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Supporting Information

Rapid and High-Precision Photoinduced 3D Printing Enabled by Thioacetal Mediated Cationic Degenerate Chain Transfer Polymerization

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Contents

Experimental Section

Materials

Isobutyl vinyl ether (IBVE, 98%, Adamas), diethylene glycol divinyl ether (DDE, 98%, Yuanye), cyclohexyl vinyl ether (CHVE, 98%, Energy-chemical), 2,3-dihydrofuran (DHF, 99%, Yuanye), ethyl vinyl ether (EVE, 98%, TCI), propoxyethylene (PVE, 99%, Aladdin), *n*-butyl vinyl ether (BVE, 98%, Amethyst), *n*-butyl mercaptan (97%, Macklin), benzyl mercaptan (98%, Energy-chemical), 2-methyl-2-propanethiol (99%, Aladdin), cyclohexanethiol (98%, Adamas), 4-fluorothiophenol (98%, Adamas), *p*-toluenesulfonic acid (99%, Parameter), triphenylamine (99.89%, Bidepharm), phosphorus oxychloride ($POCl_3$, 98%, Meryer), N,N-dimethylformamide (DMF, 99%, Energy Chemical), tertbutyl potassium dioxide (99.9%, Aladdin), methyltriphenylphosphonium iodide (98%, Energy-chemical), 3-(methylthio)aniline (98%, Bidepharm), sulfuric acid (AR, Yonghua), sodium nitrite (AR, Sinopharm Chemical Reagent Co., Ltd), Potassium Iodide (99.19%, Bidepharm), sodium thiosulfate (98%, Bidepharm), triethylamine (AR, Qiangsheng), tris(2-methylphenyl)phosphine (98%, Yuanye), palladium(II)acetate (99.9%, Macklin), caesium carbonate (99.9%, Adamas), methyl trifluoromethanesulfonate (98%, Bidepharm), potassium hexafluorophosphate (99%, Leyan), calcium hydride (CaH_2, 98.5%, Macklin), dichloromethane (DCM, 99%, Qiangsheng), trichloromethane (AR, Qiangsheng), petroleum ether (PE, 99%, Qiangsheng), ethyl acetate (EA, 99%, Qiangsheng), acetonitrile (MeCN, 99%, Qiangsheng), acetone (99%, Qiangsheng), methanol (MeOH, 99%, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng). All monomers were used as received unless otherwise indicated.

The 405 nm LED light strip used in polymerization (λ_{max} = 405 nm, 12 W m^{-1}) was purchased from Shenzhen Huahe Lighting Co., Ltd China. The light intensity to the polymerization solution was 1.1 mW cm^{-2}. The DLP 3D printer (Anycubic Photon D2) with a purple LED light (λ_{max} = 405 nm, 1.0 mW cm^{-2}) was purchased from Shenzhen Anycubic Technology Co., Ltd, China.

Characterization

NMR

The nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker 300 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard.

SEC

The number-average molecular weight (M_n) and molecular weight distribution ($Đ$) of polymers were determined by TOSOH HLC-8420 Size Exclusion Chromatography (SEC) equipped with refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm) columns arranged in series, which can separate polymers in the molecular weight range of 500 - 1.9×10^5 g mol^{-1}. Tetrahydrofuran (THF) served as the eluent with a flow rate of 0.35 mL min^{-1} at 40 °C. SEC samples were injected using a TOSOH HLC-8420 SEC plus auto sampler. Data acquisition was performed using EcoSEC software and molecular weights were calculated with polystyrene (PS) standards.

ATR-FTIR

The C=C conversion of the different monomers in the study on polymerization of DDE and DHF was monitored by an online infrared analyzer Nicolet iS20. Monomer conversion was calculated based on the reduction in intensity of the C=C vibration peak at approximately 1619 cm^{-1}.

SEM

Morphology of the precision model sample was characterized via a Hitachi SU8010 scanning electron microscope (SEM) with an operation voltage of 5 kV.

Mechanical Properties Testing

The mechanical tests were carried on an electronic tensile machine (TopHung) with a 50-N load cell. Tensile tests were performed at room temperature under a crosshead speed of 2.0 mm min^{-1}. The testing samples were prepared by 3D printing (a length of 50 mm, a gage length of 16 mm, a width of 8.3 mm, a gage width of 4 mm and a thickness of 1.7 mm). Tensile strength was calculated by dividing the maximum load (N) by the average original cross-sectional area (m^2) in the gage length segment of the specimen and elongation at break was obtained by dividing the extension at the point of specimen rupture by the original gage length and multiplying by 100.

ESR

ESR measurements were carried out on a JEOL JES-X320 ESR spectrometer at room temperature. General instrument parameters are as follows: microwave power, 1 mW, macrowave frequency, 9425 MHz, modulation frequency, 100 kHz, modulation amplitude, 1 G, field scan range, 300 G, center field, 3360 G.

DMA

The mechanical properties of the 3D-printed materials were measured using a TA Instruments Q850 dynamic mechanical analyzer (DMA). A gas cooling accessory (GCA) was employed to cool the sample to -30 °C, followed by an isothermal hold for 1 min. The temperature was then ramped from -30 °C to 100 °C at a rate of 3 °C/min, while the frequency was maintained constant at 1 Hz. Dog-bone-shaped specimens were fabricated using a DLP 3D printer. The glass transition temperature (T_g) was determined as the peak temperature of the tan δ curve at 1 Hz.

