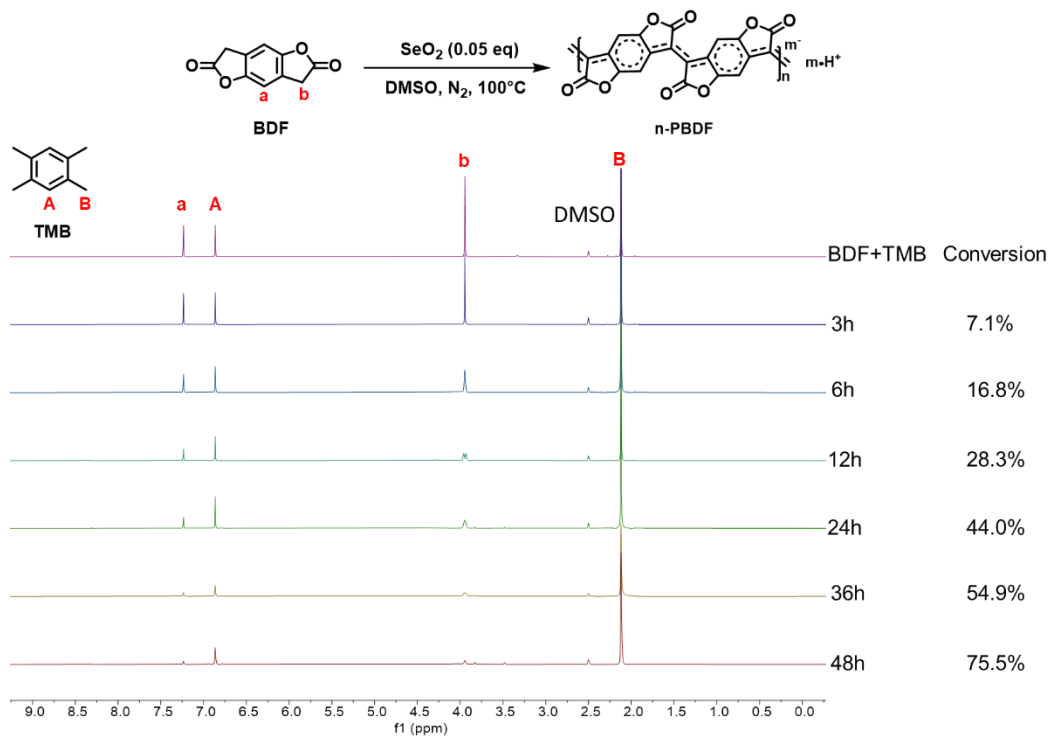


Figure S11 ^1H NMR spectrum of polymerization of BDF (15 mg mL^{-1}) with SeO_2 (0.05 eq) in $\text{DMSO}-d_6$ at 100°C for different time under nitrogen. TMB was used as a reference.

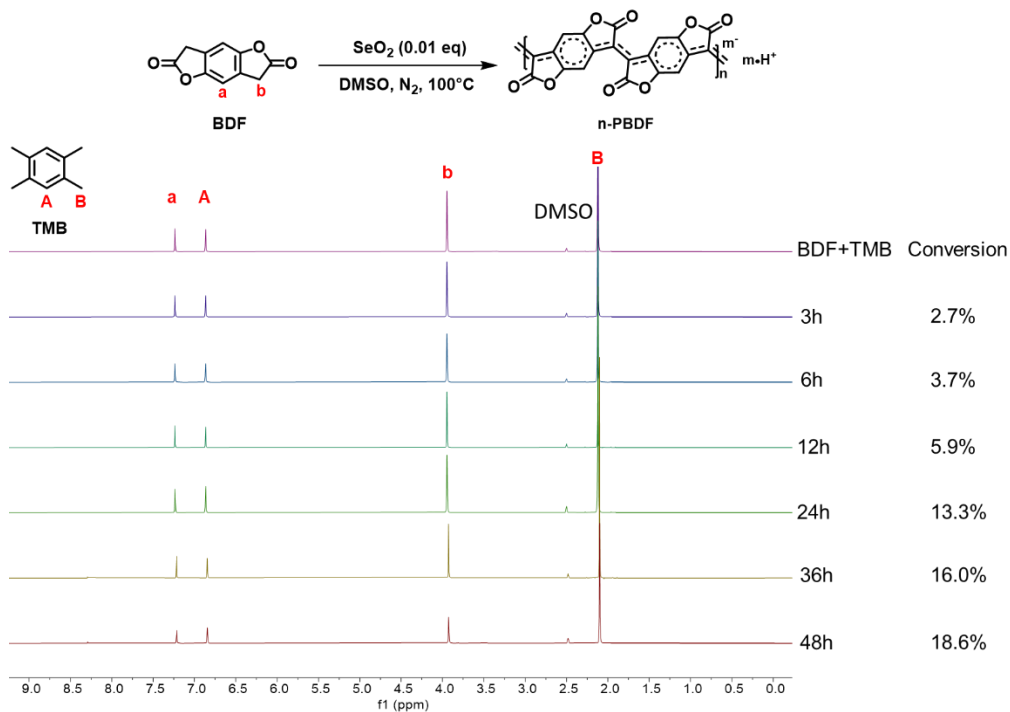


Figure S12 ^1H NMR spectrum of polymerization of BDF (15 mg mL^{-1}) with SeO_2 (0.01 eq) in $\text{DMSO}-d_6$ at 100°C for different time under nitrogen. TMB was used as a reference.

DMSO- d_6 at 100 °C for different time under nitrogen. TMB was used as a reference.

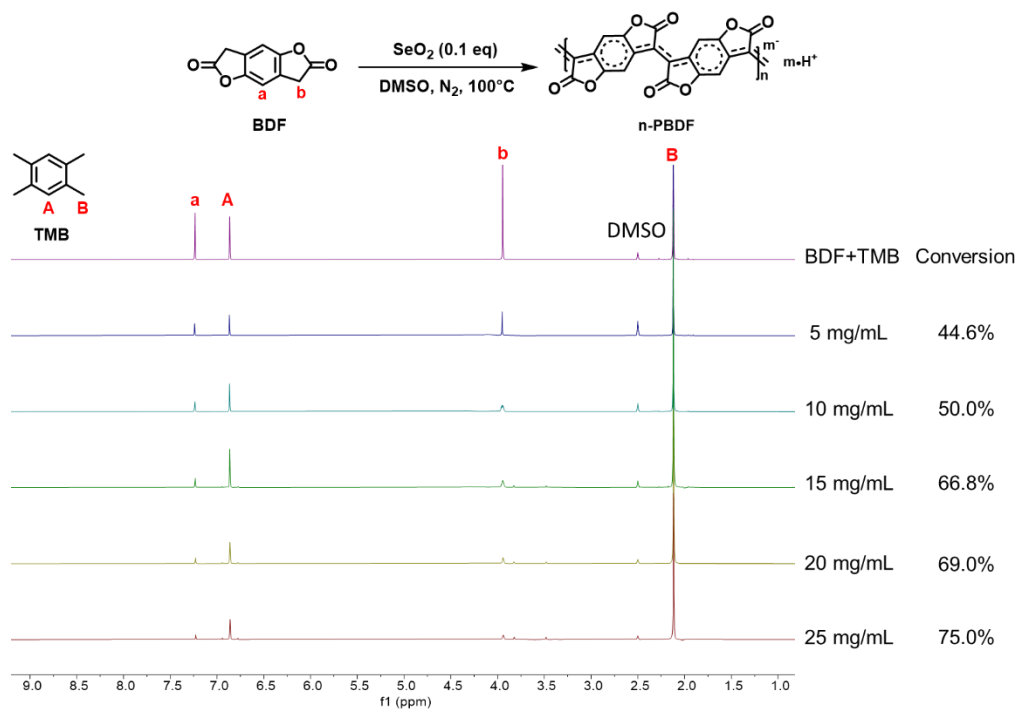


Figure S13 ¹H NMR spectrum of polymerization of different BDF monomer concentration with SeO₂ (0.1 eq) in DMSO- d_6 at 100 °C for 24 hours under nitrogen. TMB was used as a reference.

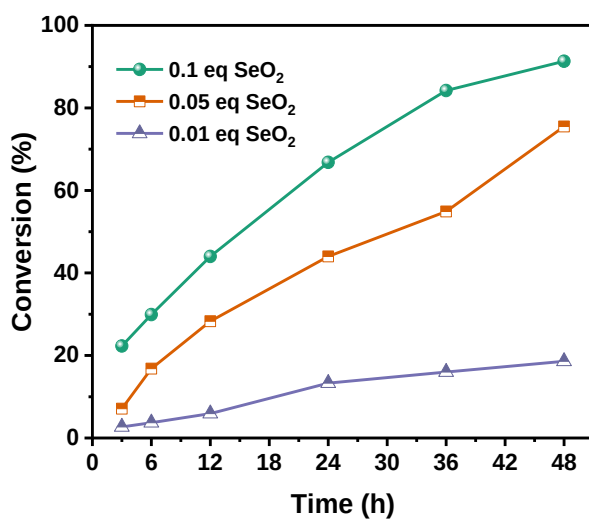


Figure S14 Time-dependent conversion of BDF monomer in polymerization by using 0.1, 0.05, and 0.01 equiv. SeO₂ (calculated from NMR).

Dynamic Light Scattering (DLS) measurements of n-PBDF polymer

In order to further understand the polymerization kinetics and mechanisms, we try to obtain the molecular weight information of the polymers. However, n-PBDF polymer is almost exclusively soluble in DMSO, and conventional GPC mobile phase is not applicable for its molecular weight measurement, such as tetrahydrofuran and chloroform. Therefore, we use Dynamic Light Scattering (DLS) measurements to characterize polymer hydrodynamic diameter under different polymerization time and understand the polymerization kinetics.

A general procedure for Dynamic Light Scattering (DLS) characterization of polymerization: BDF monomer (750 mg, 3.944 mol, 1 equiv.) and SeO₂ (43.8 mg, 0.394 mmol, 0.1 equiv.) were dissolved in DMSO (50 mL) under nitrogen atmosphere. The reaction mixture was heated to 100 °C with vigorous stirring. 0.1 mL of mixture was extracted from the reaction solution at different reaction times (3, 6, 12, 24, 36, and 48 hours) and diluted to 5 mL. In order to eliminate the interference of SeO₂ and elemental selenium on the results of DLS measurements, L-ascorbic acid (2 equiv. of SeO₂) was added to reduce the possible residual SeO₂. The mixtures were diluted 10 times again and then centrifuged to remove the selenium particles (10000 rpm, 10 min, 2 times). The dilute solutions were filtered using a 1-μm nylon filter before being analyzed with DLS instrument.

Table S2 Dynamic light scattering (DLS) analysis of hydrodynamic diameter distribution of n-PBDF particles under different polymerization time.

Sample	Polymerization time (h)	Average diameter (nm)
n-PBDF ink from 0.1 eq SeO ₂	3	55.3 ± 0.9
	6	58.9 ± 0.7
	12	70.3 ± 1.2
	24	75.2 ± 1.8
	36	90.5 ± 0.6
	48	113.2 ± 4.5

