Supplementary Information (SI) for Chemical Science.

Supporting Information For

Ultrafast and High-Precision 3D Printing via Type-I-Initiated Xanthate-Mediated RAFT Polymerization

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Experimental Section

Materials

Butyl acrylate (BA, 99%, Aladdin, passed through a neutral alumina column prior to use), poly(ethylene glycol) diacrylate ($PEGDA_{200}$, Shanghai yuanye Bio-Technology Co., Ltd), diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (TPO, 98%, TCI), curcumin (98%, Adamas), sodium hydroxide (NaOH, 98%, Qiangsheng), carbon disulfide (CS_2, 99.9%, Alfa Aesar), ethanol (99%, Qiangsheng), ethyl-2-bromopropionate (EBP, 98%, Alfa Aesar), ethyl 2-mercaptopropanoate (97%, Macklin), O-phenyl carbonochloridothioate (98%, Macklin), ethanethiol (98%, Macklin), ethyl acetate (EA, 99%, Qiangsheng), sodium sulfate (Na_2SO_4, 99%, Qiangsheng), neutral aluminium oxide (Al_2O_3, Qiangsheng), tetrahydrofuran (THF, 99%, Qiangsheng). All monomers were used as received unless otherwise indicated.

Instrumentation

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 for characterization of EXEP, PXEP and ETSPE; Nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker 600 MHz nuclear magnetic resonance instrument using $CDCl_3$ as the solvent and tetramethylsilane as an internal standard for characterization of PBA mediated by EXEP, PBA mediated by PXEP and PBA mediated by ETSPE.

The number-average molecular weight (M_n) and molecular weight distribution ($Đ$) of polymers were determined by TOSOH HLC-8420GPC EcoSEC Elite equipped with refractive index and UV detectors using two TSKgel SuperHM-M (6.0mm I.D. × 15 cm) columns arranged in series, and it can separate polymers in the molecular weight range 500–4 × 10^6 g mol^{-1}. One TSKgel guardcolumn SuperH-H (4.6mm I.D. × 3.5 cm) was used as guardcolumn. Tetrahydrofuran (THF) was served as the eluent with a flow rate of 0.6 mL min^{-1} at 40 °C. Data acquisition was performed using EcoSEC Elite-WS software and molecular weights were calculated with polystyrene (PS) standards.

Vinyl bond conversion was calculated based on the absorbance of the peak at 1405 cm^{-1} assigned to the in plane bending vibration of the =C-H group. The reaction was conducted using 405 nm LED purple light (6 mW cm^{-2}) and was monitored by an online infrared analyzer Thermo Scientific Nicolet iS20 FTIR spectrometer equipped with room temperature detectors. Analysis was performed using OMNIC software.

The mechanical properties tests were carried on using a TH-8201S machine with a 5 kN load cell. Tensile tests were performed at room temperature under a crosshead speed of 2.0 mm min^{-1}. Dumbbell-shaped tensile specimens followed the GB/T 1040 standard with an overall length of 77.5 mm, a gauge length of 25 mm, an overall width of 10 mm, a width at the center of 5 mm, and a thickness of 2 mm and were fabricated using a M-One Pro 3D printer. To match the limited printing area, all dimensions of the specimens were uniformly scaled down to 75% of the original size while maintaining the same geometric shape. Stress–strain curves were calculated based on the measured cross-sectional area. 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.

A TA instruments Q850 dynamic mechanical analyzer (DMA) was used to obtain mechanical property measurements on the 3D printed materials, The gas cooling accessories (GCA) was used to adjust the temperature to -30 °C and subsequently hold isothermal conditions for 1 minutes. The temperature was then ramped to 100 °C at a rate of 4 °C/min while the frequency was held constant at 1 Hz, using a displacement of 30 μm.

The 405 nm LED light source used in polymerization (λ_{max} = 405 nm, 60 mW cm^{-2}) was purchased from Zhong Shan Tian Dou Electric Factory. The LCD 3D printer (M-One Pro) with a purple LED light (λ_{max} = 405 nm, 6 mW cm^{-2}) and the photocuring oven (λ_{max} = 405 nm, rated power = 60 W) (Cure 3D) were purchased from Ningbo Makex Digital Technology Co., Ltd.

Synthesis of ethyl 2-((ethoxycarbonothioyl) thio) propanoate (EXEP). NaOH (2.00 g, 50 mmol) was dissolved in 85 mL ethanol by stirring in a 250 mL flask. Then carbon disulfide (4.57 g, 60 mmol) was added dropwise. The solution was stirred at room temperature for another 30 minutes, then ethyl-2-bromopropionate (8.10 g, 45 mmol) was added and the solution was stirred for 3 hours. The resulting yellow solution was evaporated to remove the solvent and then washed with brine (saturated, 100 mL) and extracted with ethyl acetate (2 × 80 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated to dryness to yield the pure product as a yellow oil (9.1 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (q, 2 H), 4.38 (q, 1 H), 4.21 (q, 2 H), 1.57 (d, 3 H), 1.42 (t, 3 H), 1.29 (t, 3 H).

Synthesis of ethyl 2-((phenoxycarbonothioyl) thio) propanoate (PXEP). Sodium hydroxide (0.4 g, 10 mmol) was dissolved by water in a round-bottom flask and then ethyl 2-mercaptopropanoate (0.83 g, 6.2 mmol) was added and stirred for 30 min. After that, O-phenyl carbonochloridothioate (0.86 g, 5 mmol) was added to the mixture dropwise and stirred for 3 h. The mixture was washed with brine (saturated, 50 mL) and extracted by 100 mL ethyl acetate. The organic phase was dried by anhydrous sodium sulfate. Crude product was obtained after evaporating the organic solvent under reduced pressure. The product was finally purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate 20/1 v/v) and shown as yellow liquid (499 mg, 37%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.36 (m, 2 H), 7.35 – 7.23 (m, 1 H), 7.14 – 7.03 (m, 2 H), 4.48 (q, 1 H), 4.24 (qd, 2 H), 1.66 (d, 3 H), 1.29 (t, 3 H).