Synthesis of butyl(1-isobutoxyethyl)thioether (1a)

IBVE (14.6 mL, 112 mmol) and *n*-butanethiol (24.0 mL, 224 mmol) were dissolved in dry CH_2Cl_2 (31.4 mL), followed by the addition of *p*-toluenesulfonic acid monohydrate (45 mg, 0.26 mmol). The reaction mixture was stirred at -40 °C for 1 hour. Upon completion, the reaction mixture was diluted with diethyl ether and washed successively with 5 wt% $NaHCO_3$ and water. The organic phase was dried and concentrated under reduced pressure. The crude product was purified by vacuum distillation (1.13 mmHg, bp = 46 °C) to afford **1a** as a colorless liquid (16.7 g, 87.6mmol, 78% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ : 4.66 (q, *J* = 6.4 Hz, 1H), 3.42 (dd, *J* = 9.0, 6.9 Hz, 1H), 3.18 (dd, *J* = 9.0, 6.4 Hz, 1H), 2.67-2.47 (m, 2H), 1.84 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.67-1.48 (m, 5H), 1.41 (d, *J* = 7.9 Hz, 2H), 0.97-0.86 (m, 9H).

Synthesis of *t*-butyl(1-isobutoxyethyl)thioether (1b)

Compound **1b** was synthesized following the same procedure as for **1a**. The crude product was purified by silica gel column chromatography using petroleum ether as the eluent to afford **1b** as a colorless oil (52% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ : 4.95

(q, J = 6.5 Hz, 1H), 3.28 (qd, J = 8.7, 6.6 Hz, 2H), 1.82 (dp, J = 13.4, 6.7 Hz, 1H), 1.51 (d, J = 6.5 Hz, 3H), 1.37 (s, 9H), 0.92 (dd, J = 6.7, 1.7 Hz, 6H).

Synthesis of cyclohexyl(1-isobutoxyethyl)thioether (1c)

Compound **1c** was synthesized following the same procedure as for **1a**. The crude product was purified by silica gel column chromatography (petroleum ether) to afford **1c** as a colorless oil (60% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 4.78 (q, J = 6.4 Hz, 1H), 3.38 (dd, J = 8.9, 6.8 Hz, 1H), 3.22 (dd, J = 8.9, 6.4 Hz, 1H), 2.86 (tt, J = 10.2, 3.8 Hz, 1H), 1.99 (m, 1H), 1.92 (m, 1H), 1.82 (m, J = 6.7 Hz, 1H), 1.71 (m, 2H), 1.55 (m, 1H), 1.53 (d, J = 6.4 Hz, 3H), 1.40-1.21 (m, 5H), 0.92 (dd, J = 6.7, 1.9 Hz, 6H).

Synthesis of benzyl(1-isobutoxyethyl)thioether (1d)

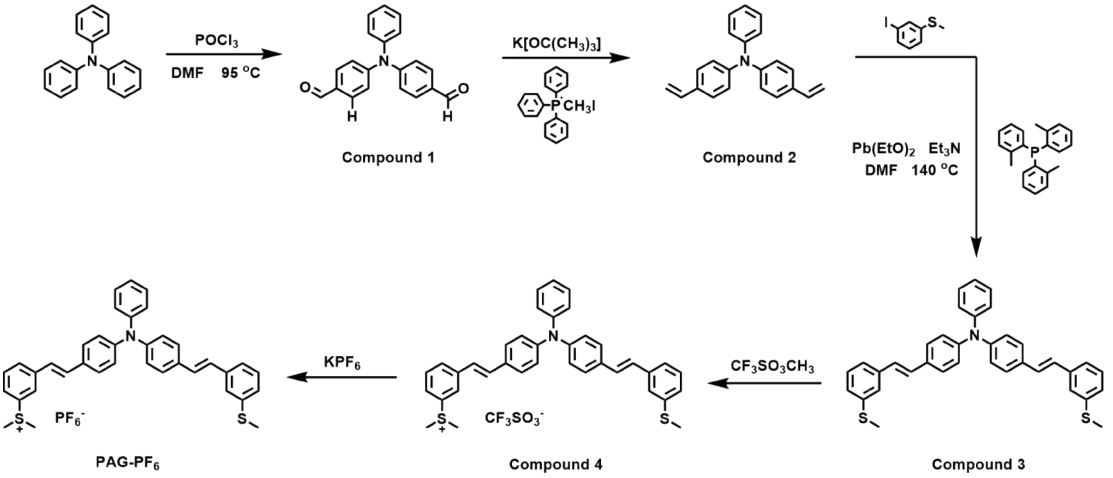
Compound **1d** was synthesized following the same procedure as for **1a**. The crude product was purified by silica gel column chromatography (petroleum ether) to afford **1d** as a colorless oil (64% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ : 7.37-7.16 (m, 5H), 4.64 (q, J = 6.4 Hz, 1H), 3.85-3.69 (m, 2H), 3.37 (dd, J = 8.9, 6.8 Hz, 1H), 3.19 (dd, J = 8.9, 6.4 Hz, 1H), 1.84 (dp, J = 13.4, 6.7 Hz, 1H), 1.51 (d, J = 6.4 Hz, 3H), 0.92 (dt, J = 6.5, 3.2 Hz, 6H).

Synthesis of 1-[(*p*-fluorophenyl)(1-isobutoxyethyl)thioether (1e)

In a two-necked flask (100 mL) under N_2 atmosphere, $Pd(OAc)_2$ (2.5 mmol), freshly distilled THF (30 mL), IBVE (50 mmol), and 4-fluorobenzenethiol (50 mmol), were added sequentially. The reaction mixture was stirred at 45 °C for 20 hours. The mixture was then filtered through Celite using ethyl acetate as the eluent. The crude product was purified by silica gel column chromatography (petroleum ether) to afford **1e** as a colorless oil (83% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ : 7.50-7.39 (m, 2H), 7.05-6.93 (m, 2H), 4.80 (q, J = 6.3 Hz, 1H), 3.63 (dd, J = 9.1, 6.8 Hz, 1H), 3.20 (dd, J = 9.1, 6.4 Hz, 1H), 1.85 (dh, J = 13.3, 6.7 Hz, 1H), 1.45 (d, J = 6.3 Hz, 3H), 0.92 (dd, J = 6.7, 5.2 Hz, 6H).