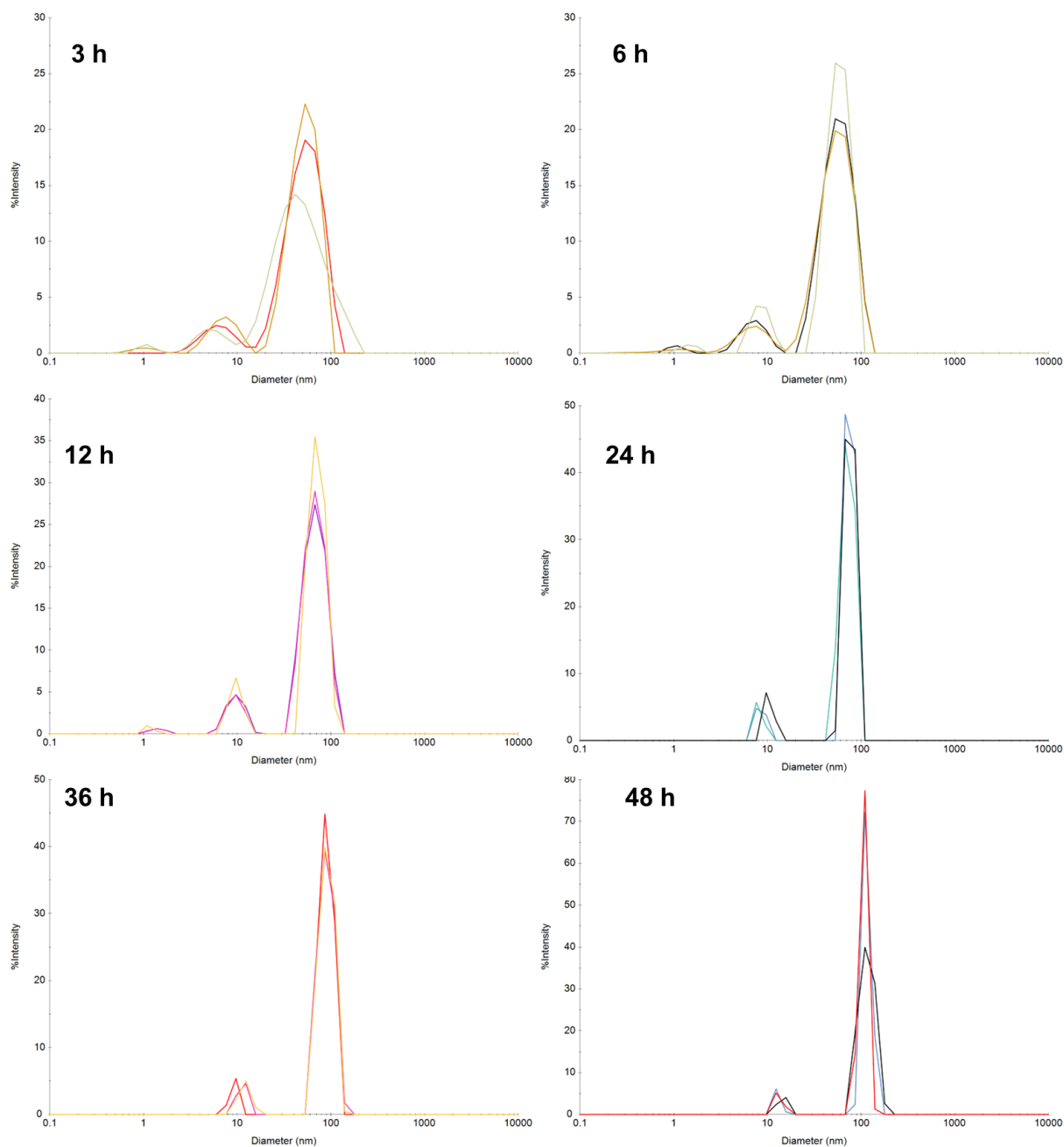


Figure S15 Dynamic light scattering (DLS) analysis of hydrodynamic diameter distribution of n-PBDF particles under different reaction times in 0.1 eq SeO₂ catalyzed polymerization.

5. Model reaction study

To understand the mechanism of oxidative polymerization of n-PBDF, model reactions were studied which involved the oxidation of benzofuran-2(3H)-one (BF; also known as 2-coumaranone) by using SeO₂ as an oxidizing agent. The BF (6.0 mg) and SeO₂ (1 equiv. in 0.6 mL DMSO-*d*₆) were charged into an NMR tube under a nitrogen atmosphere. The mixture was then heated to different temperatures (100 °C, 60 °C, and room temperature) for several hours. As for comparison, the same model reactions were conducted by using TMQ and Cu(OAc)₂ as oxidants to further compare the oxidative reactivity. ¹H NMR spectra at different reaction times were conducted to monitor the reaction process (**Figures S16-S18**). As a result, SeO₂ showed higher conversion of BF in model reaction than TMQ and Cu(OAc)₂ at both room temperature and high temperature. BF can achieve almost 100% conversion even at room temperature after 24 hours when SeO₂ was used as an oxidant (**Figure S19**). These results demonstrated that SeO₂ has stronger oxidative activity than TMQ and Cu(OAc)₂ in the model reaction.

However, careful analysis of the SeO₂-mediated model reaction revealed that the expected (E)-2H,2'H-[3,3'-bibenzofuranylidene]-2,2'-dione (BFD; known as isoxindigo) was not the major product, but the minor product (**Figure S20**). To identify the structure of the major product, we scaled up the synthesis of the model reaction and separated the major product. **Figure S21** shows the scale up synthesis of the model reaction and its corresponding phenomena. The brick red solid was obtained after filtration and characterized by Se 3d XPS (**Figure S22**), which demonstrated that elemental selenium was formed and was the reductant product of SeO₂ in the model reaction. The major product was separated and identified as carboxylic acid M6 by ¹H NMR, ¹³C NMR, and HRMS (**Figures S23-S25**). To detect the formation of intermediate M5, we conducted the model reaction at 100 °C and the reaction mixture was immediately sent to HRMS (APCI⁺) characterization after stirring for 20 min without any water treatment. To stabilize the intermediate M5 as much as possible and inhibit its hydrolysis, molecular sieves (3A) were added to the model reaction to adsorb water molecules. As shown in **Figure S26**, the intermediate M5 was detected in the mixture, which directly proves the formation of the intermediate M5. Based on the above

results, we propose the mechanisms of the model reaction, as shown in **Figures S27**.

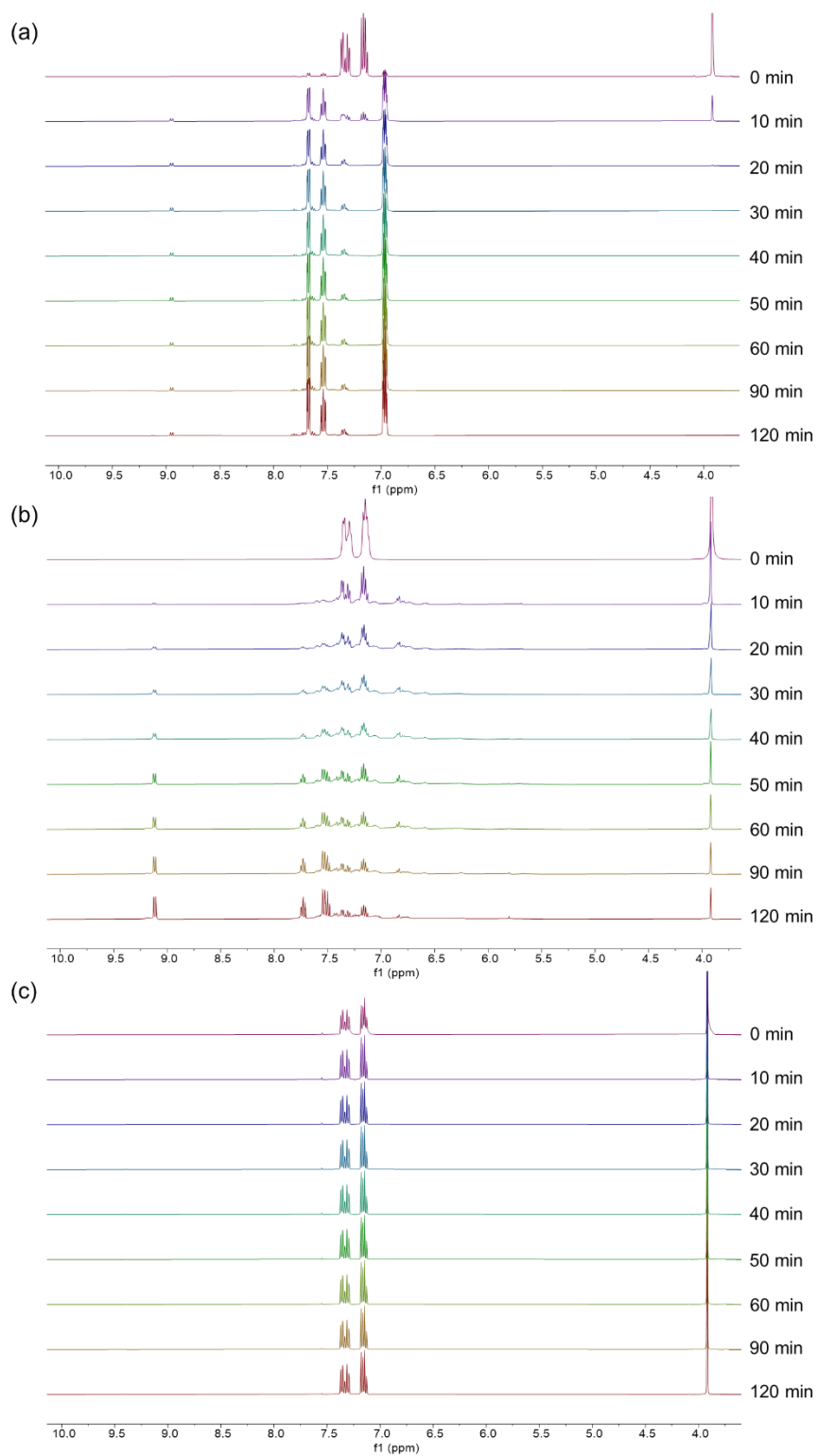


Figure S16 Time-dependent ^1H NMR spectrum of model reaction: BF_3 with one equivalent (a) SeO_2 , (b) $\text{Cu}(\text{OAc})_2$, and (c) TMQ in $\text{DMSO}-d_6$ at 100°C .

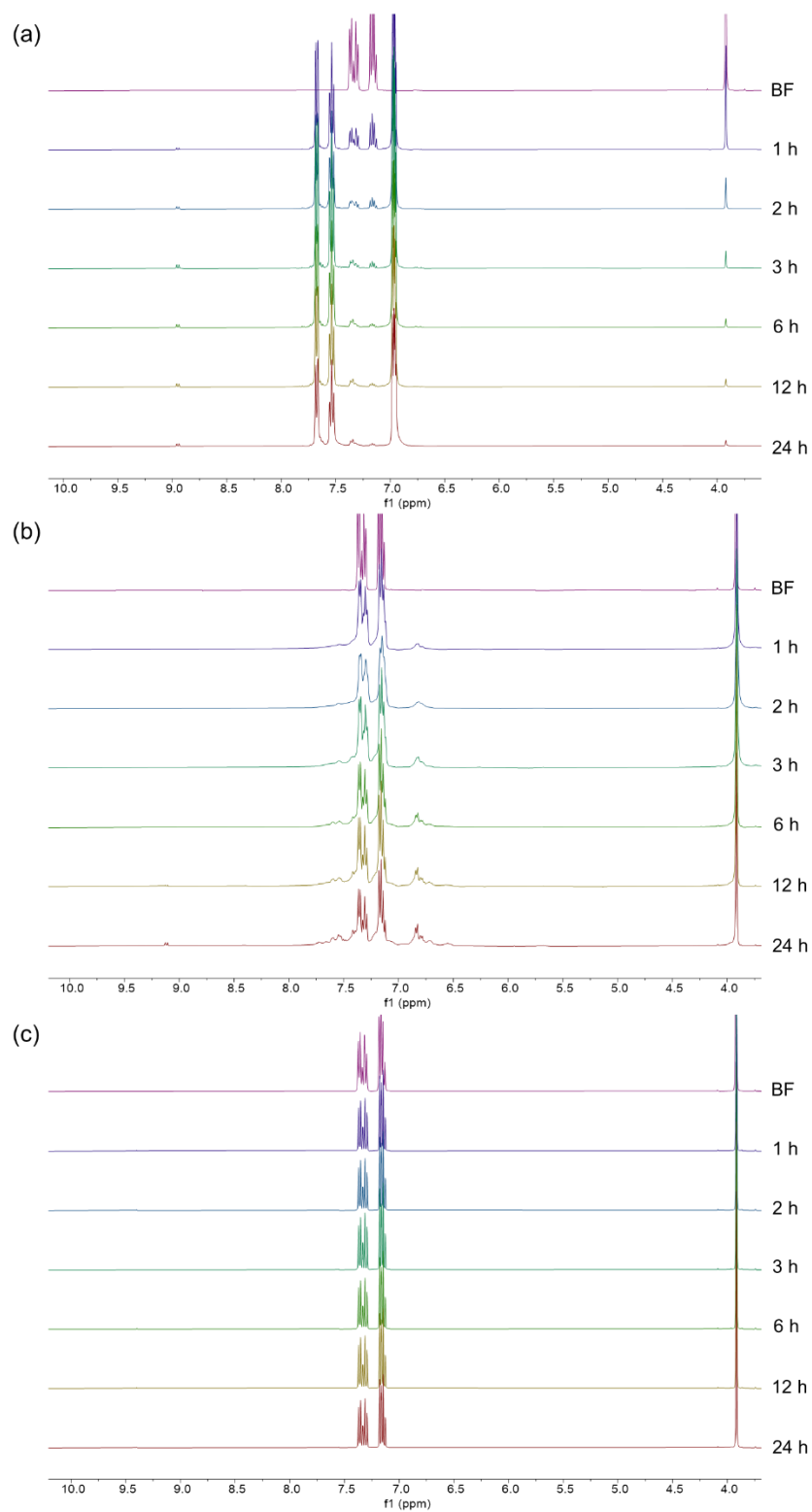


Figure S17 Time-dependent ^1H NMR spectrum of model reaction: BF with one equivalent (a) SeO_2 , (b) $\text{Cu}(\text{OAc})_2$, and (c) TMQ in $\text{DMSO}-d_6$ at 60°C .

