Supporting Information for:

Sulfur-Rich Polymer with Nano Particles: High Refractive Index Dual Tone Photoresist

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Contents

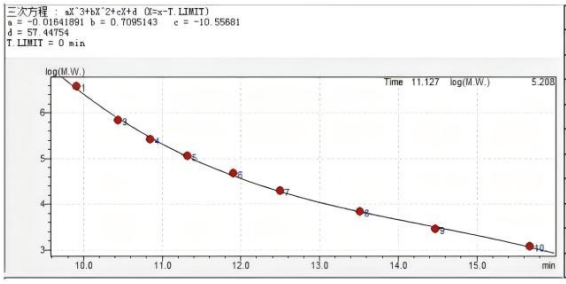
Materials and Characterization

Materials

All monomers were purchased from Admas-beta except THPOPMA. Ultra-dry Pyridine, Ultra-dry DMF, Ultra-dry DMAc, and Ultra-dry NMP were purchased from Admas-beta, Nano TiO_2 (~20 nm) was dispersed in PGMEA with 50% solid weight, the dispersion was purchased from Shenzhen Nagata Masura Tech Ltd., Other materials were purchased from Bide chemicals and used without any further treatment.

Characterization

1. NMR (Varian MERCURY 400 NMR spectrometer at 298K, ^1H, 400 MHz) and gel permeation chromatography (GPC, Shimadzu Prominence LC-20A) were used to determine the structures of polymers obtained. The solvent used in NMR spectra were $CDCl_3$ with tetramethylsilane as internal standard.
2. The molecular weights and polydispersity indexes were carried out on Shimadzu Prominence LC-20A, equipped with Prominence RID-20A refractive index detectors and a Prominence SPD-20A UV-Vis detector (250 nm wavelength), GPC was conducted at 20 ℃ using THF as mobile phase by using PMMA as standard.
3. DSC curves were recorded by Shimadzu DSC-60Plus instrument at a heating/cooling rate of 20 °C min^{-1} at temperatures ranging from -20 to 140 °C.
4. Raman spectra were recorded by DXR ThermoFisher Scientific with 532 nm laser excitation.
5. Element Analysis was performed using Elementar Vario Micro Cube.
6. Optical transmittance spectra were recorded by PerkinElmer Lambda 1050+.
7. Refractive Index data were recorded by F20-UV Filmetrics (KLA company, USA).
8. Film thickness was measured by Profilometry of Bruker Dektak XTL.
9. Optical Microscope images were recorded by Olympus BX53M

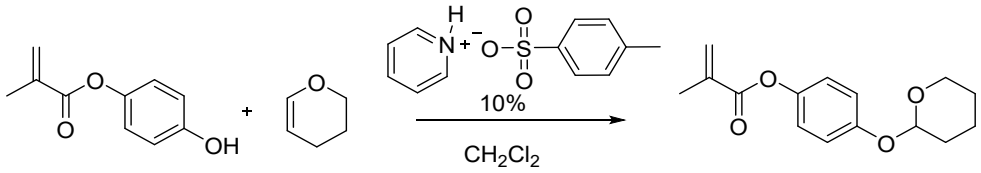


Number	Time (min)	Molecular weight (kg · mol $^{-1}$)
1	9.915	3730
2	10.417	1470
3	10.441	678
4	10.850	257
5	11.329	112
6	11.909	46.5
7	12.502	19.8
8	13.521	6.93
9	14.474	2.9
10	15.677	1.2

Figure S1. The GPC calibration curve of standard samples.

Synthesis of THPOPMA

The 4-hydroxyphenyl methacrylate 1.78g and 3,4-dihydro-2H-pyran 1.6g dissolved in 50 mL CH_2Cl_2, the 10 % catalyst of pyridinium 4-methylbenzenesulfonate 0.25 g added to the solution subsequently. The solution stirred for 24h at room temperature, the reaction mixture was quenched with 200 mL water, and then extracted with ethyl acetate (50 mL) for 3 times. The combined extracts were washed with brine, dried over Na_2SO_4 and filtered. After the solvent was removed under vacuum, the residue was purified by flash chromatography to give the desired product.