Synthesis of dimethyl(3-((E)-4-((4-((E)-3-(methylthio)styryl)phenyl)(phenyl)amino)styryl)phenyl)sulfonium hexafluorophosphate(PAG-PF_6)

The synthesis of PAG-PF_6 was according to Scheme S1.



Scheme S1. Synthesis route of PAG-PF_6.

Synthesis of compound 1: Phosphorus oxychloride (153.3 g, 1 mol) was added dropwise to a solution of triphenylamine (10.1 g, 0.1 mol) in anhydrous DMF (76 mL) under an ice-water bath. The reaction mixture was then stirred at 95 °C for 12 hours under argon. After cooling, the mixture was poured into ice water and neutralized with 20 wt% NaOH to pH ≈ 8. The product was extracted with ethyl acetate, washed with brine (×3), dried over anhydrous sodium sulfate, and concentrated. Purification by silica gel chromatography (petroleum ether/ethyl acetate = 10:1, v/v) afforded compound **1**

(yellow-green solid, 15.13 g, 50.2%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ : 9.89 (s, 2H), 7.85 (d, J = 8.7 Hz, 4H), 7.47 (t, J = 7.9 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.24-7.20 (m, 2H), 7.17 (d, J = 8.6 Hz, 4H).

Synthesis of compound 2: Potassium tert-butoxide (5.60 g, 50 mmol) and methyltriphenylphosphine bromide (20.2 g, 50 mmol) were added to anhydrous THF (200 mL) at 0 °C under an argon atmosphere with stirring. The mixture was stirred for 30 min, after which a solution of compound 1 (6.03 g, 20 mmol) in anhydrous THF (50 mL) was added dropwise. The reaction mixture was stirred for an additional 30 min and then allowed to warm to room temperature and stirred for 6 h. The reaction was quenched with ice water, and the mixture was extracted with dichloromethane. The combined organic layers were washed with brine (×3), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (petroleum ether) to afford compound **2** as a white solid (4.61 g, 77.5%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ : 7.45-7.26 (m, 6H), 7.12-6.90 (m, 7H), 6.67 (dd, J = 17.7, 11.0 Hz, 2H), 5.70 (d, J = 17.6 Hz, 2H), 5.17 (d, J = 10.9 Hz, 2H).

Synthesis of compound 3: Compound 2 (1 g, 3.367 mmol), triethylamine (1.02 g, 10.1 mmol), 3-iodothiobenzyl ether (2.1 g, 8.42 mmol), tris(*o*-methylphenyl)phosphorus (76.7 mg, 2.53 mmol), and palladium acetate (18.9 mg, 0.84 mmol) were dissolved in anhydrous DMF (10 mL) under an argon atmosphere. The reaction mixture was heated at 140 °C under reflux for 24 hours. After cooling to room temperature, the reaction was quenched by the addition of deionized water (100 mL). The mixture was extracted with dichloromethane, and the organic layers were washed with brine (×3), dried over anhydrous anhydrous sodium sulfate and concentrated. Purification by silica gel column chromatography (petroleum ether/dichloromethane = 3:1, v/v) afforded compound **3** as a yellow solid (0.85 g, 46.7%). ^{1}H NMR (DMSO-d_6, 300 MHz): δ : 7.54 (d, J = 8.7 Hz, 4H), 7.46 (s, 2H), 7.41-7.18 (m, 8H), 7.19-7.05 (m, 7H), 7.01 (d, J = 8.6 Hz, 4H), 2.50 (s, 6H).

Synthesis of compound 4: Compound 3 (1.08 g, 2 mmol) and cesium carbonate (1.30 g, 4 mmol) were dissolved in anhydrous dichloromethane (50 mL) under an argon atmosphere. The reaction mixture was cooled to -78 °C using an ice－ethanol bath and protected from light. A solution of methyl trifluoromethanesulfonate (0.656 g, 4 mmol) was added dropwise. The mixture was stirred at -78 °C for 1 h and then allowed to warm to room temperature and stirred for an additional 12 h. The reaction was quenched with water, and the organic phase was separated and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (dichloromethane/MeOH = 10:1–5:1, v/v) to afford compound **4** as a yellow solid (0.45 g, 43.2%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ : 8.10 (s, 1H), 7.75 (t, J = 8.8 Hz, 2H), 7.57 (t, J = 7.9 Hz, 1H), 7.49-7.33 (m, 5H), 7.33-7.19 (m, 5H), 7.17-6.90 (m, 11H), 3.39 (s, 6H), 2.51 (s, 3H).

Synthesis of PAG-PF$_6$: Compound 4 (0.20 g, 0.28 mmol) was dissolved in acetone (5 mL) and added dropwise into a saturated aqueous solution of potassium hexafluorophosphate (25 mL). The resulting precipitate was collected by filtration and reprecipitated three times under the same conditions. The final product was collected and dried to afford PAG-PF_6 as a yellow solid (0.158 g, 78.9%). ^1H NMR ($CDCl_3$, 300 MHz): δ : 8.00 (s, 1H), 7.81 (d, *J* = 6.2 Hz, 1H), 7.63 (d, *J* = 6.7 Hz, 2H), 7.49-7.34 (m, 5H), 7.34-7.20 (m, 5H), 7.19-6.89 (m, 11H), 3.31 (s, 6H), 2.51 (s, 3H).

General procedure for photopolymerization of IBVE

All polymerizations were conducted in a nitrogen-filled glovebox. Monomers were dried over CaH_2 for at least 12 hours, distilled under nitrogen, subjected to three freeze－pump－thaw cycles, and stored in the glovebox. In a typical experiment, IBVE (0.65 mL, 500.8 mg, 5 mmol), 1a (9.52 mg, 0.05 mmol), PAG-PF_6 (0.106 mg, 1.5×10^{-4} mmol) and DCM (0.3 mL) were added to a 4 mL Teflon vial ($[IBVE]_0$:$[1a]_0$:$[PAG\text{-}PF_6]_0$ = 100:1:0.003). The mixture was irradiated with a 405 nm LED (1.1 mW cm^{-2}) at 25 °C under stirring for the desired time. The reaction was quenched by dilution with THF and addition of trace methanol. Monomer conversion was determined gravimetrically.