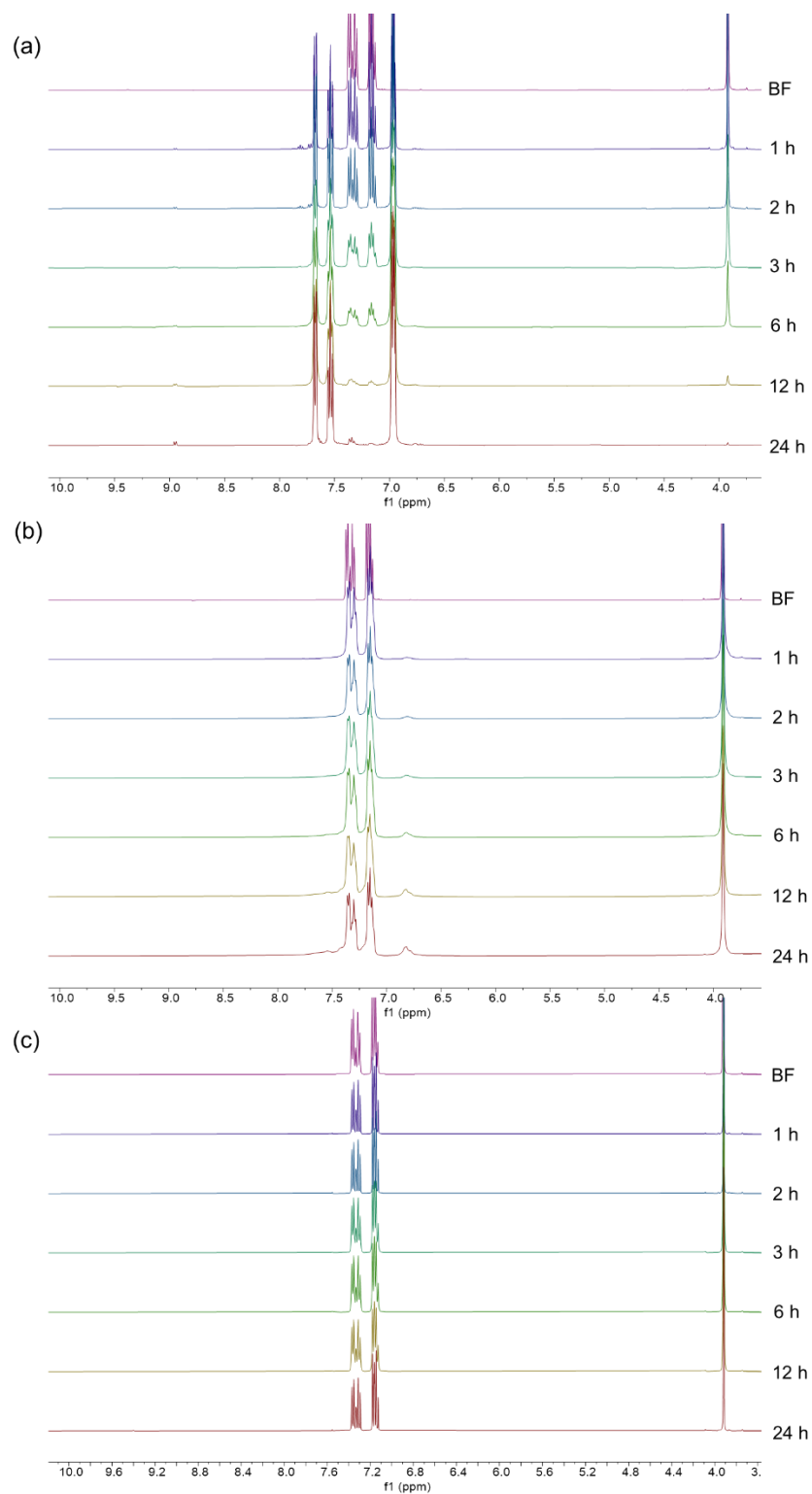


Figure S18 Time-dependent ^1H NMR spectrum of model reaction: BF with one equivalent (a) SeO_2 , (b) $\text{Cu}(\text{OAc})_2$, and (c) TMQ in $\text{DMSO-}d_6$ at RT.

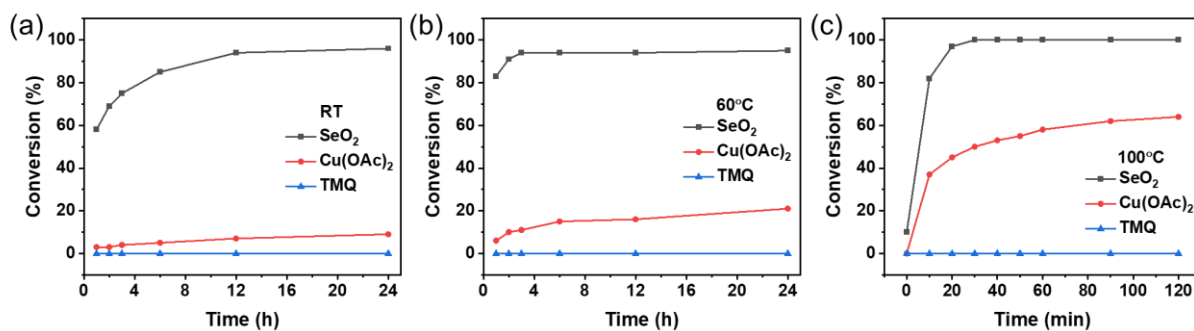


Figure S19 Time-dependent conversion of BF in model reaction by using SeO₂, TMQ, and Cu(OAc)₂ as an oxidizing agent: (a) RT, (b) 60 °C and (c) 100 °C (calculated from NMR).

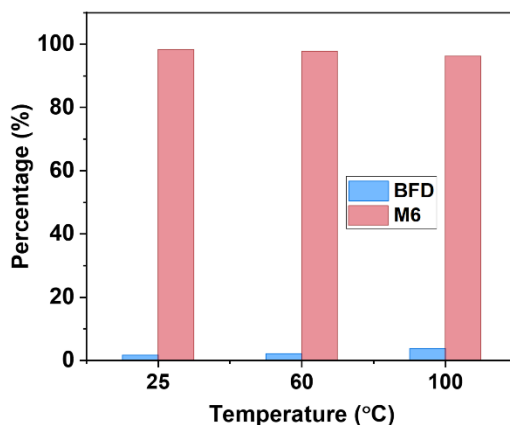


Figure S20 The percentage of BFD (minor product) and carboxylic acid M6 (major product) in SeO₂-mediated model reaction at different temperatures. Based on the NMR integrals of the peaks at 8.96 ppm of BFD and 6.95–6.99 ppm of M6, the percentages of the two compounds were calculated from their NMR integrals. After reacting at room temperature for 24 hours, the percentage of BFD calculated to be 1.7% and the percentage of M6 calculated to be 98.3%; After reacting at 60 °C for 24 hours, the percentage of BFD and M6 are calculated to be 2.2% and 97.8%, respectively; After reacting at 100 °C for 2 hours, the percentage of BFD and M6 are calculated to be 3.8% and 96.2%, respectively.

Scale up synthesis of model reaction:

Under nitrogen atmosphere, benzofuran-2(3H)-one (0.500 g, 3.73 mmol, 1.0 equiv.) and SeO_2 (0.413 g, 3.73 mmol, 1.0 equiv.) were dissolved in DMSO (20 mL), and the mixture was stirred at room temperature for 24 h. The mixture turned a brick red. After the reaction was complete, the precipitate was filtered and dried under a vacuum, which was characterized by Se XPS. The organic phase was dissolved in EA (100 mL), washed with water ($50 \text{ mL} \times 3$), and then concentrated under reduced pressure. The residue was dissolved in NaHCO_3 aqueous solution (100 mL) and extracted with DCM (100 mL). The DCM phase dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to obtain BFD. The aqueous phase was acidified with 1 M HCl and extracted with EA (100 mL). The obtained organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure to give compound M6 as a yellow solid (400 mg, 80 %). ^1H NMR ($\text{DMSO}-d_6$, 400 MHz, ppm): δ 10.90 (s, 1H), 7.66–7.69 (dd, $J_1 = 8.0$, $J_2 = 8.0$ Hz, 1H), 7.52–7.56 (m, 1H), 6.95–9.99 (m, 2H). ^{13}C NMR ($\text{DMSO}-d_6$, 100 MHz, ppm): δ 188.87, 167.01, 159.62, 136.64, 129.92, 119.68, 119.63, 117.23. ESI-HRMS: calcd. for $[\text{M}-\text{H}]^-$: 165.0193; Found: 165.0195.

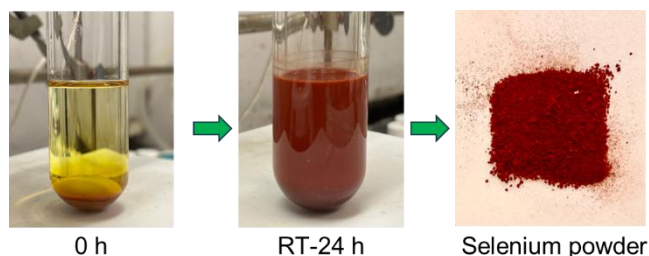


Figure S21 The reaction phenomena of the SeO_2 -mediated model reaction and the obtained brick red precipitate. The color difference of the selenium formed in polymerization and model reaction is due to different selenium allotropes. Selenium forms several allotropes that interconvert with temperature changes, depending somewhat on the rate of temperature change.^[3] The similar phenomenon of different color of Selenium precipitate obtained at different temperature has been reported in the literature.^[4]

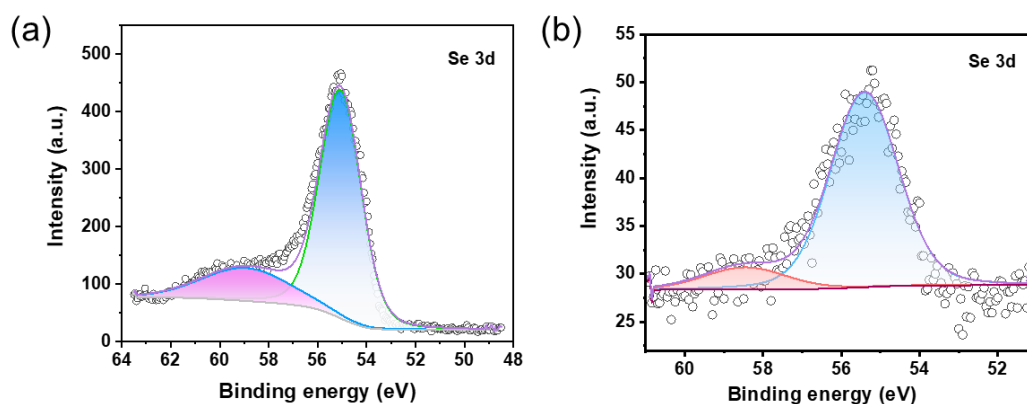


Figure S22 The Se 3d XPS spectrum of (a) the brick red precipitate in the model reaction and (b) the unpurified n-PBDF polymer films. The binding energy of the Se 3d peak of pure selenium was 55.5 eV, while the higher binding energy at 59.9 eV was the Se 3d peak in SeO₂.

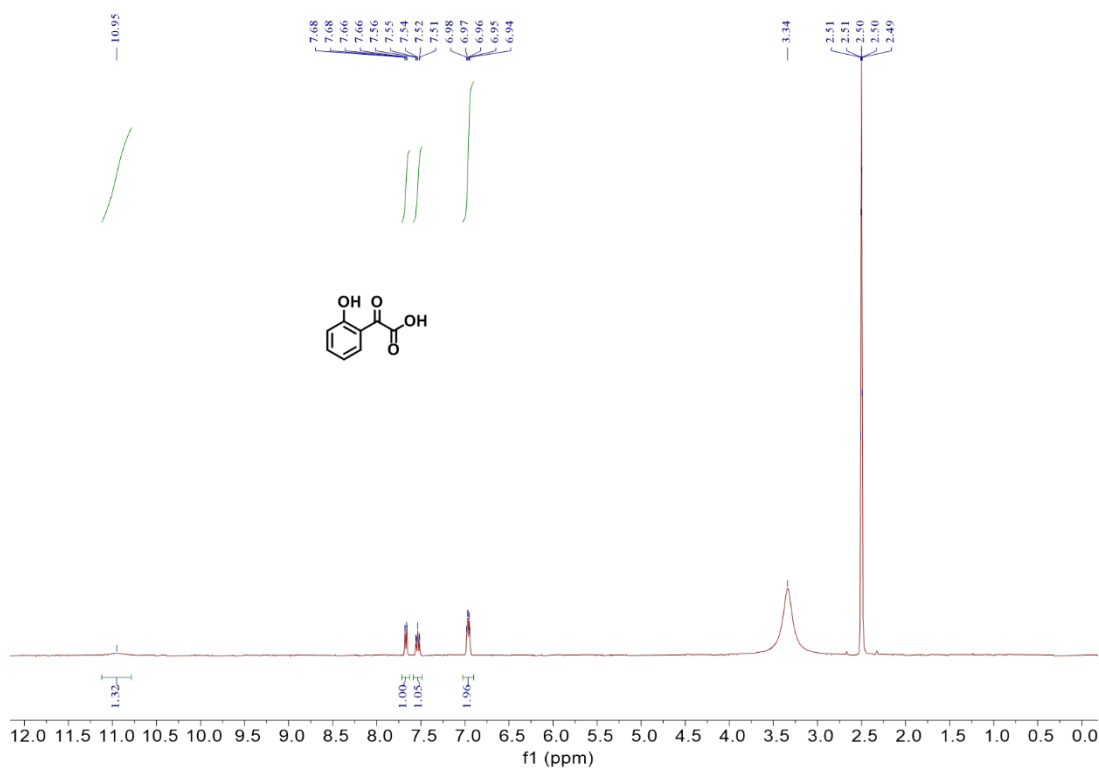


Figure S23 ¹H NMR spectrum of acid M6 in DMSO-*d*₆.