Synthesis of 2-ethylthiocarbonylsulfanyl-propionic acid ethyl ester (ETSPE). Ethanethiol (13.76 g, 222 mmol) was dissolved in 50 mL tetrahydrofuran by stirring in a 500 mL flask. Then aqueous sodium hydroxide solution (17%, 8.88 g NaOH in 43.36 g H_2O) was added and stirred for 30 min. After that, carbon disulfide (18.58 g, 244 mmol) was added dropwise and the solution was stirred for 1 h. Subsequently, ethyl-2-bromopropionate (41.09 g, 227 mmol) was added dropwise and the solution was stirred for 24h. The mixture was washed with brine (saturated, 100 mL) and extracted by ethyl acetate (2 × 100 mL). The organic phase was dried by anhydrous sodium sulfate. Crude product was obtained after evaporating the organic solvent under reduced pressure. The product was finally purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate 50/1 v/v) and shown as yellow liquid (5.7 g, 11%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.81 (q, 1 H), 4.20 (q, 2 H), 3.37 (q, 2 H), 1.60 (d, 3 H), 1.36 (t, 3 H), 1.28 (t, 3 H).

RAFT polymerization of BA. Butyl acrylate (BA) and RAFT agents were mixed in the desired ratio. Then around 300 mg of the resulting solution was transferred into a 2 mL ampoule bottle. The mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen. Polymerization was carried out under 405 nm purple LED irradiation (60 mW cm^{-2}) for the desired reaction time. The reaction was then quenched by exposing the ampoule bottle to oxygen. THF was added to dissolve the product. The polymer was obtained after evaporate the solvent and monomer under reduced pressure at 25 °C. Monomer conversion was determined by gravimetrical method, while the molecular weight and molecular weight distribution were analyzed by GPC.

Chain extension of PBA. The product obtained from RAFT polymerization of BA was used as a macro-CTA. A mixture was placed in a 2mL ampoule bottle with a molar ratio of $[BA]_0$:$[macro\text{-}CTA]_0$ = 70:1. The mixture was degassed by three freeze-pump-thaw cycles and purged with nitrogen. Polymerization was carried out under 405 nm purple LED irradiation (60 mW cm^{-2}) for the desired reaction time. The reaction was then quenched by exposing the ampoule bottle to oxygen. THF was added to dissolve the product. The polymer was obtained after evaporate the solvent and monomer under reduced pressure at 25 °C. Monomer conversion was determined by gravity, while the molecular weight and molecular weight distribution were analyzed by SEC.

Calculation formula of 3D printing speed. Dumbbell-shaped samples (a length of 31 mm, a gage length of 10 mm, a width of 4 mm, a gage width of 2 mm and a thickness of 2 mm) were printed with different target layer thickness 0.05 mm, 0.1 mm, 0.2 mm, exposure time per layer and varied molecular ratio of PEGDA, RAFT agents and TPO. Target sample thickness was 2.0mm. Measure actual sample thickness and input this value into the following formula:

$$v\,(cm\ h^{-1}) = 360 \times \frac{Target\ layer\ thickness\ (mm)}{Exposure\ time\ per\ layer\ (s)} \times \frac{Actual\ sample\ thickness\ (mm)}{Target\ sample\ thickness\ (mm)}$$

Online infrared analysis. Solutions for online infrared analysis were prepared by mixing different proportions of PEGDA, RAFT agents and TPO. The mixture was uniformly mixed and dissolved by oscillator for online infrared analysis under 405 nm LED light irradiation (6 mW cm^{-2}) and open to air.

Setting of 3D printing. A 3D object was designed and exported as an .stl file. The .stl file was opened using XMicro software. The Z lift distance was set to 10 mm and both lift speed and retract speed was set to very fast. The print area was set to 6.4 × 3.6 cm. The light intensity was set to high. The Shrinkage rate was set to 99.7%. Target layer thickness was set in XMicro software and exposure time per layer was set on the control panel of the 3D printer.

3D printing of dumbbell-shaped samples for mechanical tensile testing:

For the formula of PEGDA$_{200}$, EXEP and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$ = 100:0.5:0.15, 100:1:0.15 and 100:1:0.3, parameters were set as below: 0.1 mm thickness of per layer, 1 second exposure time per layer, 0.1 seconds light off time, 1 second bottom exposure time.

For the formula of PEGDA$_{200}$, EXEP and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$ = 100:5:0.15, parameters were set as below: 0.1 mm thickness of per layer, 2 seconds exposure time per layer, 0.1 seconds light off time, 2 seconds bottom exposure time.

For the formula of PEGDA$_{200}$, EXEP and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$ = 100:10:0.15, parameters were set as below: 0.1 mm thickness of per layer, 3 seconds exposure time per layer, 0.1 seconds light off time, 3 seconds bottom exposure time.

For the formula of PEGDA$_{200}$, EXEP and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$ = 100:20:0.15, parameters were set as below: 0.1 mm thickness of per layer, 6 seconds exposure time per layer, 0.1 seconds light off time, 6 seconds bottom exposure time.

For the formula of PEGDA$_{200}$, PXEP and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[PXEP]$_0$:[TPO]$_0$ =100:1:0.3, parameters were set as below: 0.1 mm thickness of per layer, 2 seconds exposure time per layer, 0.1 seconds light off time, 2 seconds bottom exposure time.

For the formula of PEGDA$_{200}$, ETSPE and TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[ETSPE]$_0$:[TPO]$_0$ =100:1:0.3, parameters were set as below: 0.2 mm thickness of per layer, 5 seconds exposure time per layer, 0.1 seconds light off time, 5 seconds bottom exposure time.

3D printing of the precision model:

For the formula of PEGDA$_{200}$, EXEP, TPO and curcumin with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$:[curcumin]$_0$ = 100:1:0.3:0.0028, the parameter was set as below: 0.1 mm thickness of per layer, 2 seconds exposure time per layer, 0.1 seconds light off time, 2 seconds bottom exposure time.

For the formula of PEGDA$_{200}$, EXEP, TPO with a molar ratio of [PEGDA$_{200}$]$_0$:[EXEP]$_0$:[TPO]$_0$ = 100:1:0.3, the parameter was set as below: 0.1 mm thickness of per layer, 1 seconds exposure time per layer, 0.1 seconds light off time, 1 seconds bottom exposure time.