Chain extension of PIBVE

PIBVE prepared with $[IBVE]_0$:$[1a]_0$:$[PAG\text{-}PF_6]_0$ = 50:1:0.003 was used as a macro-CTA. IBVE (5 mmol), PIBVE (0.05 mmol), PAG-PF_6 (5×10^{-4} mmol), and CH_2Cl_2 (0.3 mL) were mixed ($[IBVE]_0$:$[PIBVE]_0$:$[PAG\text{-}PF_6]_0$ = 100:1:0.01) and irradiated with a 405 nm LED (1.0 mW cm^{-2}) at 25 °C for 24 h. The reaction was quenched as described above.

Photopolymerization of printing resins for online infrared analysis

Printing resins for online infrared analysis were prepared by mixing different proportions of DDE, DHF, Thioacetal and PAG-PF_6. The mixture was uniformly mixed and dissolved by an oscillator for online infrared analysis under 405 nm LED light irradiation of the DLP 3D printer (1.0 mW cm^{-2}) and open to air.

3D printing procedure

A resin mixture (≈ 30 mL) containing DDE, DHF, 1a and PAG-PF$_6$ with a molar ratio of $[\text{DDE}]_0$:$[\text{DHF}]_0$:$[\text{ 1a}]_0$:$[\text{PAG-PF}_6]_0$ = 50:50:1:0.025 was poured into the sink of the DLP 3D printer. Then, the mold.stl file was imported into the printer. The printing parameters were set as follow: exposure time per layer: 10 s; target per layer thickness: 0.1 mm; 1 bottom layer and 15 s exposure time for bottom layer; 1 for anti-alias; 5 mm Z lift height; 2 mm s^{-1} Z lift speed; 2 mm s^{-1} Z retract step speed. Then the printing process was started. Printed objects were washed with ethyl acetate and post-cured under 405 nm irradiation (60 mW cm^{-2}) for 1 hour.

Dumbbell-shaped mold samples for tensile testing

Printing resin (≈ 30 mL) containing DDE, IBVE/DHF/CHVE, Thioacetal and PAG-PF$_6$ at various molar ratios was prepared and poured into the sink of the DLP 3D printer. A dumbbell-shaped mold (.stl file) was imported into the printer. The printing parameters were set as follow, the exposure time per layer was adjusted according to the minimum curing time required to obtain well-defined objects; target per layer thickness: 0.1 mm; one bottom layer and exposure time (same exposure time for per layer) for bottom layer; 1 for anti-alias; 5 mm Z lift height; 2 mm s^{-1} Z lift speed; 2 mm s^{-1} Z retract step speed. After printing, the specimens were removed, washed with ethyl acetate, and post-cured under 405 nm LED irradiation (60 mW cm^{-2}) for 1 hour.

Additional data

Table S1. Mechanical properties of printed samples using printing resin consisting of different post-curing time under a fixed molar ratio of $[DDE]_0:[DHF]_0:[1a]_0:[PAG\text{-}PF_6]_0 = 50:50:1:0.025$.

Entry	Post-curing time	Strain at break ε_b (%)	Stress at break σ_b (MPa)	Young's modulus (MPa)
1	10 min	21.21 ± 0.41	16.61 ± 1.42	237.82 ± 6.61
2	30 min	19.10 ± 1.40	19.06 ± 3.10	294.41 ± 17.90
3	60 min	17.26 ± 0.67	21.98 ± 0.90	332.02 ± 14.07
4	120 min	17.94 ± 1.23	23.05 ± 0.45	338.59 ± 5.37

Table S2. Storage modulus of printed samples using printing resin consisting of DDE, DHF, **1a** and $PAG\text{-}PF_6$ with different molar ratios.

Entry	$[DDE]_0:[DHF]_0:[1a]_0:[PAG\text{-}PF_6]_0$	Strain at break ε_b (%)	Stress at break σ_b (MPa)	Young's modulus (MPa)
1	50:50:0:0.025	15.57±1.39	22.52±0.63	331.75±6.15
2	50:50:1:0.025	17.26 ± 0.67	21.98 ± 0.90	332.02 ± 14.07
3	50:50:5:0.025	21.35 ± 1.31	13.70 ± 0.25	188.22 ± 4.33
4	50:50:10:0.025	22.39 ± 0.32	6.76 ± 0.29	46.95 ± 1.46
5	30:70:1:0.025	38.10 ± 0.81	20.98 ± 0.73	356.32 ± 15.86
6	30:70:5:0.025	40.61 ± 0.29	16.23 ± 0.67	240.03 ± 7.87
7	30:70:10:0.025	40.27 ± 1.31	5.13 ± 0.04	16.83 ± 0.83
8	70:30:1:0.025	13.45 ± 1.31	17.82 ± 0.72	262.22 ± 12.11
9	70:30:10:0.025	15.18 ±1.31	6.73 ± 0.49	62.07 ± 3.07
10	100:0:1:0.025	5.94 ± 0.12	14.93 ± 1.16	326.44 ± 7.93
11	100:0:5:0.025	8.28 ± 0.42	13.83 ± 0.16	228.40 ± 8.28
12	100:0:10:0.025	9.63 ± 0.14	4.30 ± 0.08	51.14 ± 0.97

Table S3. Mechanical properties of printed samples in Figure 6C using printing resin consisting of different thioacetal initiators under a fixed molar ratio of $[\mathrm{DDE}]_0$:$[\mathrm{DHF}]_0$:$[\mathrm{Thioacetal}]_0$:$[\mathrm{PAG\text{-}PF_6}]_0$ = 50:50:5:0.025.