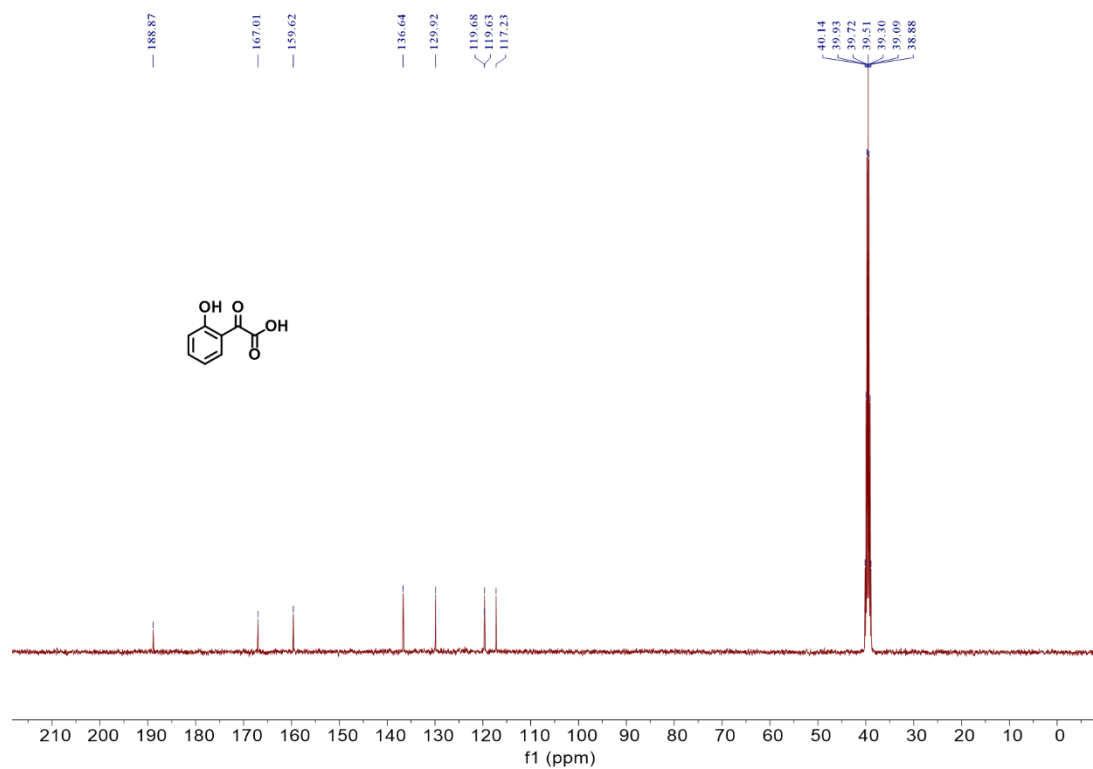


Figure S24 ^{13}C NMR spectrum of acid M6 in $\text{DMSO-}d_6$.

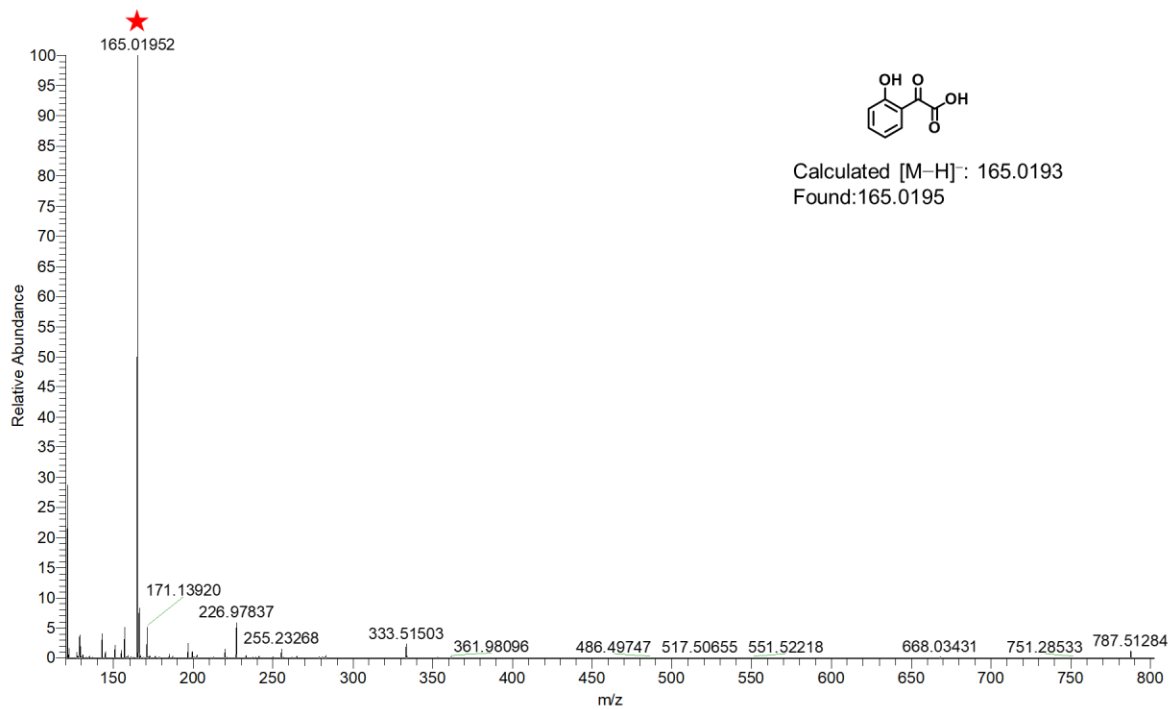


Figure S25 High resolution mass spectrum (ESI^-) of acid M6.

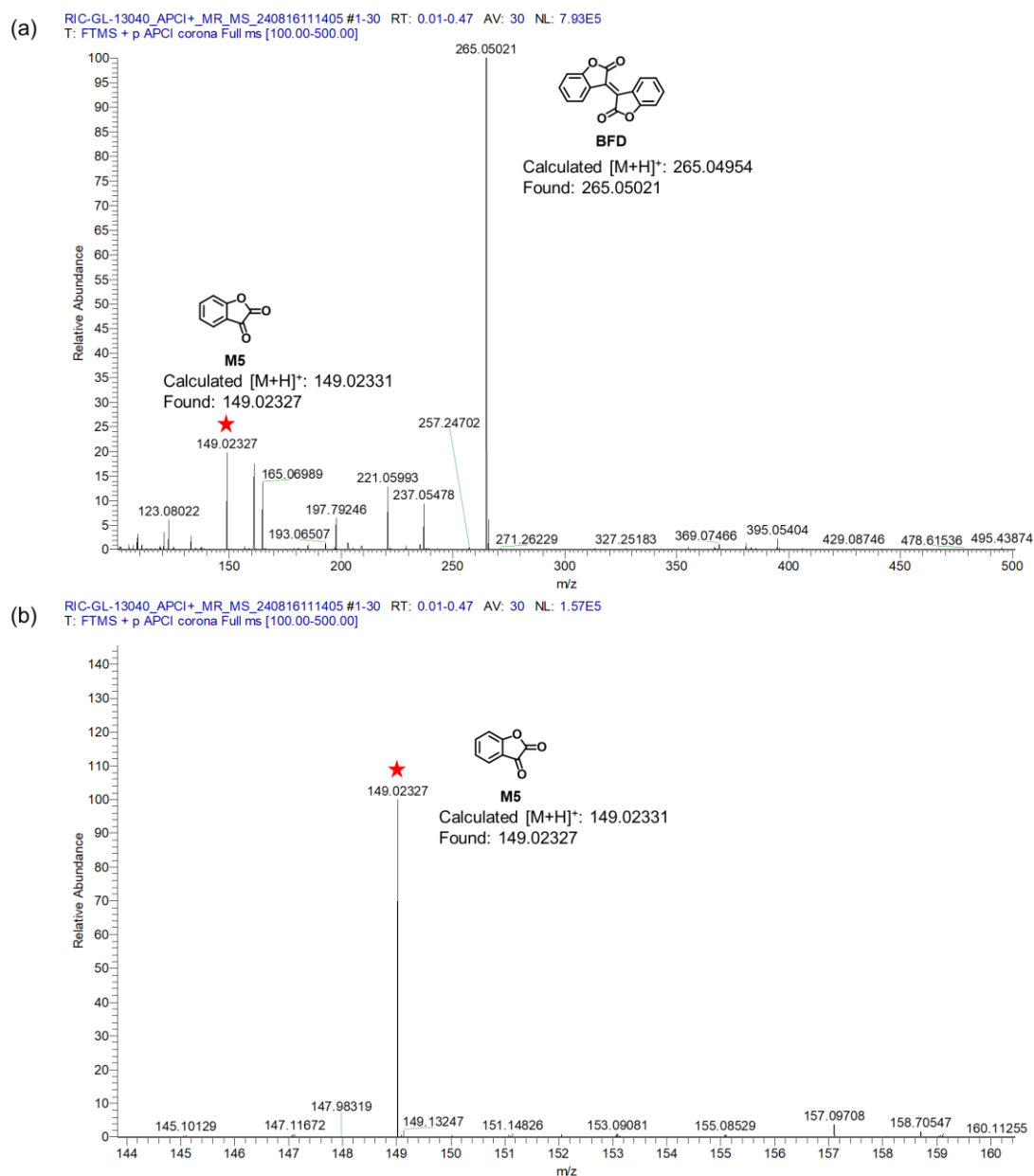


Figure S26 High resolution mass spectra (APCI⁺) of the reaction mixture of model reaction with the added of molecular sieves (3A): (a) full spectrum and (b) zoom in spectrum.

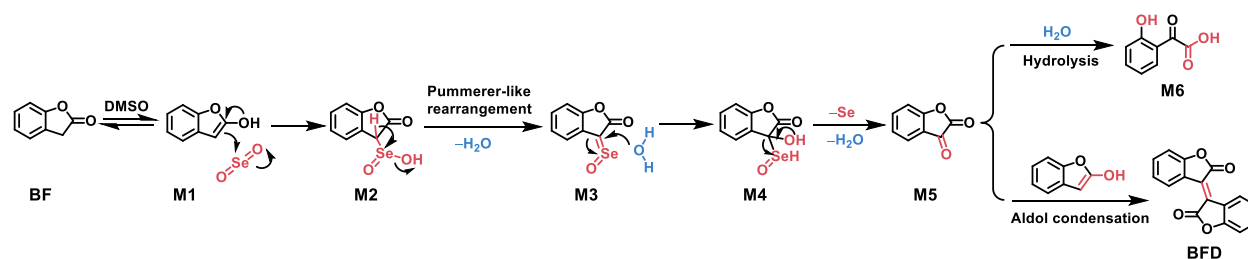


Figure S27 The proposed mechanisms of SeO₂-mediated model reaction.

6. Theoretical calculation

To elucidate the mechanistic differences between model reaction and polymerization, Yet Another Reaction Program (YARP) methodology is applied to locate the transition states (TSs) and activation energies in the mechanism pathways.^[5] YARP is capable of characterizing reactions by several algorithms, including generating geometries by conformational sampling for double-ended transition state searches, approximating TSs by low-level calculations, and refining these TSs by Berny optimization and Intrinsic Reaction Coordinate calculations at high-level DFT.^[6] In this study, CREST and xTB are used for conformational sampling and low-level calculations.^[7] All the geometries and energies of this work are optimized at B3LYP-D3/6-31G** level of theory with PCM model of DMSO as solvent by Gaussian 19 package.^[8] **Figures S28-S33** show the free energy diagrams of the two pathways from the diketones to the corresponding final products in the model reaction and the polymerization process.