3D printing of the hollow grid model:

For the formula of $PEGDA_{200}$, EXEP and TPO and curcumin with a molar ratio of $[PEGDA_{200}]_0$:$[EXEP]_0$:$[TPO]_0$:$[curcumin]_0$ = 100:1:0.3:0.0028, the parameter was set as below respectively: 0.05 mm thickness of per layer, 1 seconds exposure time per layer, 0.1 seconds light off time, 1 seconds bottom exposure time; 0.1 mm thickness of per layer, 2 seconds exposure time per layer, 0.1 seconds light off time, 2 seconds bottom exposure time; 0.2 mm thickness of per layer, 2 seconds exposure time per layer, 0.1 seconds light off time, 2 seconds bottom exposure time.

After the printing process, the build stage was removed carefully and the printed objects were washed by EA and dried for further use. All printing process above was performed at room temperature and open to air. Finally, all the printed objects were followed by curing in the photocuring oven for 10 minutes.

Additional Results

Table S1. Build speed of 3D printing resin formulations with $[PEGDA_{200}]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:1:x.

Entry	**TPO**	**Target Layer Thickness (mm)**	**Exposure Time Per Layer (s)**	**Actual Thickness (mm)**	**Printing Speed (cm h^{-1})**
1	0.1	0.05	3	1.85±0.03	5.55
2	0.1	0.05	2	1.82±0.03	8.19
3	0.1	0.05	1	—	—
4	0.1	0.1	3	1.80±0.03	10.80
5	0.1	0.1	2	1.79±0.03	16.11
6	0.1	0.1	1	—	—
7	0.1	0.2	3	1.66±0.02	19.92
8	0.1	0.2	2	—	—
9	0.15	0.05	1	1.79±0.04	16.11
10	0.15	0.1	2	1.77±0.02	15.93
11	0.15	0.1	1	1.68±0.02	30.24
12	0.15	0.2	2	1.69±0.03	30.42
13	0.15	0.2	1	—	—
14	0.3	0.05	1	1.85±0.02	16.65
15	0.3	0.1	1	1.80±0.02	32.40
16	0.3	0.2	2	1.69±0.02	30.42
17	0.3	0.2	1	—	—

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

Table S2. Build speed of 3D printing resin formulations with $[PEGDA_{200}]_0:[ETSPE]_0:[TPO]_0$ = 100:a:b.

Entry	ETSPE	TPO	Target Layer Thickness (mm)	Exposure Time Per Layer (s)	Actual Thickness (mm)	Printing Speed (cm h^{-1})
1	1	0.15	0.05	4	2.06±0.04	4.64
2	1	0.15	0.05	3	—	—
3	1	0.15	0.1	6	2.05±0.02	6.15
4	1	0.15	0.1	5	—	—
5	1	0.15	0.2	7	1.95±0.04	10.03
6	1	0.15	0.2	6	—	—
7	1	0.3	0.05	3	2.04±0.03	6.12
8	1	0.3	0.05	2	—	—
9	1	0.3	0.1	5	2.04±0.01	7.34
10	1	0.3	0.1	4	1.98±0.01	8.91
11	1	0.3	0.1	3	—	—
12	1	0.3	0.2	6	1.96±0.02	11.76
13	1	0.3	0.2	5	1.94±0.02	13.97
14	1	0.3	0.2	4	—	—
15	1	0.5	0.05	3	2.07±0.04	6.21
16	1	0.5	0.05	2	—	—
17	1	0.5	0.1	4	2.03±0.04	9.14
18	1	0.5	0.1	3	—	—
19	1	0.5	0.2	4	1.93±0.01	17.37
20	1	0.5	0.2	3	—	—
21	5	0.15	0.1	120	—	—
22	10	0.15	0.1	120	—	—
23	20	0.15	0.1	120	—	—

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

Table S3. Build speed of 3D printing resin formulations with $[PEGDA_{200}]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:x:0.15.

Entry	EXEP	Target Layer Thickness (mm)	Exposure Time Per Layer (s)	Actual Thickness (mm)	Printing Speed (cm h^{-1})
1	5	0.05	2	1.89 ± 0.02	8.51
2	5	0.05	1	—	—
3	5	0.1	2	1.79 ± 0.02	16.11
4	5	0.1	1	—	—
5	5	0.2	3	1.65 ± 0.03	19.80
6	5	0.2	2	—	—
7	10	0.05	3	1.83 ± 0.01	5.49
8	10	0.05	2	—	—
9	10	0.1	3	1.76 ± 0.01	10.56
10	10	0.1	2	—	—
11	10	0.2	5	1.67 ± 0.01	12.02
12	10	0.2	4	1.63 ± 0.03	14.67
13	10	0.2	3	—	—
14	20	0.05	5	1.81 ± 0.03	3.26
15	20	0.05	4	—	—
16	20	0.1	6	1.76 ± 0.04	5.28
17	20	0.1	5	—	—
18	20	0.2	8	1.63 ± 0.05	7.34
19	20	0.2	6	——	——

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

Table S4. Build speed of 3D printing resin formulations with $[\text{PEGDA}_{200}]_0$:$[\text{EXEP}]_0$ = 100:x.

Entry	EXEP	Target Layer Thickness (mm)	Exposure Time Per Layer (s)	Actual Thickness (mm)	Printing Speed (cm h^{-1})
1	1	0.05	40	1.91±0.03	0.430
2	1	0.05	30	—	—
3	1	0.1	50	1.80±0.06	0.648
4	1	0.1	40	—	—
5	1	0.2	70	1.75±0.01	0.900
6	1	0.2	50	1.74±0.04	1.25
7	1	0.2	40	—	—
8	5	0.05	20	1.88±0.04	0.846
9	5	0.05	15	—	—
10	5	0.1	30	1.81±0.04	1.09
11	5	0.1	20	1.78±0.03	1.60
12	5	0.1	15	—	—
13	5	0.2	40	1.73±0.03	1.56
14	5	0.2	30	1.73±0.04	2.08
15	5	0.2	20	—	—
16	10	0.05	15	1.85±0.05	1.11
17	10	0.05	10	—	—
18	10	0.1	20	1.81±0.03	1.63
19	10	0.1	15	—	—
20	10	0.2	20	1.65±0.05	2.97
21	10	0.2	15	—	—
22	20	0.05	15	1.88±0.04	1.13
23	20	0.05	10	—	—
24	20	0.1	20	1.81±0.04	1.63
25	20	0.1	15	—	—
26	20	0.2	20	1.67±0.02	3.01
27	20	0.2	15	—	—

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

Table S5. Build speed of 3D printing resin formulations with $[PEGDA_{200}]_0$:$[TPO]_0$ = 100:x.