Entry	Thioacetal	Strain at break ε_b (%)	Stress at break σ_b (MPa)	Young's modulus (MPa)
1	1a	21.35 ± 1.31	13.70 ± 0.25	188.22 ± 4.33
2	1b	16.04 ± 0.54	14.89 ± 1.20	257.58 ± 12.68
3	1c	23.29 ± 1.52	16.48 ± 0.23	245.61 ± 11.38
4	1d	22.69 ± 0.62	16.31 ± 0.42	240.47 ± 13.08
5	1e	16.11 ± 0.63	17.62 ± 0.97	285.31 ± 22.46

Table S4. Mechanical properties of printed samples in Figure 6D using printing resin consisting of different monomers under a fixed molar ratio of $[\mathrm{DDE}]_0$:$[\mathrm{Monomer}]_0$:$[\mathrm{1a}]_0$:$[\mathrm{PAG\text{-}PF_6}]_0$ = 50:50:5:0.025.

Entry	Monomer	Strain at break ε_b (%)	Stress at break σ_b (MPa)	Young's modulus (MPa)
1	DHF	21.35 ± 1.31	13.70 ± 0.25	188.22 ± 4.33
2	CHVE	28.00 ± 0.39	3.32 ± 0.11	12.22 ± 0.16
3	IBVE	7.84 ± 0.81	1.37 ± 0.19	17.29 ± 0.40

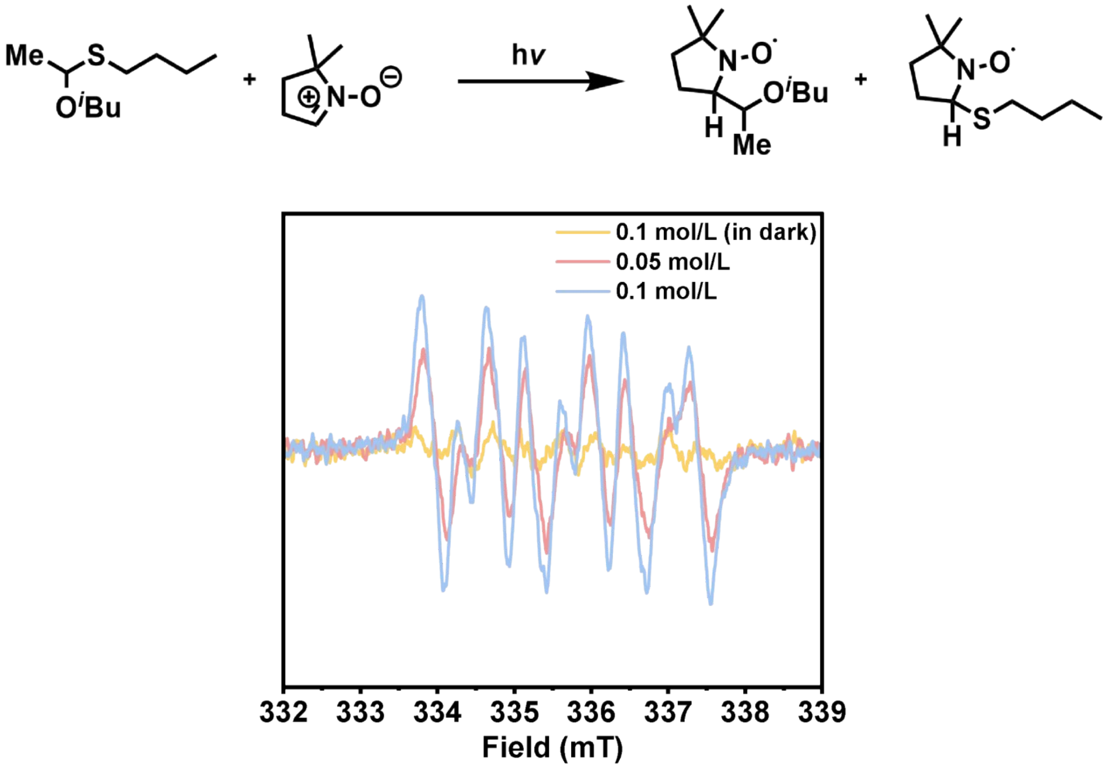


Figure S1. ESR spectra of DMPO and 1a at different concentrations in diethylene glycol dimethyl ether. $[1a]_0$:$[DMPO]_0$ = 1:3.