Scheme S1. Synthesis of THPOPMA

2.33g (89 % yield), colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (dd, *J* = 9.2, 6.6 Hz, 4H), 6.32 (s, 1H), 5.73 (s, 1H), 5.38 (t, *J* =4.0 Hz ,1H), 3.93-3.88 (m, 1H), 3.62-3.59 (m, 1H), 2.05 (s, 3H), 2.00-1.97 (m, 1H), 1.88-1.84 (m, 2H), 1.71-1.61 (m, 3H).

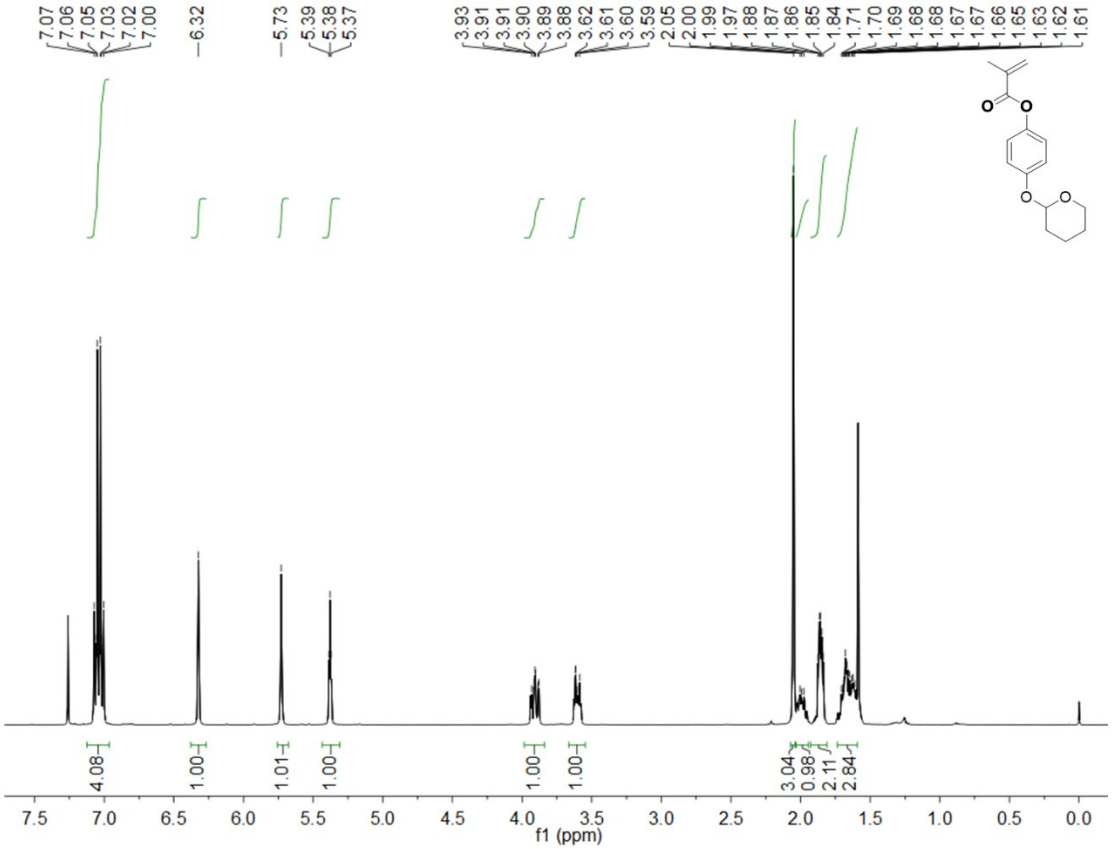


Figure S2. ^{1}H NMR spectrum of THPOPMA

Table S1. Screening of Reaction Conditions for the Polymerization of Phenyl Methacrylate with Sulfur[a]

Entry	Monomer : S	Solvent	Time	Conversion[b]	S %[c]	Mn kg mol $^{-1}$	PDI [d]
1	2:1	DMF	24 h	60	38.5	2.1 k	1.31
2	2:1	DMAc	24 h	79	37.6	2.7 k	1.44
3	2:1	NMP	6 h	>99	43.6	3.1 k	1.64
4	5:1	NMP	6 h	>99	32.7	4.1 k	1.45

5	10:1	NMP	6 h	>99	30.7	4.3 k	1.33

[a]Unless otherwise specified, reaction condition: S_8 0.256 g (1mmol); monomer and PhSNa feed ratio according to the different condition; 2 mL of solvent; under argon. [b]Conversion was calculated from unreacted sulfur. [c]S % content was determined by element analysis. [d]Mn and PDI was determined by GPC

Table S2. Elemental analysis of synthesized sulfur containing polymers.