Entry	TPO	Target Layer Thickness (mm)	Exposure Time Per Layer (s)	Actual Thickness (mm)	Printing Speed (cm h^{-1})
1	0.1	0.05	2	2.12±0.02	9.54
2	0.1	0.05	1	—	—
3	0.1	0.1	2	2.08±0.03	18.72
4	0.1	0.1	1	—	—
5	0.1	0.2	3	1.99±0.03	23.88
6	0.1	0.2	2	—	—
7	0.15	0.05	1	2.10±0.03	18.90
8	0.15	0.1	1	2.02±0.02	36.36
9	0.15	0.2	2	1.97±0.03	35.46
10	0.15	0.2	1	—	—
11	0.3	0.05	1	2.08±0.02	18.72
12	0.3	0.1	1	2.00±0.04	36.00
13	0.3	0.2	2	1.93±0.02	34.74
14	0.3	0.2	1	—	—

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

Table S6. Build speed of 3D printing resin formulations with $[PEGDA_{200}]_0$:$[PXEP]_0$:$[TPO]_0$ = 100:1:x.

Entry	$[TPO]_0$	Target Layer thickness (mm)	Exposure Time Per Layer (s)	Actual thickness (mm)	Printing speed (cm h^{-1})
1	0.1	0.05	2	1.82±0.01	8.19
2	0.1	0.05	1	—	—
3	0.1	0.1	3	1.78±0.02	10.68
4	0.1	0.1	2	—	—
5	0.1	0.2	6	1.69±0.03	10.14
6	0.1	0.2	5	1.68±0.03	12.10
7	0.1	0.2	4	1.66±0.03	14.94
8	0.1	0.2	3	—	—
9	0.3	0.05	2	1.86±0.02	8.37
10	0.3	0.05	1	1.83±0.03	16.47
11	0.3	0.1	3	1.83±0.01	10.98
12	0.3	0.1	2	1.79±0.01	16.11
13	0.3	0.1	1	—	—
14	0.3	0.2	3	1.71±0.01	20.52
15	0.3	0.2	2	1.70±0.02	30.60
16	0.3	0.2	1	—	—
17	0.5	0.05	2	1.87±0.02	8.42
18	0.5	0.05	1	1.84±0.02	16.56
19	0.5	0.1	2	1.81±0.01	16.29
20	0.5	0.1	1	1.76±0.01	31.68
21	0.5	0.2	2	1.70±0.02	30.60
22	0.5	0.2	1	—	—

Objects were considered to be not well defined if a) the material did not adhere to the build stage, b) the material was printed with different thickness, c) The surface of the object has many cracks or gaps.

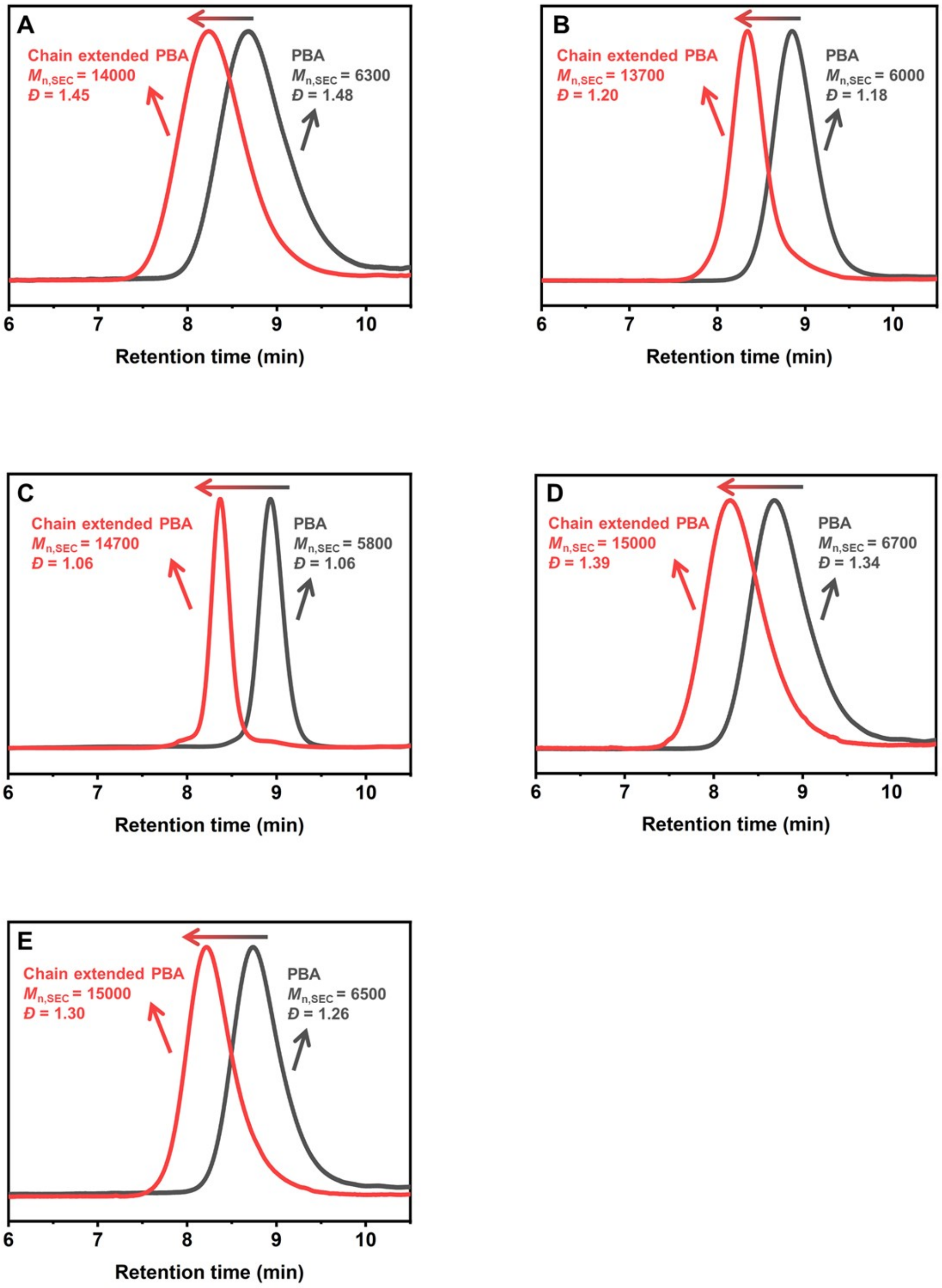

Figure S1. SEC curves of chain extension using PBA prepared from **Table 1**.