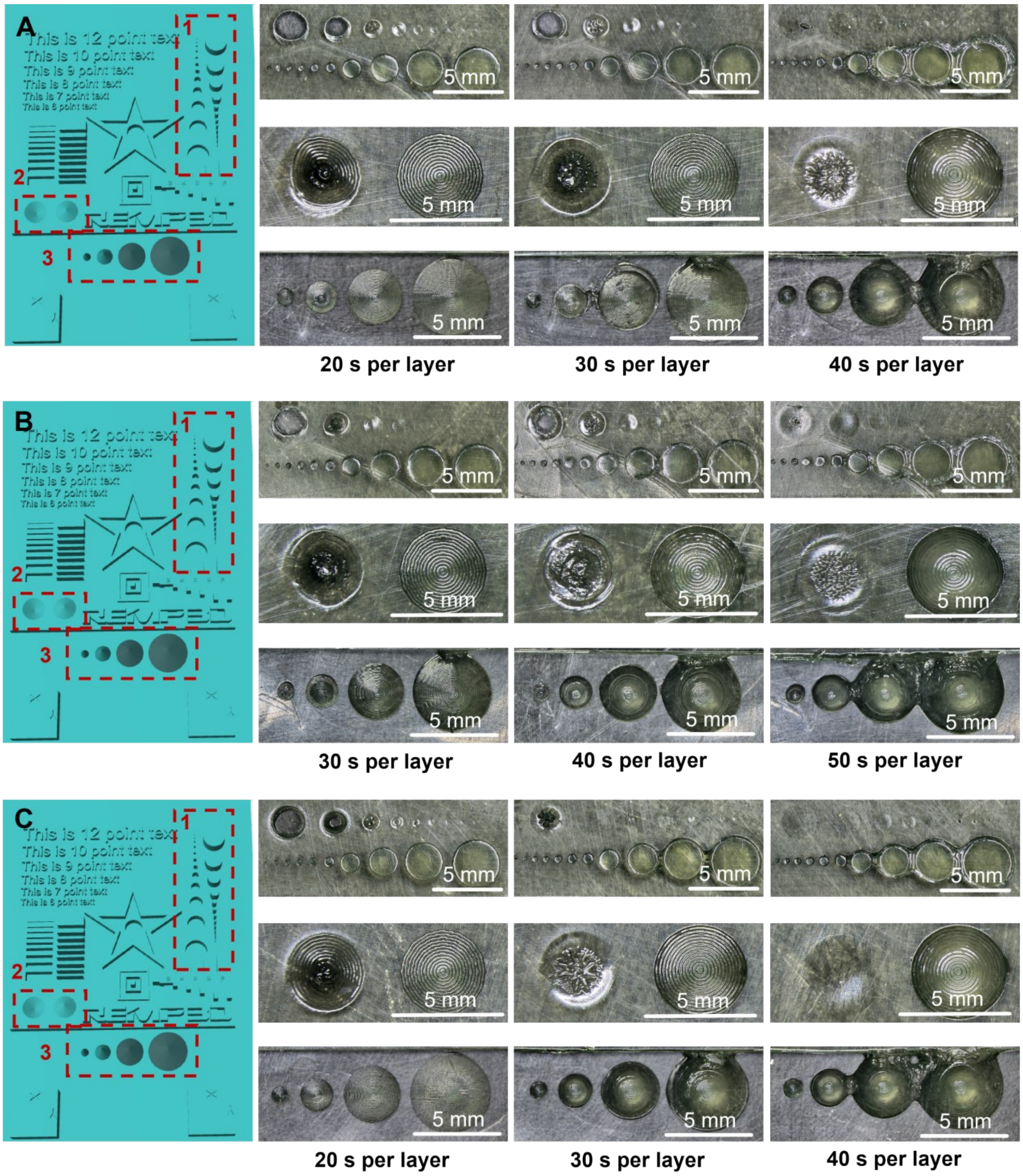


Figure S2. Comparison chart of precision models with different curing times and molar ratios of $[DDE]_0$:$[DHF]_0$:$[1a]_0$:$[PAG\text{-}PF_6]_0$: (A) 50:50:5:0.025; (B) 50:50:10:0.025; (C) 70:30:5:0.025.

(A) Immediately after printing

(B) Storage in the dark for 3 h

(C) Post-curing for 30 minutes

Figure S3. Dimensions of the printed specimens (20 × 10 × 2 mm) under different curing conditions: (A) immediately after printing, (B) after storage in the dark for 3 h, and (C) after 30 min of UV post-curing.

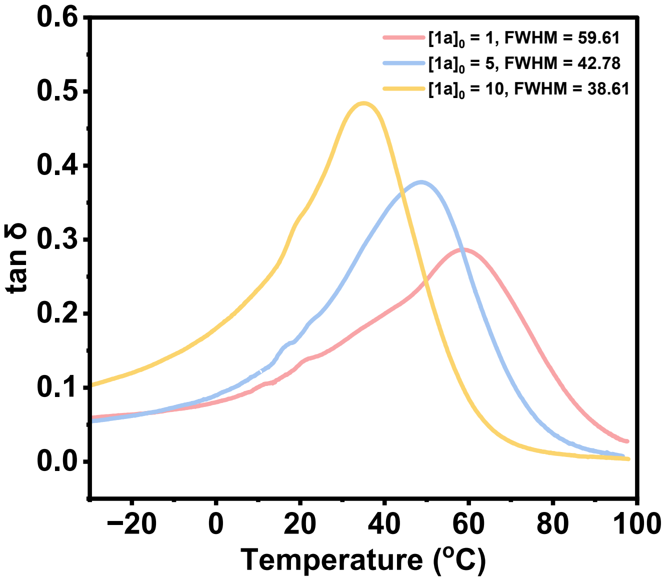


Figure S4. Tanδ versus temperature curves of dumbbell-shaped specimens printed using $[DDE]_0:[DHF]_0:[1a]_0:[PAG\text{-}PF_6]_0 = 50:50:x:0.025$.

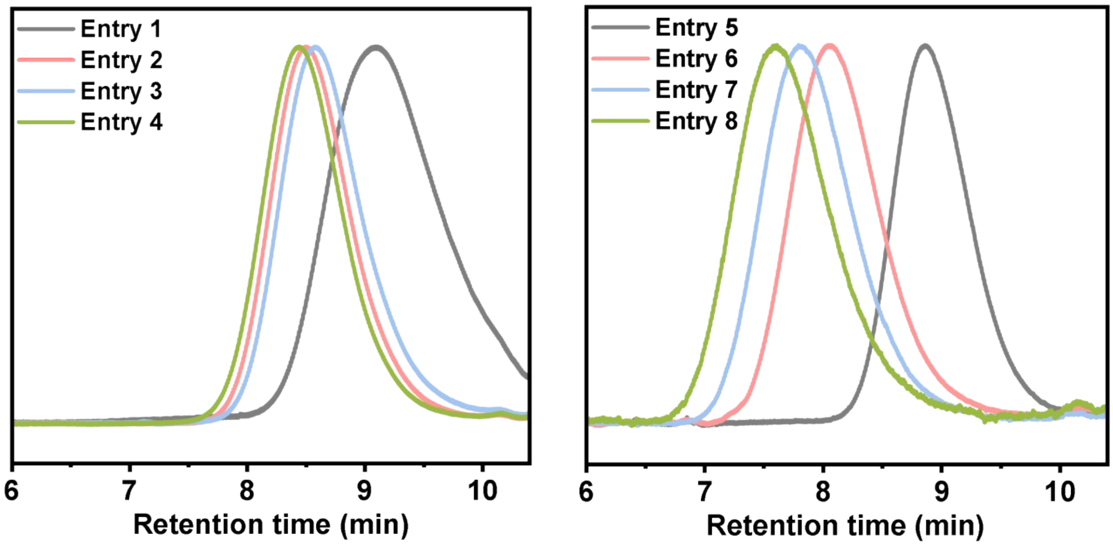


Figure S5. SEC traces of PIBVEs obtained in **Table 1**.