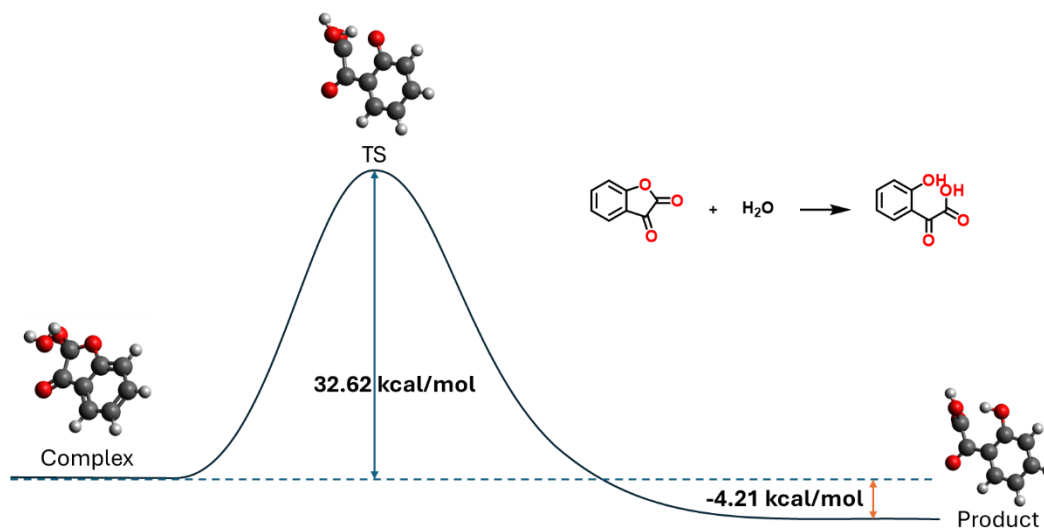


Figure S28 The free energy diagram of the hydrolysis process of diketone in model reaction.

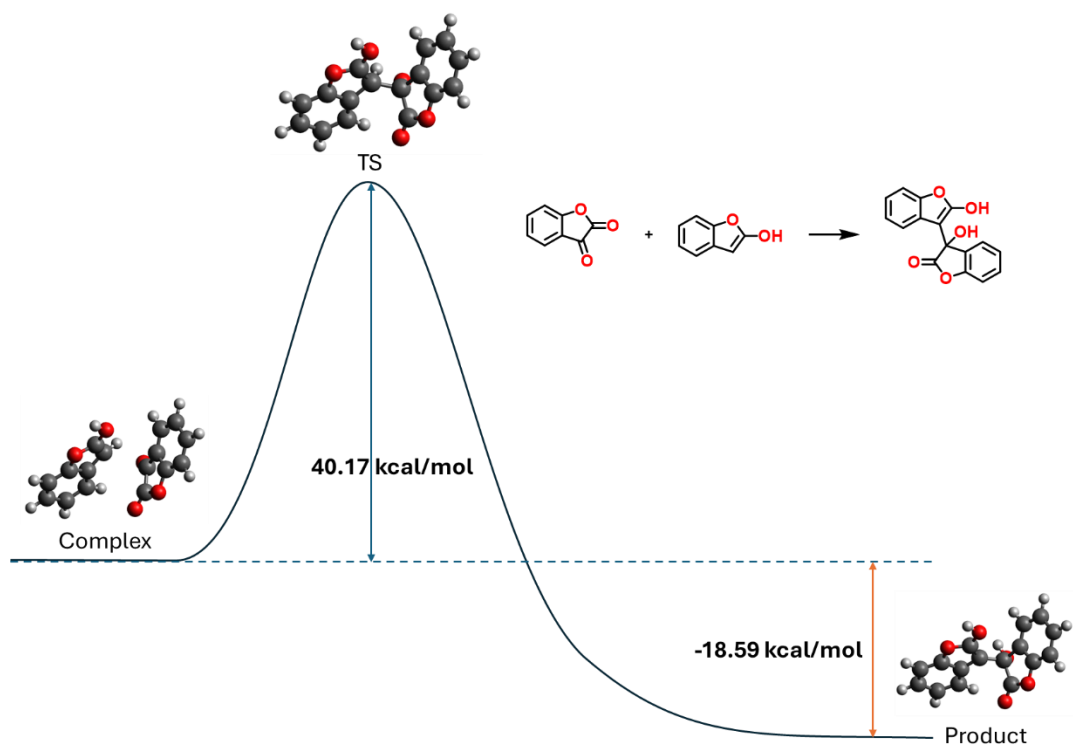


Figure S29 The free energy diagram of the aldol condensation process in model reaction.

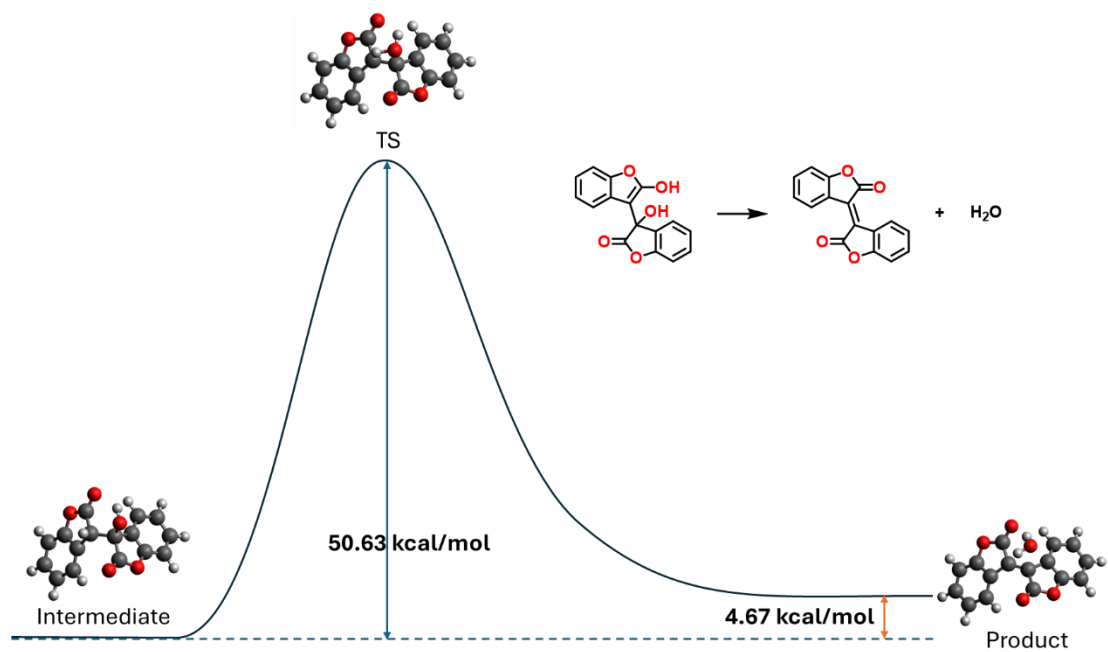


Figure S30 The free energy diagram of the dehydration process of aldol condensation intermediate in model reaction.

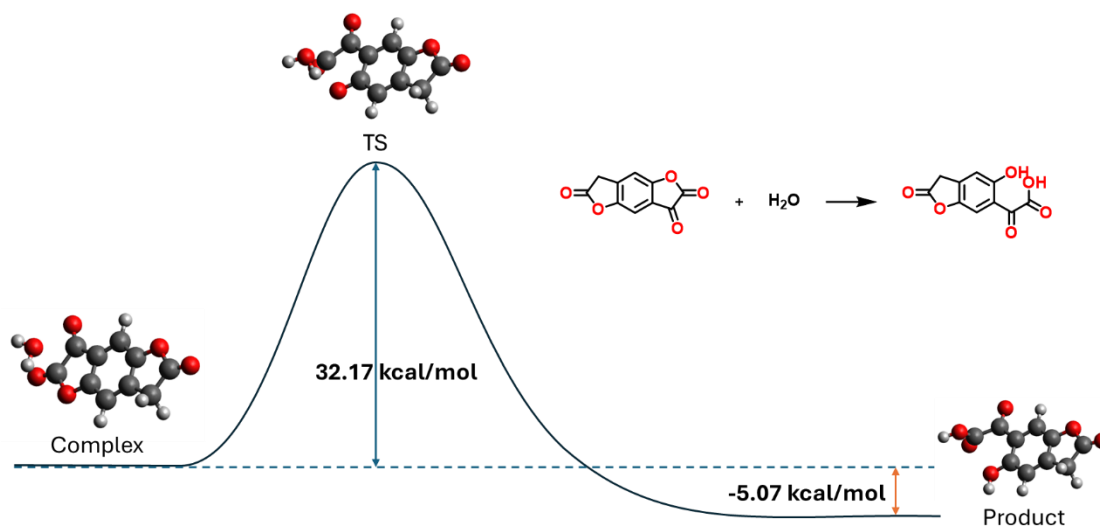


Figure S31 The free energy diagram of the hydrolysis process of diketone in the polymerization process.

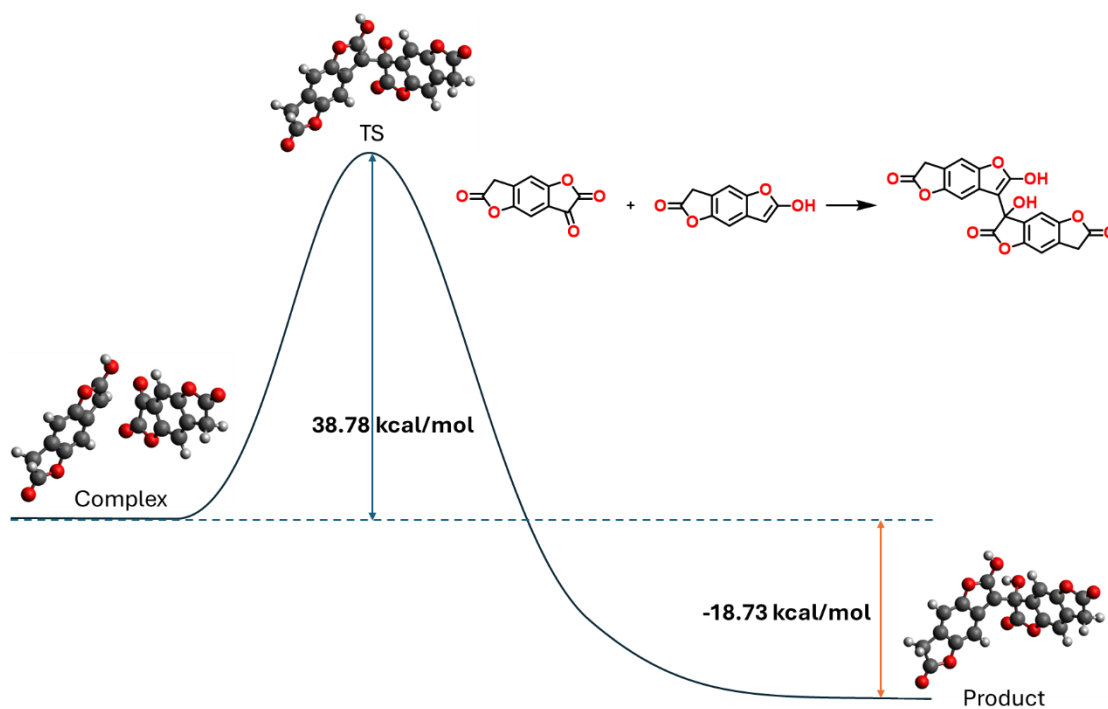


Figure S32 The free energy diagram of the aldol condensation process in the polymerization process.

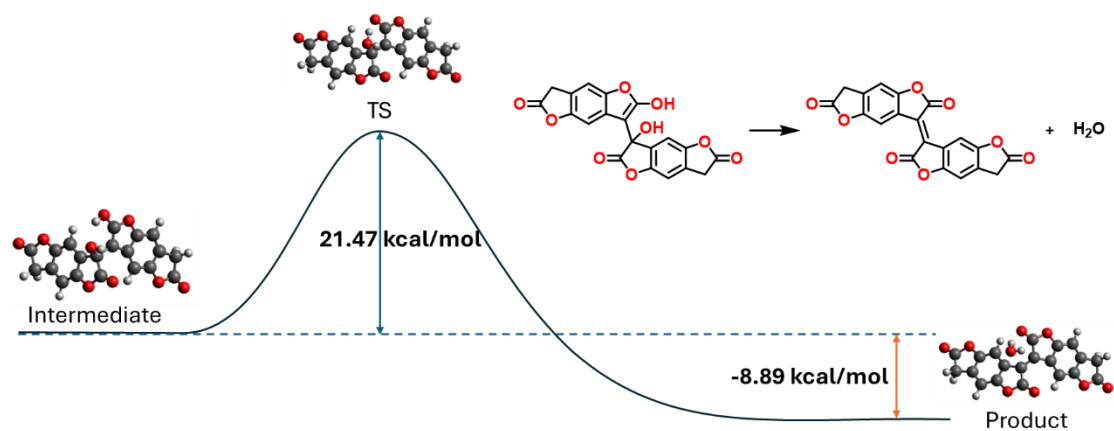


Figure S33 The free energy diagram of the dehydration process of aldol condensation intermediate in the polymerization process.