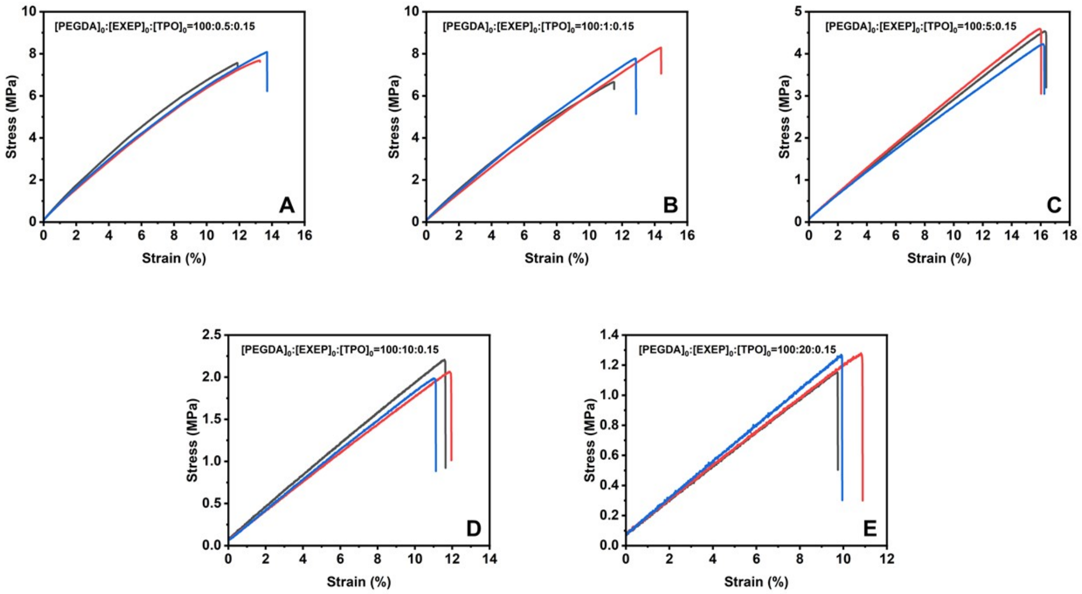

Figure S2. The stress and strain curves of samples prepared with a molar ratio of A) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:0.5:0.15; B) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:1:0.15; C) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:5:0.15; D) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:10:0.15; E) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:20:0.15.

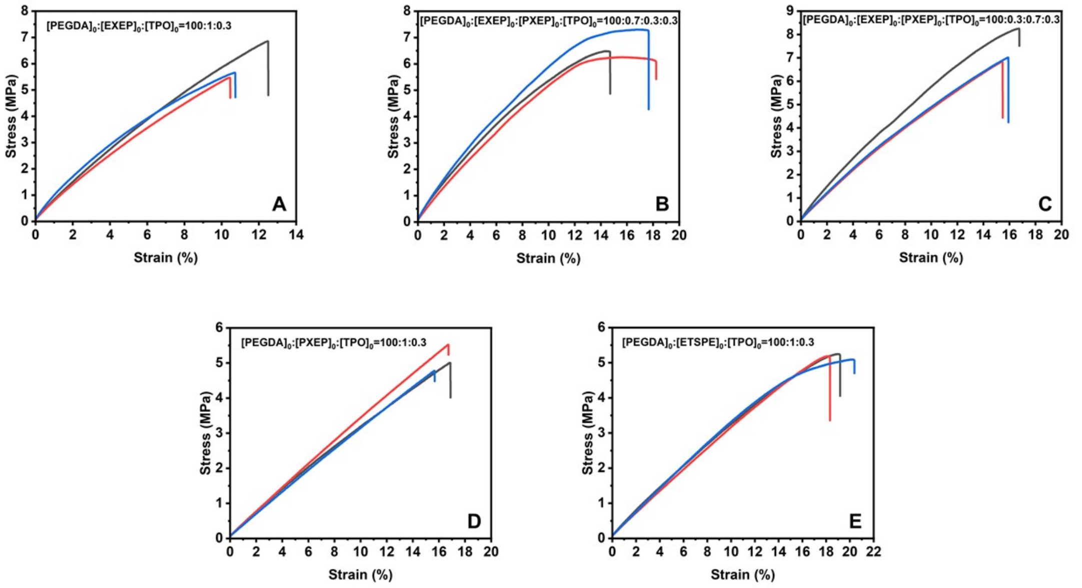

Figure S3. The stress and strain curves of samples prepared with a molar ratio of A) $[PEGDA]_0$:$[EXEP]_0$:$[TPO]_0$ = 100:1:0.3; B) $[PEGDA]_0$:$[EXEP]_0$:$[PXEP]_0$:$[TPO]_0$ = 100:0.7:0.3:0.3; C) $[PEGDA]_0$:$[EXEP]_0$:$[PXEP]_0$:$[TPO]_0$ = 100:0.3:0.7:0.3; D) $[PEGDA]_0$:$[PXEP]_0$:$[TPO]_0$ = 100:1:0.3; E) $[PEGDA]_0$:$[ETSPE]_0$:$[TPO]_0$ = 100:1:0.3.

Table S7. Tensile test of samples printed by the formulation consisting of $[\mathrm{PEGDA}_{200}]_0$:$[\mathrm{EXEP}]_0$:$[\mathrm{TPO}]_0$ = 100:x:0.15.