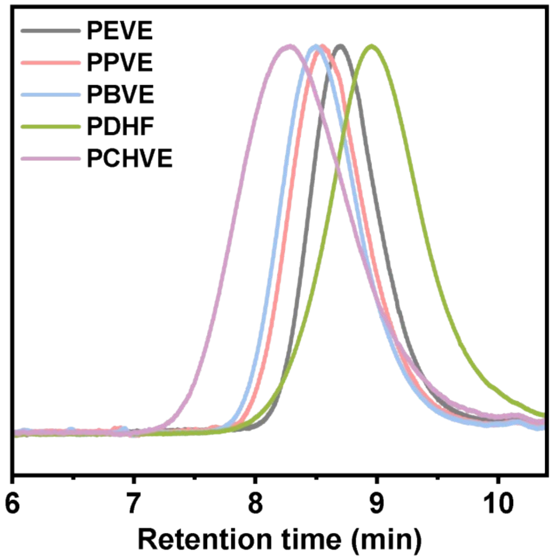


Figure S6. SEC traces of polymers obtained in **Table 2**.

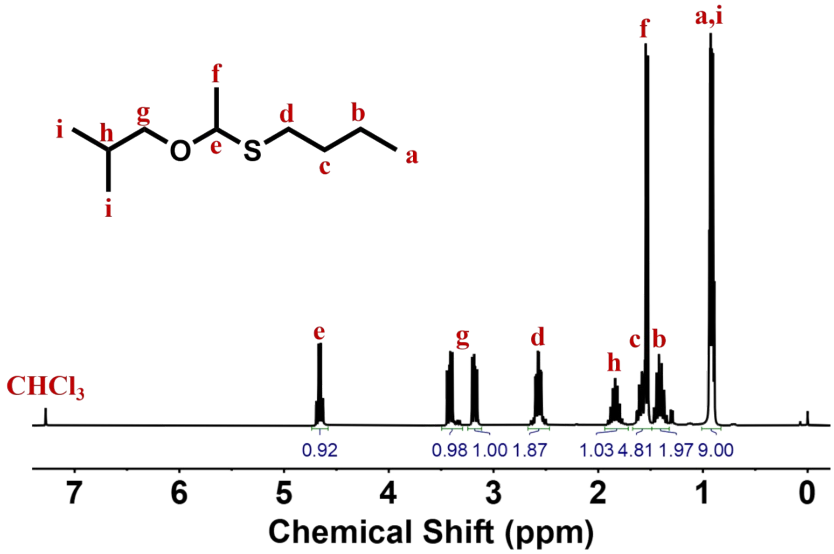


Figure S7. ^{1}H NMR spectrum (in $CDCl_3$) of **1a**.

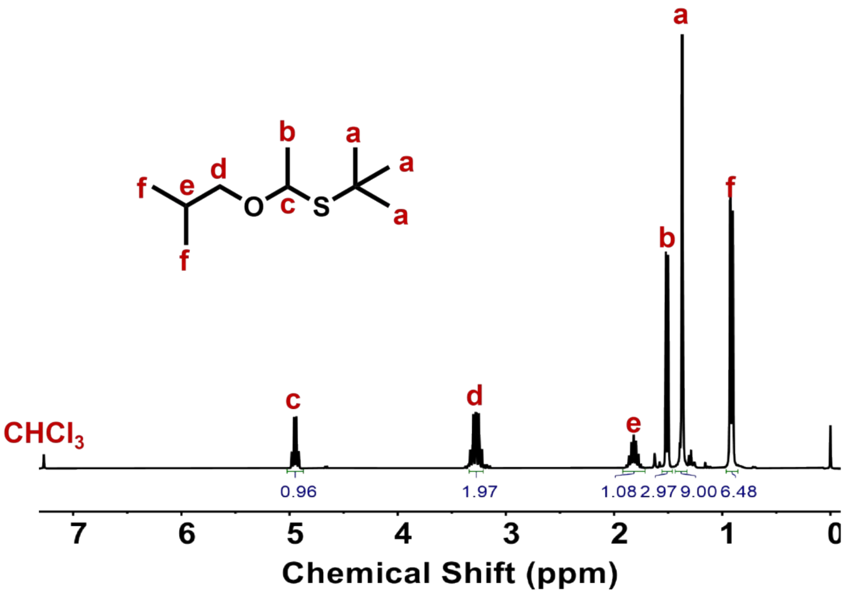


Figure S8. ^{1}H NMR spectrum (in $CDCl_3$) of **1b**.

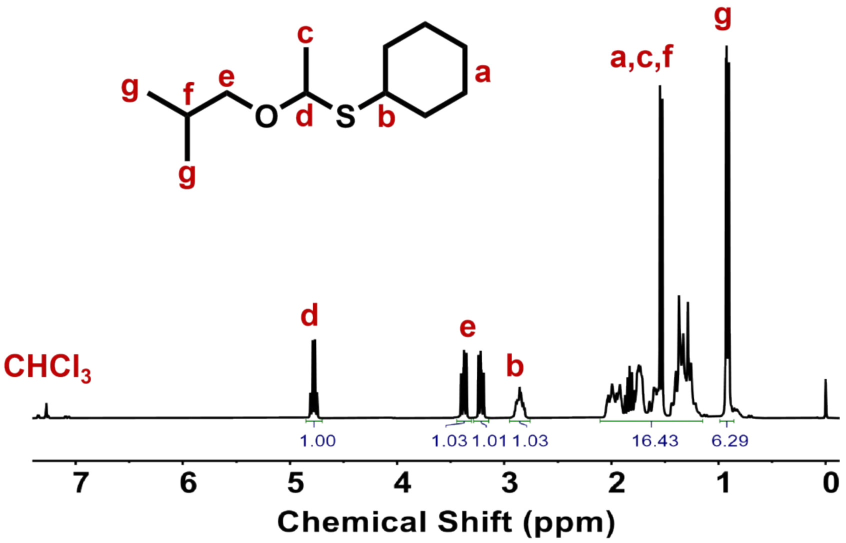


Figure S9. ^{1}H NMR spectrum (in $CDCl_3$) of **1c**.