7. Mechanistic understanding of polymerization

To understand whether there is no ring-opening hydrolysis structure present in SeO₂-catalyzed PBDF, we conduct the FTIR spectrum of n-PBDF polymer from both 1.0 and 0.1 equivalents SeO₂-catalyzed polymerization reaction. As shown in **Figure S34**, the FTIR spectrum of n-PBDF exhibits noticeable C=O stretching of the lactone moiety at 1781 cm⁻¹, while the characteristic band of a carboxylic acid group at 1752–1624 cm⁻¹ was absent,^[9] indicating that there is no ring-opening hydrolysis structure in SeO₂-catalyzed PBDF.

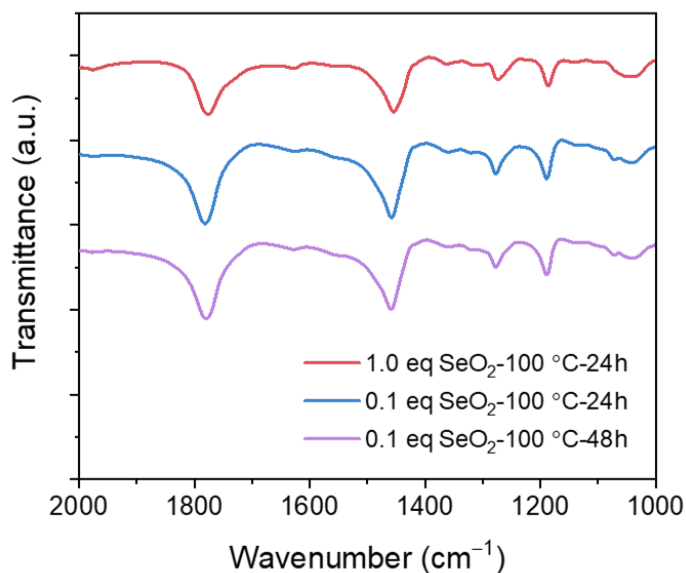


Figure S34 FTIR spectra of n-PBDF polymer from SeO₂-catalyzed polymerization.

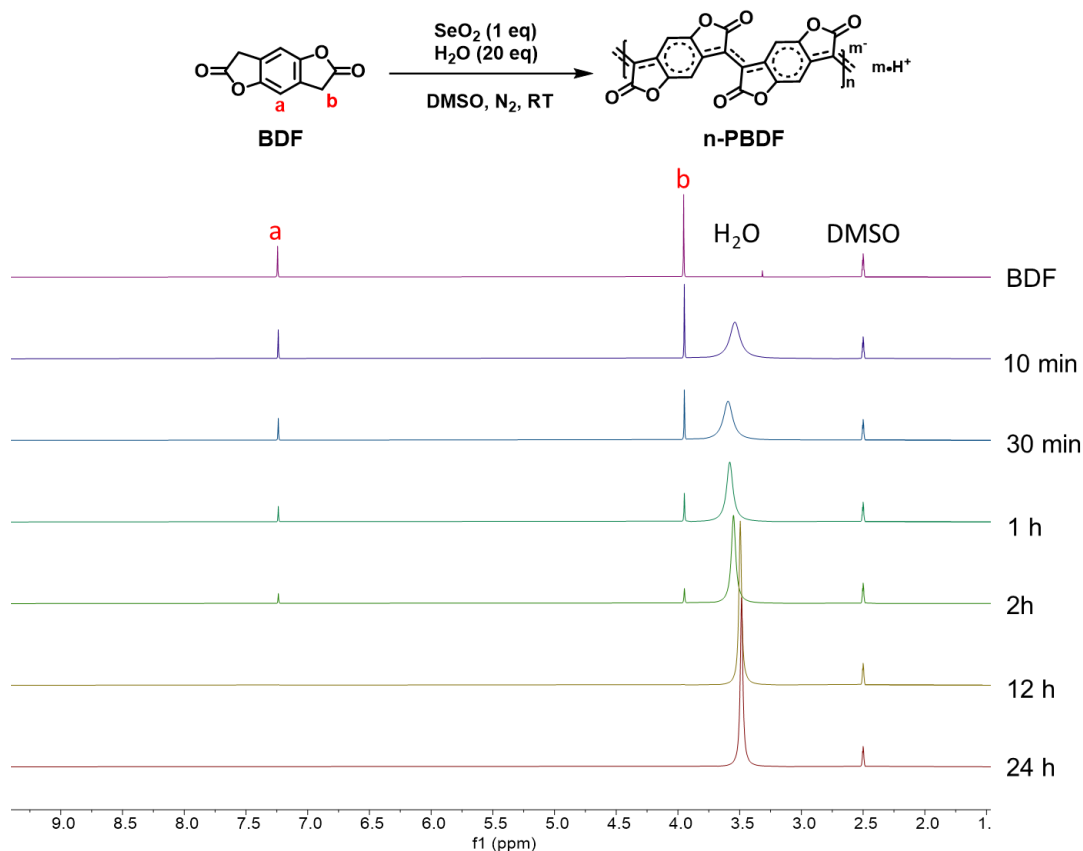


Figure S35 ¹H NMR spectrum of BDF (5 mg mL⁻¹) polymerization catalyzed by SeO₂ (1 eq) in the presence of H₂O (20 eq) added in DMSO-*d*₆ at RT. The results showed that the proton peak of the monomer was gradually consumed, and the monomer conversion reached 100% after 24 hours, suggesting the successful formation of n-PBDF. And there is no other by-product formed. These results demonstrated that water has no significant interruptive effect on the polymerization process, and the polymerization of BDF went smoothly without any side reactions of the ring-opening hydrolysis process at room temperature.

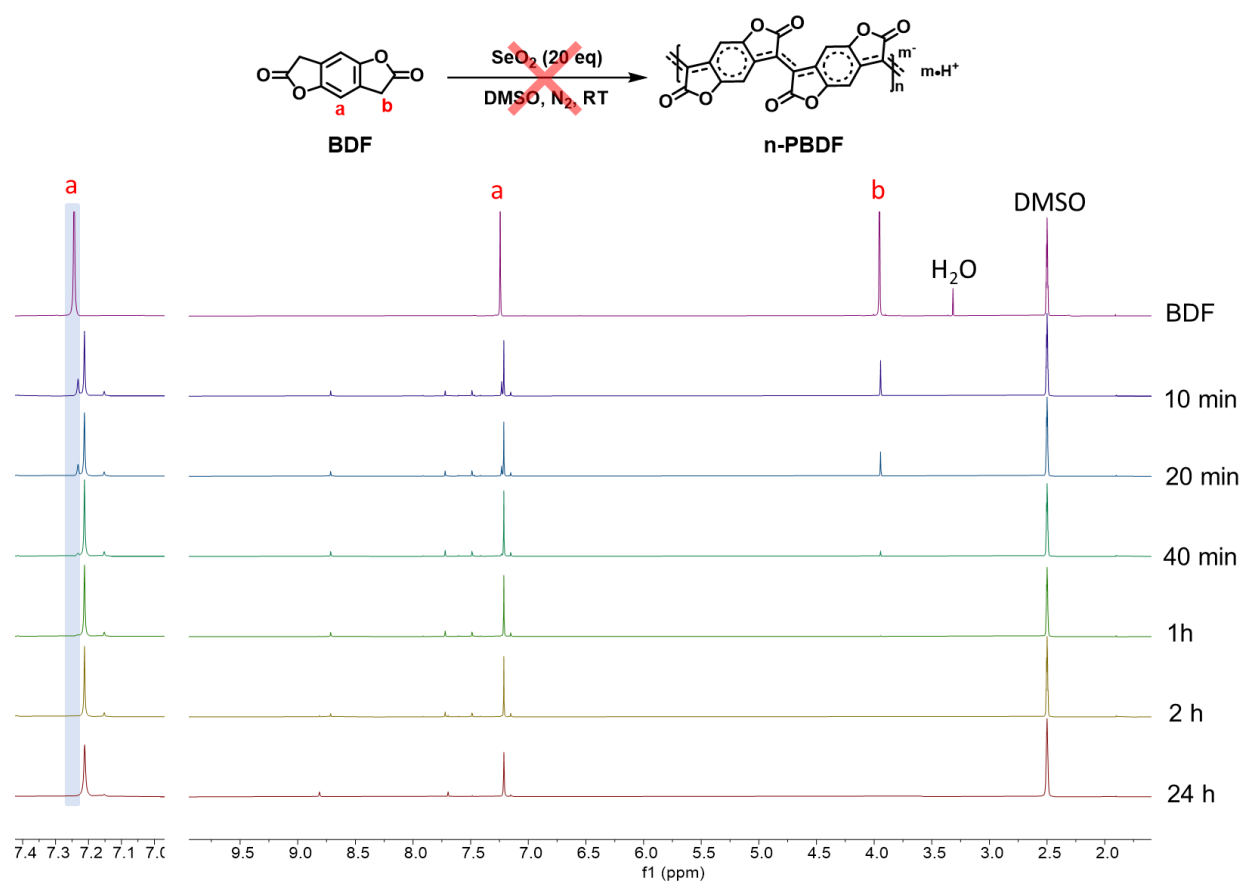


Figure S36 ^1H NMR spectrum of BDF (5 mg mL^{-1}) polymerization catalyzed by SeO_2 (20 eq) in $\text{DMSO}-d_6$ at RT. The left part shows the enlarged view of the 7.0~7.4 ppm region.

To understand the mechanism of the polymerization process, a polymerization control experiment at low concentrations of BDF monomers reacted with an excess amount of SeO_2 was performed. The mixtures of 25 mg BDF monomer (1 equiv.) and SeO_2 (20 equiv.) were dissolved in 5 ml $\text{DMSO}-d_6$ under nitrogen, and the mixture was stirred at room temperature. ^1H NMR spectra of the mixture at different reaction times were recorded (**Figure S36**). The NMR spectrums showed that the proton peaks of the monomer at 7.24 and 3.95 ppm gradually decreased with the increase in reaction time, indicating that the monomer was gradually consumed. A new major peak at 7.21 ppm and several weaker peaks in the low field region were formed. The methylene proton peak at 3.95 ppm disappeared completely after 2 h and no other proton peak in high field region appeared, indicating that all methylene groups were completely oxidized to carbonyl groups in the

presence of excess SeO_2 , and no methylene groups remained unreacted in the products. These results indicated that the polymerization process was highly inhibited.

We then analyze the composition of the resulting products. After the reaction was stirred for 24 hours, the reaction mixture was characterized by ESI-MS (**Figure S37**). Only peaks with m/z below 500 were found in the ESI-MS spectrum, indicating that chain growth of the polymerization process was inhibited and the obtained products consisted of only one or two BDF monomer fragments. We list all possible structures that do not contain methylene groups (**Figure S38**). Comparing these possible structures with the ESI-MS spectrum, we found that the main products in the mixture are BDF-dicarboxylic acid and Dimer-dicarboxylic acid. Since no obvious peaks with m/z higher than 500 were found in the ESI-MS spectrum and no other strong peaks in NMR, we deduced that the major peak at 7.21 ppm (shifted from 7.24 ppm) was derived from the BDF-dicarboxylic acid (major product), the weaker peaks in low field region (8.81 and 7.70 ppm) were assigned to Dimer-dicarboxylic acid (minor product). Obviously, these two dicarboxylic acids are the ring-opened products of their corresponding diketones.

At the initial stage of the reaction, most of the BDF monomer was rapidly oxidized to diketone, and only a few unreacted monomers were condensed with the newly formed diketone to form a dimer product. After that, all the methylene groups of the monomer and dimer were also rapidly oxidized to carbonyl groups, and thus, the polymer chains could not grow further. Therefore, in the presence of the excess amount of SeO_2 (acid condition), the hydrolysis process becomes the only pathway, obtaining the ring-opened product BDF-dicarboxylic acid (major) and Dimer-dicarboxylic acid (minor). The results of the polymerization control experiment indicate that the polymerization process involves Riley oxidation and aldol condensation, which further proves the rationality of the proposed polymerization mechanism.