$[\mathrm{EXEP}]_0$	**ε_b (%)**	**σ_b (MPa)**	**Young's modulus (MPa)**
0.5	13.0 ± 0.9	7.8 ± 0.3	68.6 ± 3.9
1	12.9 ± 1.4	7.6 ± 0.8	64.1 ± 2.8
5	16.2 ± 0.2	4.5 ± 0.2	28.1 ± 1.3
10	11.6 ± 0.4	2.1 ± 0.1	18.2 ± 0.7
20	10.2 ± 0.6	1.2 ± 0.1	11.7 ± 0.4

Table S8. Tensile test of samples printed by the formulation consisting of $[\mathrm{PEGDA}_{200}]_0$:$[\mathrm{CTA}]_0$:$[\mathrm{TPO}]_0$ = 100:x:0.3.

CTA	**ε_b (%)**	**σ_b (MPa)**	**Young's modulus (MPa)**
ETSPE	19.3 ± 1.0	5.2 ± 0.1	31.8 ± 1.0
PXEP	16.4 ± 0.7	5.1 ± 0.4	32.2 ± 1.4
$[\mathrm{EXEP}]_0$:$[\mathrm{PXEP}]_0$ = 0.3:0.7	16.1 ± 0.7	7.4 ± 0.8	52.7 ± 4.3
$[\mathrm{EXEP}]_0$:$[\mathrm{PXEP}]_0$ = 0.7:0.3	16.9 ± 1.9	6.7 ± 0.6	58.6 ± 4.8
EXEP	11.2 ± 1.1	6.0 ± 0.8	62.5 ± 4.4

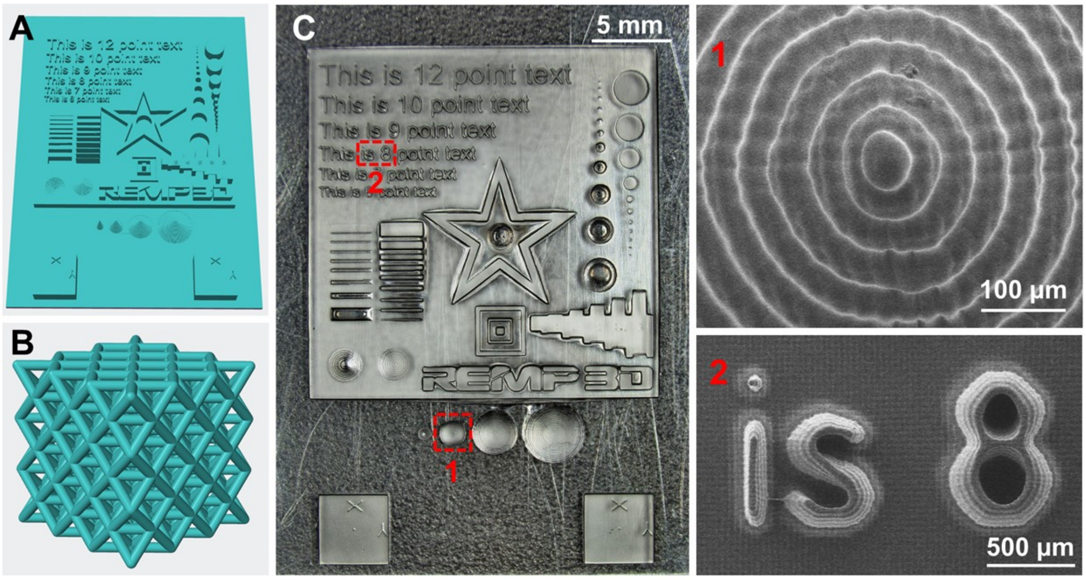

Figure S4. A) 3D Studio Max model of precision model; B) 3D Studio Max model of hollow grid model; C) Digital and SEM images of printed precision model with a molar ratio of $[\mathrm{PEGDA}_{200}]_0$:$[\mathrm{EXEP}]_0$:$[\mathrm{TPO}]_0$ = 100:1:0.3.