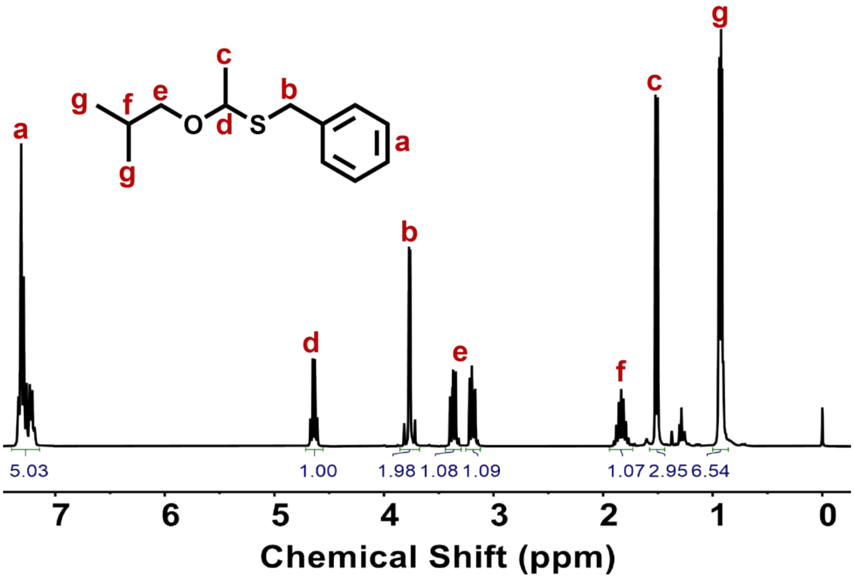


Figure S10. ^{1}H NMR spectrum (in $CDCl_3$) of **1d**.

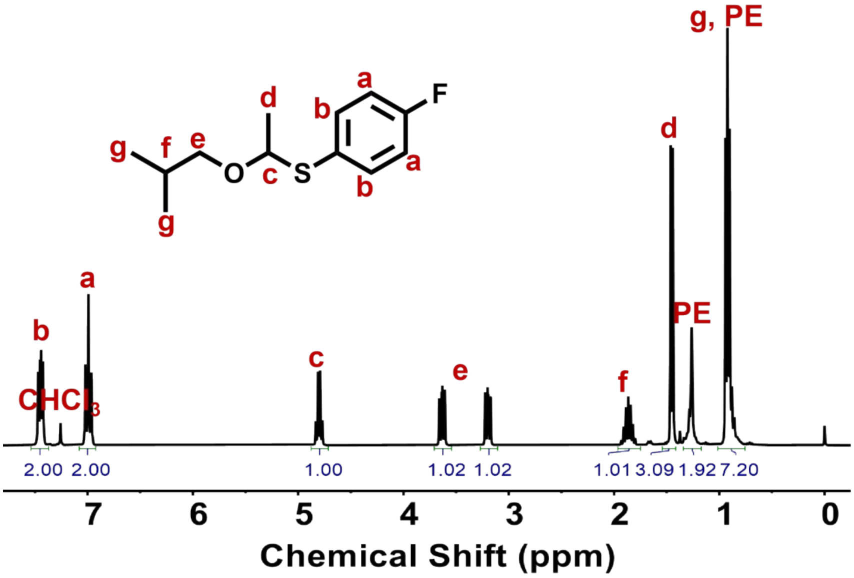


Figure S11. ^{1}H NMR spectrum (in $CDCl_3$) of **1e**.

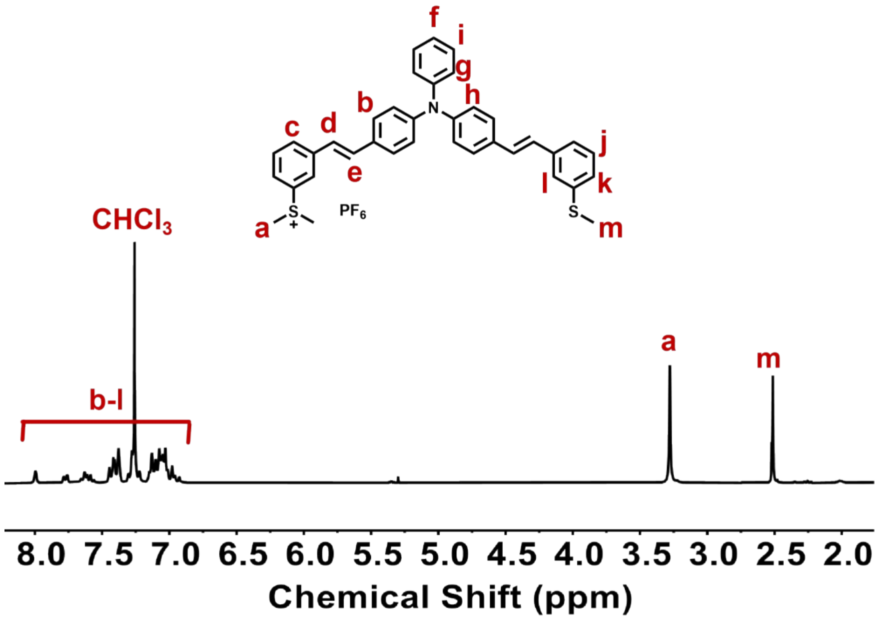


Figure S12. ^{1}H NMR spectrum (in $CDCl_3$) of PAG-PF_6.