RIC-GL-12227_ESI-_ACN+H2O_BLOCK 24H #1-35 RT: 0.01-0.50 AV: 35 NL: 1.92E7
T: FTMS - p ESI Full ms [100.00-800.00]

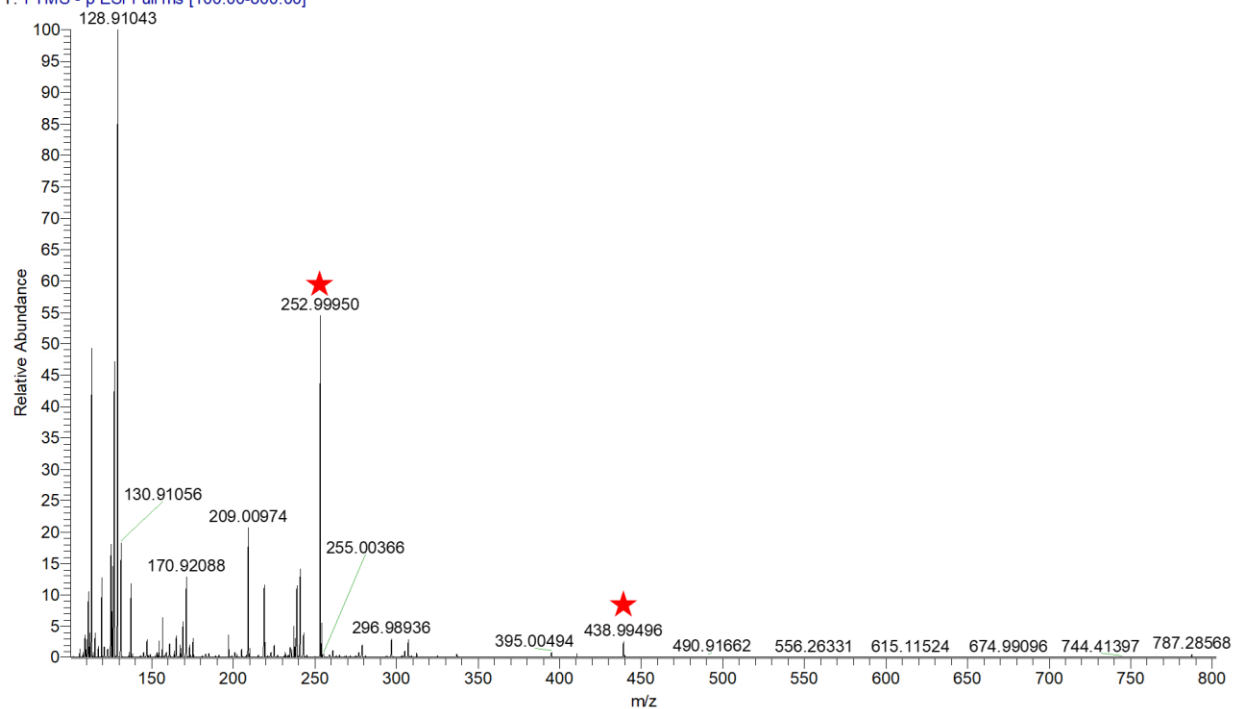


Figure S37 ESI-MS spectrum of the mixture after 24 hours of the polymerization control reaction in negative ionization mode.

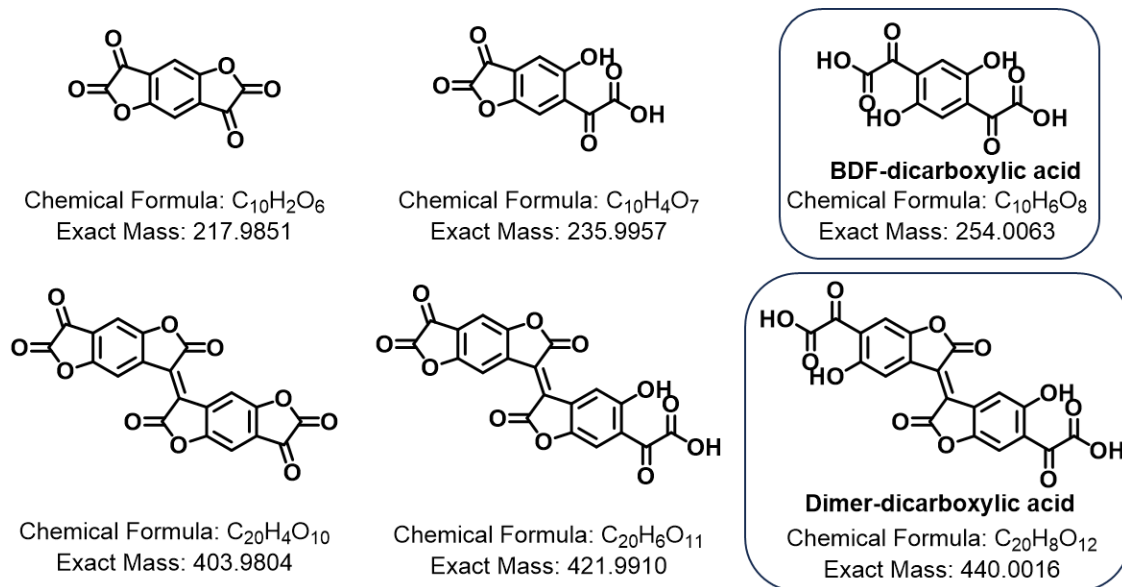


Figure S38 Compounds that consist of one and two BDF monomer fragments that do not contain methylene groups.

8. Scale-up synthesis of high-quality n-PBDF ink

SeO₂-catalyzed polymerization of n-PBDF is cost-effective and scalable, making it suitable for large-scale production. Reducing the cost of synthesis and purification is the key to large-scale synthesis, which requires a cost-effective synthetic method, low catalyst loading, high monomer conversion, and simplified purification steps. If the monomer conversion can reach 100%, the dialysis process can be avoided, and purified ink can be obtained by simple centrifugation and filtration to remove selenium particles. From the polymerization condition investigation in **Figures S9** and **S10**, when 0.3 eq SeO₂ was used to polymerize for 24 h, the monomer conversion can reach up to 100%. However, when 0.1 eq SeO₂ was used to polymerize for 24 h and 48 h, the monomer conversion reached 67% and 91%, respectively. Obviously, as few catalysts as possible should be used to achieve up to 100% monomer conversion. From results in the catalytic polymerization by batch addition of SeO₂ (**Figure S39**), when 0.1eq SeO₂ was used to polymerize for 24 h, then another 0.1eq SeO₂ was added and continued polymerized for another 24 h, up to 100% conversion of monomer can be achieved. Therefore, a demonstration of the large-scale synthesis of n-PBDF was performed by using this strategy.

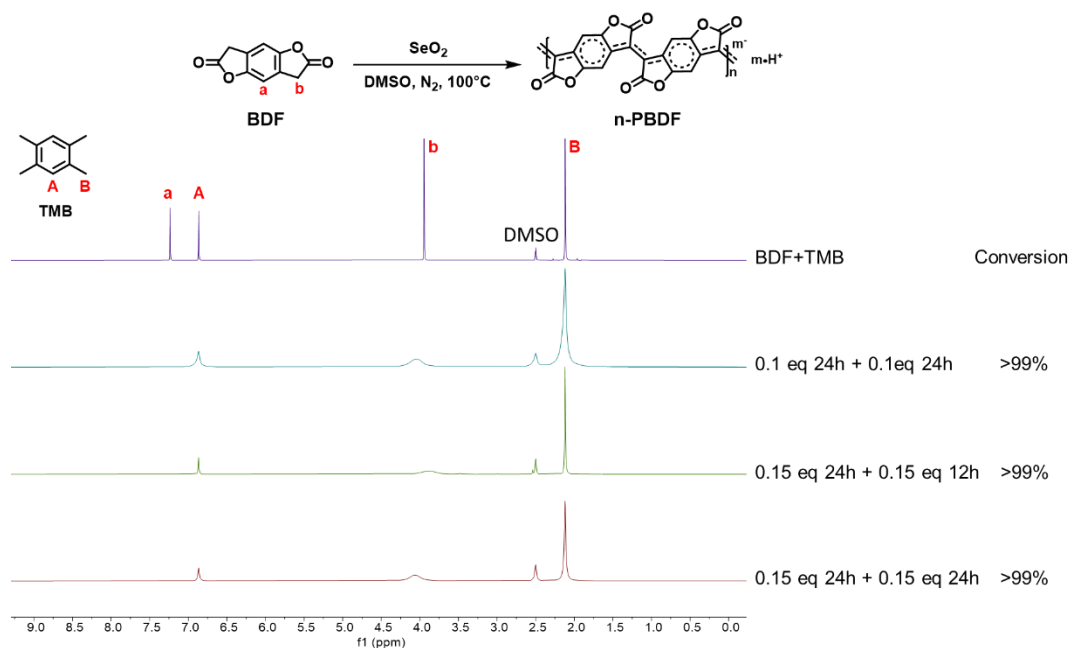


Figure S39 ¹H NMR spectrum of catalytic polymerization by batch addition of SeO₂. TMB was used as a reference.

Scale up synthesis of n-PBDF and the removal of Selenium:

The monomer 3,7-dihydrobenzo[1,2-b:4,5-b']difuran-2,6-dione (BDF) (3.0 g, 15.78 mmol, 1 eq) and SeO₂ (175.0 mg, 1.58 mmol, 0.1 eq) were dissolved in DMSO (200 mL) under nitrogen atmosphere. The mixture was stirred at 100 °C for 24 hours. Then another portion of SeO₂ (175.0 mg, 1.58 mmol, 0.1 eq) dissolved in DMSO (100 mL) was added. The mixture was continued, stirring at 100 °C for another 24 hours. After the solution was cooled to RT, the mixture formed gel. Another 200 ml of DMSO was added to dilute the mixture and stirred to homogenize it. The resulting solution was centrifuged to remove the insoluble solids (10000 rpm, 15 min, 2 times) and then filtered through a 1 µm nylon membrane in solvent filtration apparatus to obtain a homogeneous and purified n-PBDF ink. 2 mL of the obtained n-PBDF ink was taken, and the DMSO was removed under high vacuum and weighed to obtain the concentration of the polymer solution as 6 mg mL⁻¹.

The conductivities and concentration of residual selenium in polymer solutions under different purification processes were detected, and the results were summarized in **Table S3**. The concentration of selenium in polymer solutions purified only by centrifugation and filtration was as low as 0.59 ppm. If the polymer ink was dialyzed, then centrifuged and filtrated, the concentration of residual selenium in the obtained ink was as low as 0.33 ppm. It can be seen that the conductivity of the polymer ink slightly improved by the extra dialysis process. These results indicated that centrifugation and filtration are effective purification methods to remove selenium and obtain purified ink.

Table S3 Characterization of conductivities and the concentration of residual selenium in scale-up synthesized n-PBDF ink under different purification processes.

Purification method ^a	Centrifugation and filtration	Dialyzed, then centrifugation and filtration
Conductivities (S cm ⁻¹) ^b	2738 ± 126	3206 ± 218
Se concentration (ppm) ^c	0.59	0.33

^aCentrifugation: 10000 rpm, 15 min, 2 times; filtration: 1 μm nylon membrane. ^bMeasured by the Van der Pauw method. ^cMeasured by ICP-MS.

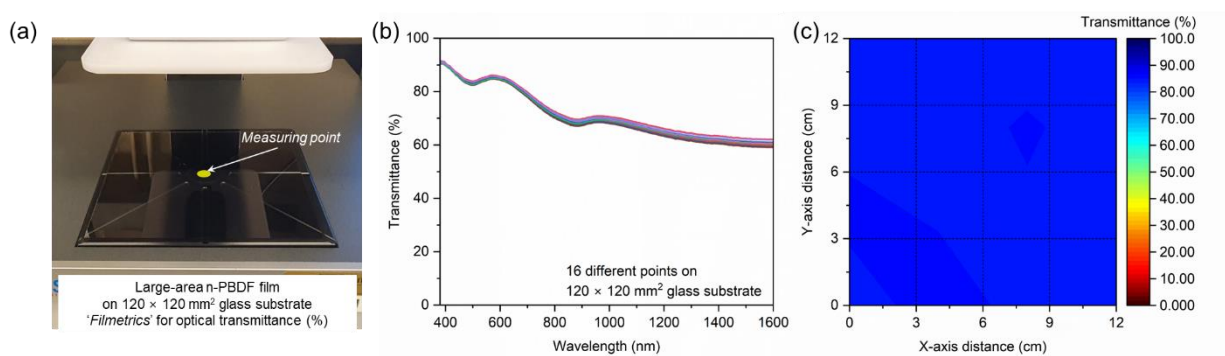


Figure S40 The transmittance of the large-area transparent n-PBDF conductive film: (a) The transmittance measurement of large-area n-PBDF film, (b) The transmittance curves of 16 different points from the large-area n-PBDF film, (c) The transmittance mapping at 550 nm of the large-area n-PBDF film.