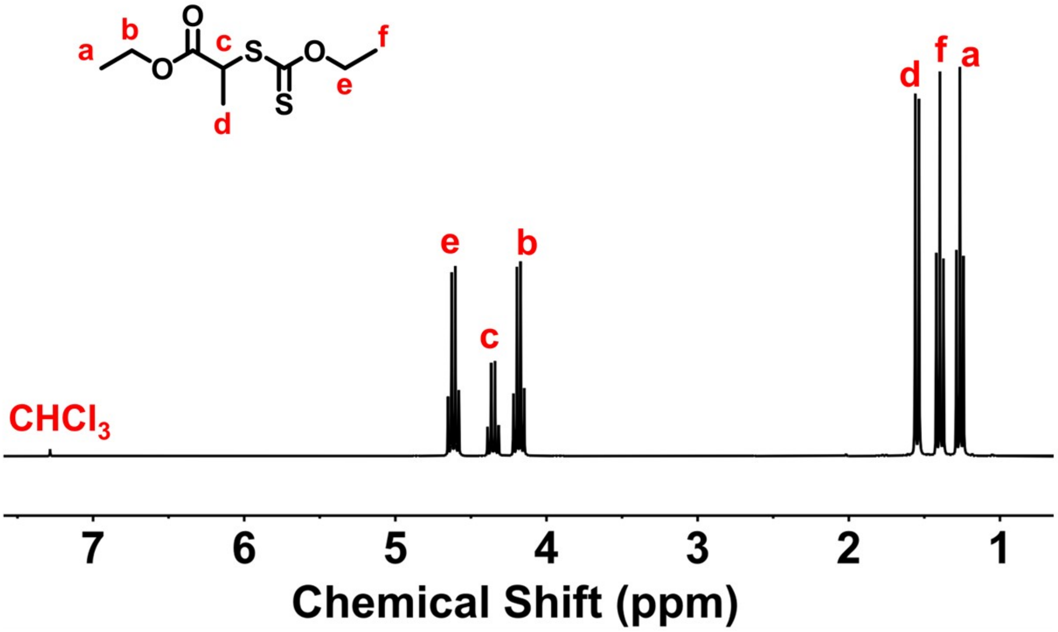

Figure S5. ^{1}H NMR spectrum (in $CDCl_3$) of **EXEP.**

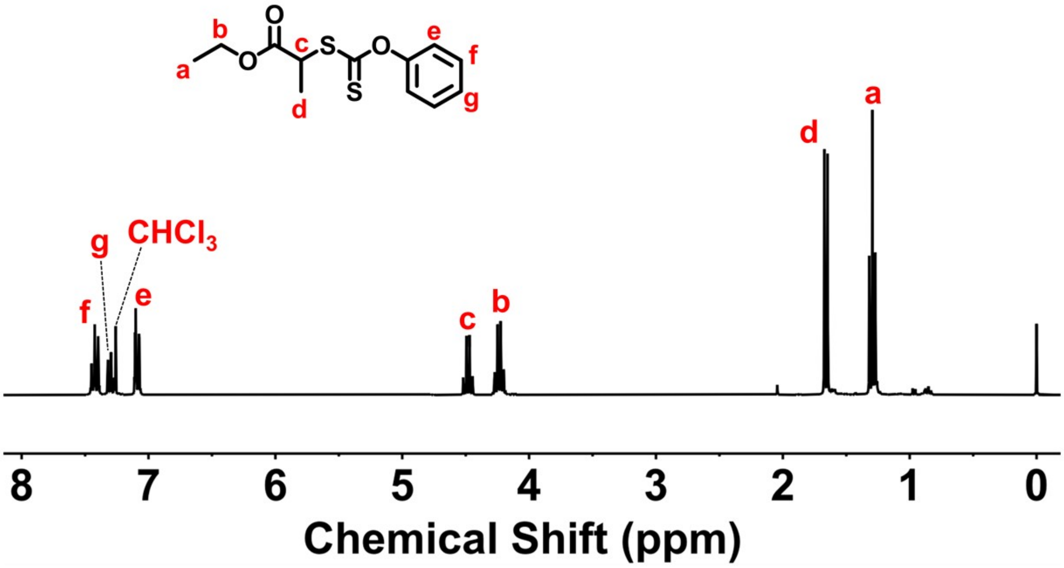

Figure S6. ^{1}H NMR spectrum (in $CDCl_3$) of **PXEP.**

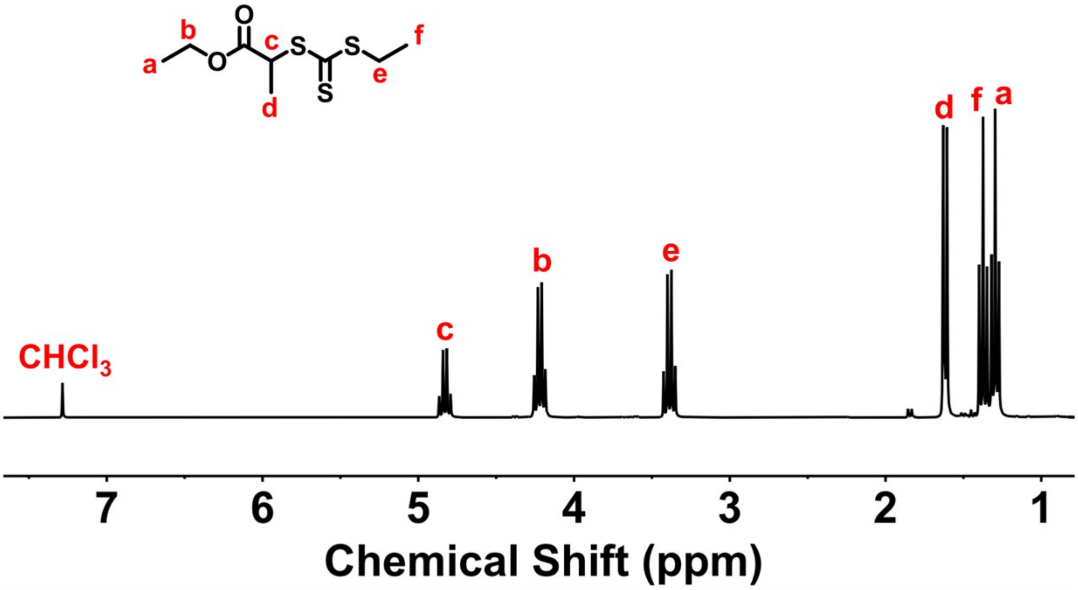

Figure S7. ^{1}H NMR spectrum (in $CDCl_3$) of **ETSPE.**

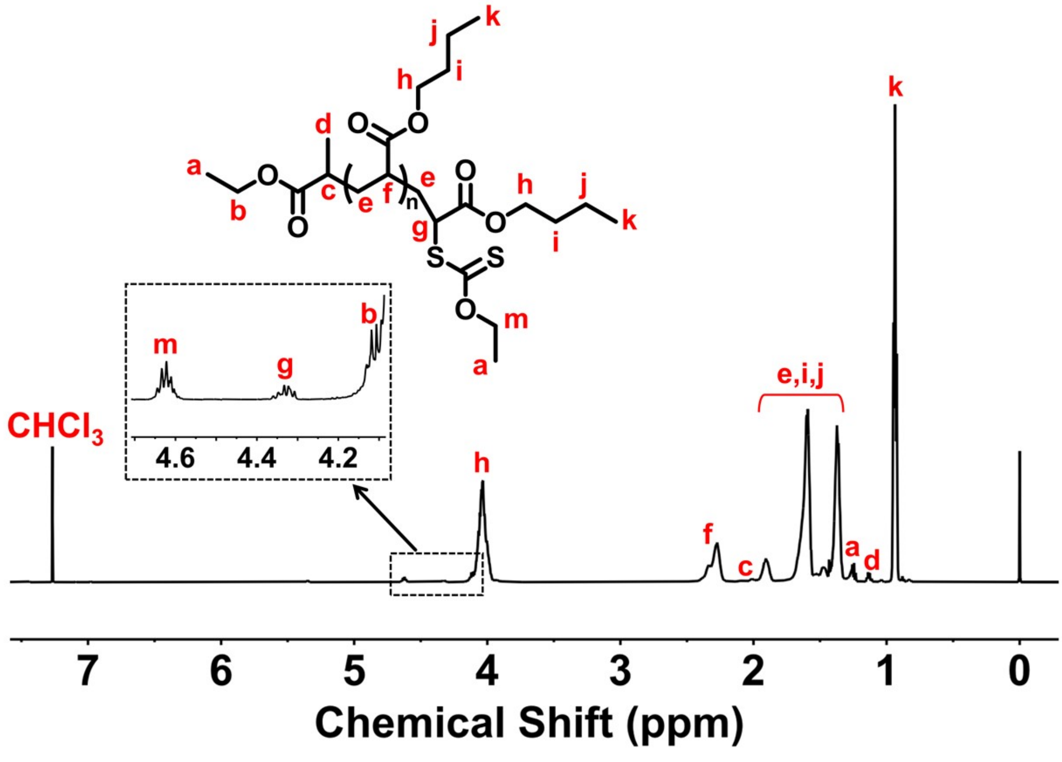

Figure S8. ^{1}H NMR spectrum (in $CDCl_3$) of PBA prepared by EXEP.

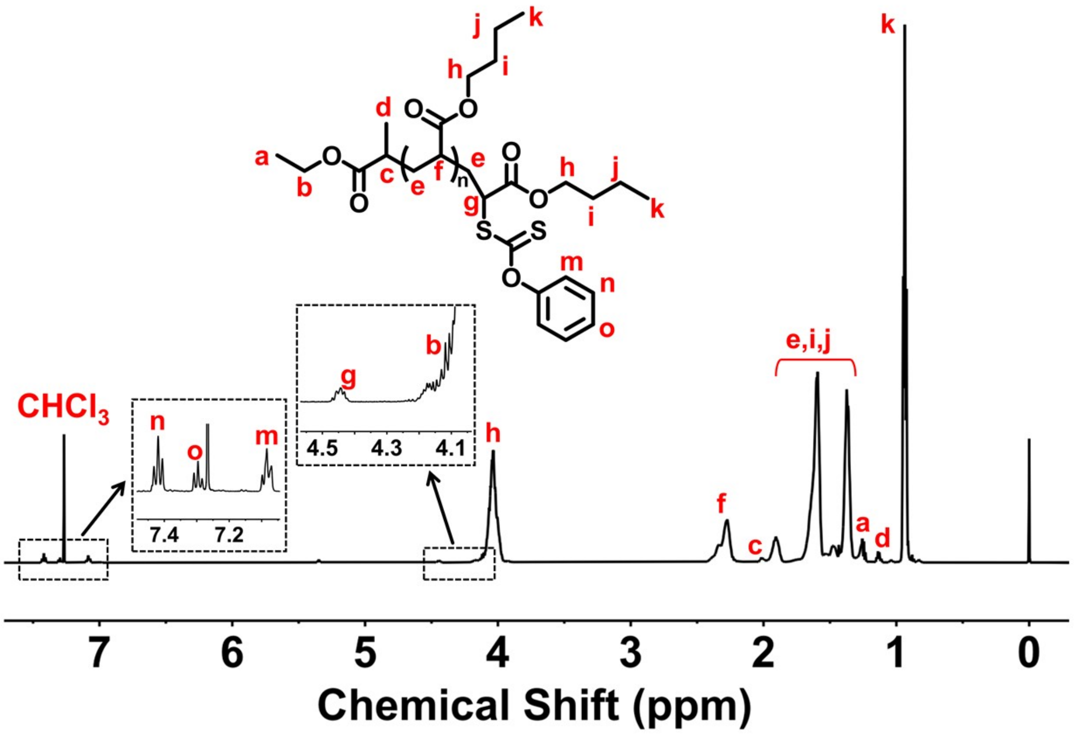

Figure S9. ^{1}H NMR spectrum (in CDCl$_3$) of PBA prepared by PXEP.

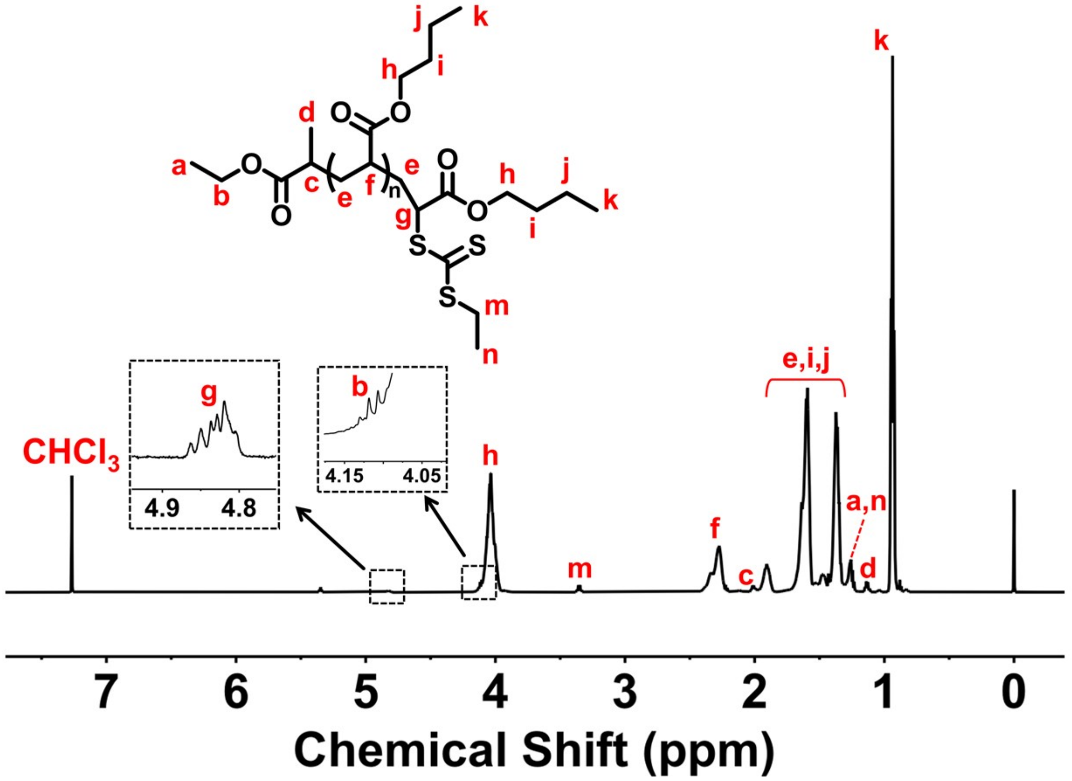

Figure S10. ^{1}H NMR spectrum (in CDCl$_3$) of PBA prepared by ETSPE.