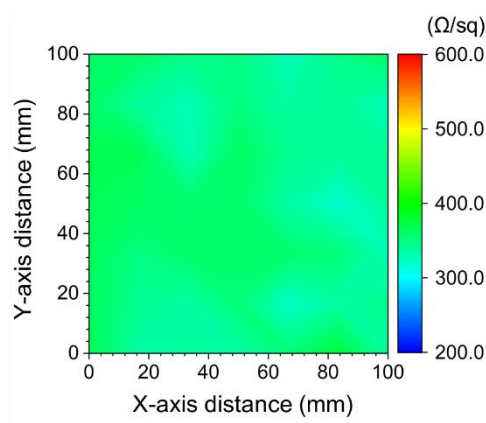


Figure S41 The square resistance mapping of the large-area transparent n-PBDF conductive film. The average square resistance of the large-area transparent conductive film is 350 Ω/sq.

Cost analysis: To better understand the synthetic cost of n-PBDF by SeO₂-catalyzed method and other relevant systems, we conduct a detailed cost calculation based on the synthetic procedures and evaluation rules published in literatures.^[10] In these cost calculations, all the raw materials, solvent and reagent used for the reaction or purification were taken into account in order to estimate the total material costs.^[10c] However, the actual expenses associated with materials production would be significantly higher than the estimated numbers, as other costs such as labor, facilities, energy, and waste treatment were ignored to simplify the calculations.^[10a,10e] Therefore, the calculations are unlikely to reflect the actual cost of mass production in industry, but can be used as a rough evaluation for cost of n-PBDF synthesis. Taking the synthesis of 1 L of 10 mg/mL n-PBDF ink as an example, **Table S4** summarized the calculated chemical synthesis cost by three different synthetic methods. It can be seen that the monomer cost takes up a large part of the total cost. The oxidant cost in SeO₂ and Cu(OAc)₂ systems are negligible compare to monomer cost. The oxidant cost of TMQ system accounts for almost 20% of the total cost when the purification cost is ignored. However, when the purification cost is considered, the total cost in TMQ and Cu(OAc)₂ systems increases significantly due to the necessary dialysis process, which is almost twice that of SeO₂ system. The cost analysis demonstrate that SeO₂-catalyzed method has significant cost advantage for large-scale production of n-PBDF.

Table S4 The calculated chemical synthesis cost for n-PBDF (1L, 10 mg mL⁻¹) by SeO₂, TMQ and Cu(OAc)₂ methods.

Synthetic method ^a	Procedure	Chemical	Price	Quantity	Cost (\$)	Total Cost (\$)
SeO ₂	Monomer	BDF ^b	25.4 \$/g	10.3 g	261.6	276.9
	Oxidant	SeO ₂ ^c	0.33 \$/g	1.2 g	0.40	
	Solvent	DMSO ^c	14.9 \$/L	1 L	14.9	
	Purification ^d	Centrifugation and filtration				276.9

TMQ	Monomer	BDF	25.4 \$/g	12.8 g	325.1	418.2
	Oxidant	TMQ ^b	4.71 \$/g	16.6 g	78.2	
	Solvent	DMSO	14.9 \$/L	1 L	14.9	
	Purification ^e	DMSO	14.9 \$/L	10 L	149	
Cu(OAc) ₂	Monomer	BDF	25.4 \$/g	12.8 g	325.1	340.5
	Oxidant	Cu(OAc) ₂ ^b	0.04 \$/g	12.2 g	0.49	
	Solvent	DMSO	14.9 \$/L	1 L	14.9	
	Purification ^e	DMSO	14.9 \$/L	10 L	149	

^aCalculated based on 99% yield for SeO₂ in this work and 80% yield for both Cu(OAc)₂ and TMQ system in literatures;^[2d,11] ^bData are from Angene Chemical Inc.; ^cData are from Thermo Fisher Scientific Inc.; ^dPurification involving centrifugation and filtration, no chemical cost; ^ePurification involving DMSO dialysis. Actually, the DMSO used in dialysis process is much more than 10 times the volume of the original ink. Although DMSO can be recycled through distillation under reduced pressure, this process also generates costs such as labor, facilities, energy, and water, etc. Therefore, here the dialysis cost is calculated based on 10 times the volume of the original ink as a compromise.

9. Generalization of SeO₂ catalyzed polymerization method

To explore the versatility of the SeO₂ oxidation method in the synthesizing of relevant n-type conjugated polymers, the sulfur and nitrogen derivatives of BDF monomer, namely 3,7-dihydrobenzo[1,2-b:4,5-b']dithiophene-2,6-dione (BDT) and 1,5-didodecyl-5,7-dihydropyrrolo[2,3-f]indole-2,6(1H,3H)-dione (BDP-C12), were synthesized according to previous literature.^[12] BDT and BDP-C12 monomers were polymerized with SeO₂ oxidant (**Figures S42-44**), and the polymerization results were summarized in **Table S5**. In the polymerization of BDT, a n-type conducting polymer, n-doped poly(benzodithiophenedione) (PBDT) was obtained due to the *in situ* n-doping process.^[12a] *In situ* n-doping process also enable the catalytic cycle of the selenium catalyst, thus high yield can be achieved by using catalytic amount of SeO₂. As shown in **Figure S43**, n-doped PBDT exhibited strong polarons/bipolarons absorption band in the NIR region, which was similar to previous reported results.^[12a] While in polymerization of BDP-C12, a semiconductive polymer PBDP-C12 without intrinsic conductivity was obtained,^[12] where only low yield was achieved by using catalytic amount of SeO₂ due to no *in situ* n-doping process and no regeneration of SeO₂ happened.

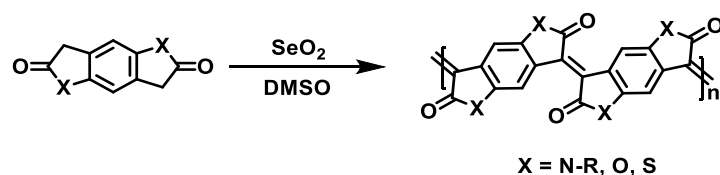


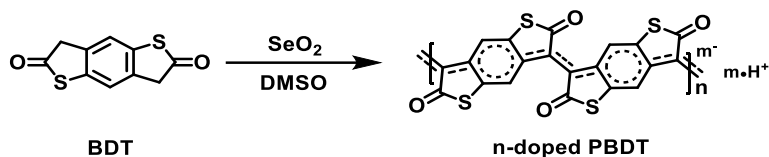
Figure S42 Synthesis of conjugated polymers PBDP, PBDF and PBDT by SeO₂ oxidation method.

Table S5 Investigation of polymerization conditions of PBDT and PBDP-C12

Polymer	SeO ₂ (equiv.)	Polymerization time (h)	Yield (%)	Conductivity (S cm ⁻¹) ^a
n-doped PBDT	1	0.5	68	1.00 ± 0.17
	0.1	24	48	0.00126 ± 0.00018
PBDP-C12	1	24	80	— ^b
	0.1	24	9	—

^aMeasured by the four-point probe method. ^bNo intrinsic conductivity.

Synthesis of Polymer n-doped PBDT



The BDT monomer (75.0 mg, 0.3374 mol, 1 equiv.) and SeO_2 (37.4 mg, 0.3374 mol, 1 equiv.) were dissolved in DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C with vigorous stirring, a viscous gel formed within 10 mins. After the polymerization for 0.5 hours, the solution was cooled to room temperature, and the mixture was diluted to 10 mL and then dialyzed against DMSO using a dialysis bag with a cut-off molecular weight of 10 kDa (Viskase, USA) to remove low molecular weight fractions. The resulting solution was centrifuged to remove the insoluble solids (10000 rpm, 15 min) and then filtered through a 1 μm nylon filter to obtain a homogeneous and purified n-doped PBDT ink. The yield of the reaction was estimated as 68% according to the volume and concentration of the solution after purification.

When SeO_2 was 0.1 eq, the same polymerization was heated to 100 °C with vigorous stirring for 24 hours. After cooled to room temperature, the mixture was dialyzed, centrifuged and filtrated to afford the purified n-doped PBDT ink. The yield of the reaction was estimated as 48% according to the volume and concentration of the solution after purification.

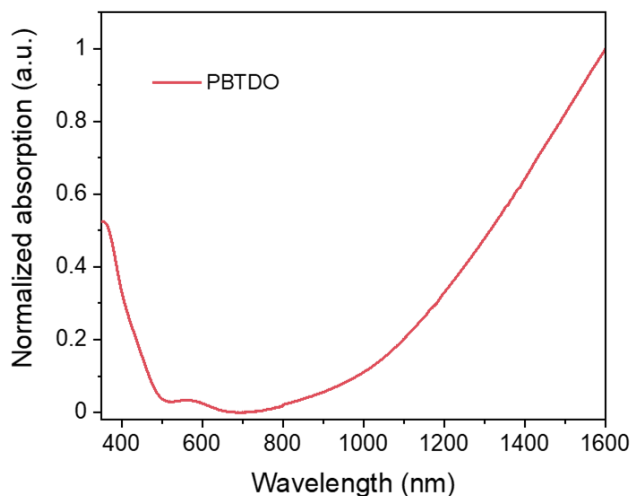
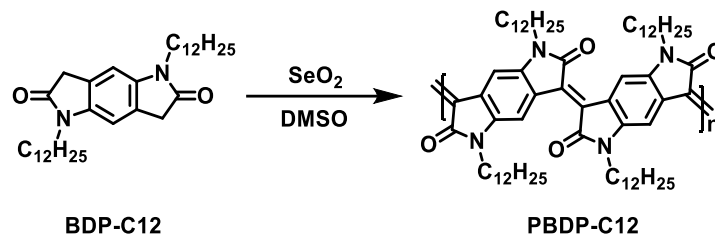


Figure S43 UV-Vis NIR spectra of n-doped PBDT in DMSO solution.

Synthesis of Polymer PBDP-C12



The BDP-C12 monomer (75.0 mg, 0.1429 mol, 1 equiv.) and SeO₂ (15.9 mg, 0.1429 mmol, 1 equiv.) were dissolved in DMSO (5 mL) under a nitrogen atmosphere. The reaction mixture was heated to 100 °C with vigorous stirring for 24 hours. After the solution was cooled to room temperature, the crude polymer was precipitated in methanol and purified by Soxhlet extraction with methanol, acetone, hexane, dichloromethane and chloroform. The dichloromethane and chloroform fraction were concentrated under reduced pressure, and the concentrated solutions were precipitated into methanol. The polymer was filtered and dried in vacuum to afford PBDP-C12 as a dark purple solid (DCM fraction 34 mg and chloroform fraction 25 mg, total yield: 80%). GPC (1,2,4-trichlorobenzene, 150 °C): DCM fraction: M_n 16.9 kDa, M_w 21.6 kDa; chloroform fraction: M_n 17.0 kDa, M_w 22.4 kDa.

When SeO₂ was 0.1 eq, the same polymerization was heated to 100 °C with vigorous stirring for 24 hours. After the same purification process, DCM fraction (4 mg) and chloroform fraction (3 mg) were obtained, total yield was 9%.

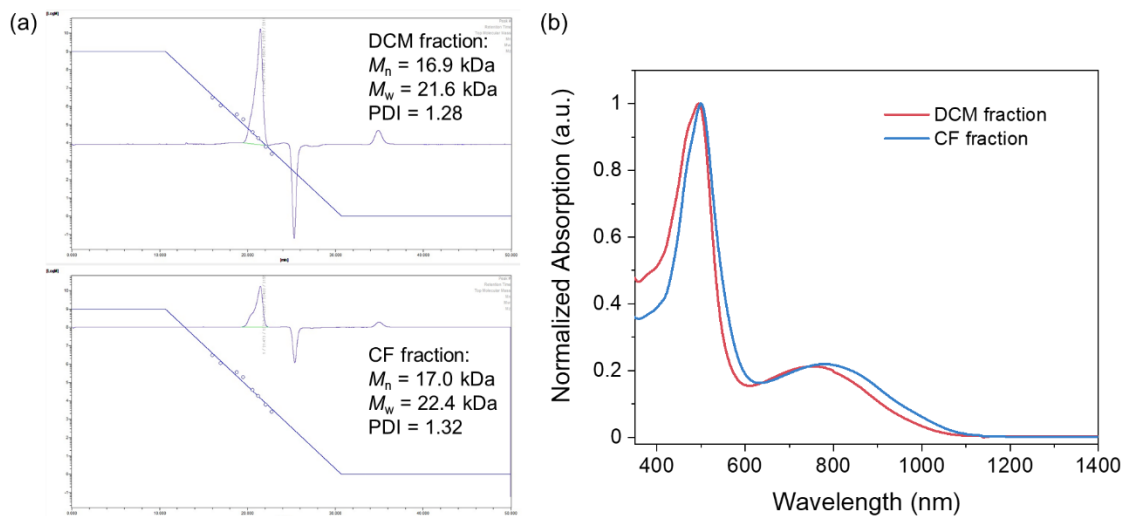


Figure S44 (a) GPC curves and (b) UV-Vis NIR spectra in chlorobenzene of PBDP-C12 polymer.

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