Monomer	Monomer : S	S (%)	C (%)	H (%)
PMA	2:1	43.6	41.4	3.3
PMA	5:1	32.7	50.3	4.0
PMA	10:1	30.7	50.5	4.1
2NMA	2:1	33.9	45.7	3.9
MMA	2:1	48.5	30.6	3.9
AdaMMA	2:1	25.8	56.1	6.5
BzMA	2:1	39.6	45.8	4.0
THPOPMA	2:1	28.8	47.3	4.7
1,3-BDBMA	2:1	38.1	38.5	4.8

Typical polymerization procedure

The sulfur 256 mg, monomer (phenyl methacrylate) 324 mg, and initiator (PhSNa) 6.6mg were added into a 25 mL Schlenk flask (in the reactor was [Monomer]: [Sulfur]: [PhSNa] = 40:20:1), followed by the addition of dry NMP 2 mL, the system turned dark red quickly. The mixture degassed by three cycles of freezing-pumping-thawing with argon, then placed under room temperature and stirred for 6 h. The system turned a clear dark solution, the solution could be precipitated by dropping the diluted into 50 ml methanol, then filtrated and collected the solid. The solid dissolved in 1 mL THF and then reprecipitated in methanol. The final polymer was dried in a vacuum oven at 45 ℃ for 24 h.

Lithography process

Positive tone: P(THPOPMA$_{40}$-S$_{20}$) 100 mg, TPS 6 mg, TiO_2 (dispersed in PGMEA with 50% solid content) 40 mg, dissolved in 1.4 mL PGMEA. Spin coated the photoresist on bare Si wafer at 1500 rpm for 20 seconds (Film thickness ~ 240 nm), a Cu mask (205*37 μm rectangle and 75 μm hole pattern) covered on the film and the exposure took under 254 nm lamp of 32w for 30 seconds, then immerged the wafer into developer (2.38% TMAH, Tetramethylammonium hydroxide) for 30 seconds, washed the wafer and spin off the water.

Negative tone: P(THPOPMA$_{40}$-S$_{20}$) 100 mg, TPS 6 mg, TiO_2 (dispersed in PGMEA with 50% solid content) 40 mg, and 30 mg trimethylolpropane triglycidyl ether dissolved in 1.6 mL PGMEA. Spin coated the photoresist on bare Si wafer at 1600 rpm for 20 seconds (Film thickness ~ 240 nm), a Cu mask (205*37 μm rectangle and 75 μm hole pattern) covered on the film and exposed under 254 nm lamp of 32w for 30 min, then immerged the wafer into *n*-butyl acetate for 1 min and spin off the solvent.

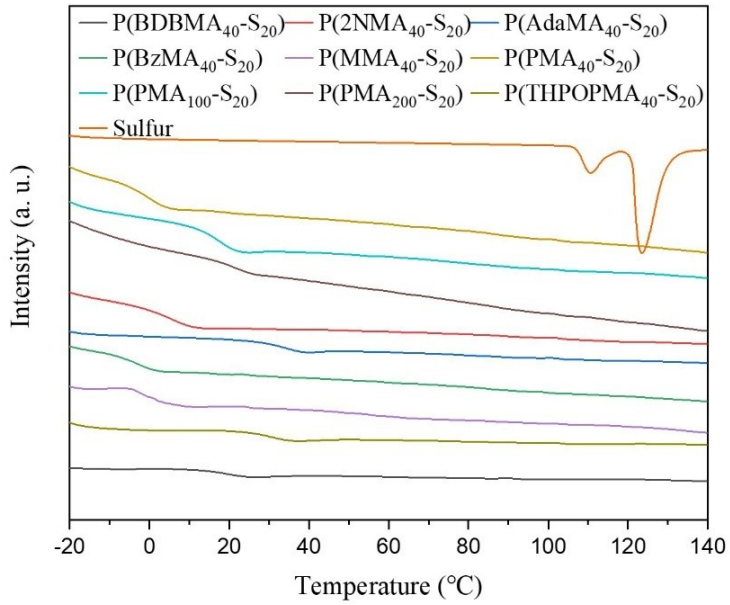


Figure S3. DSC curves of polymers

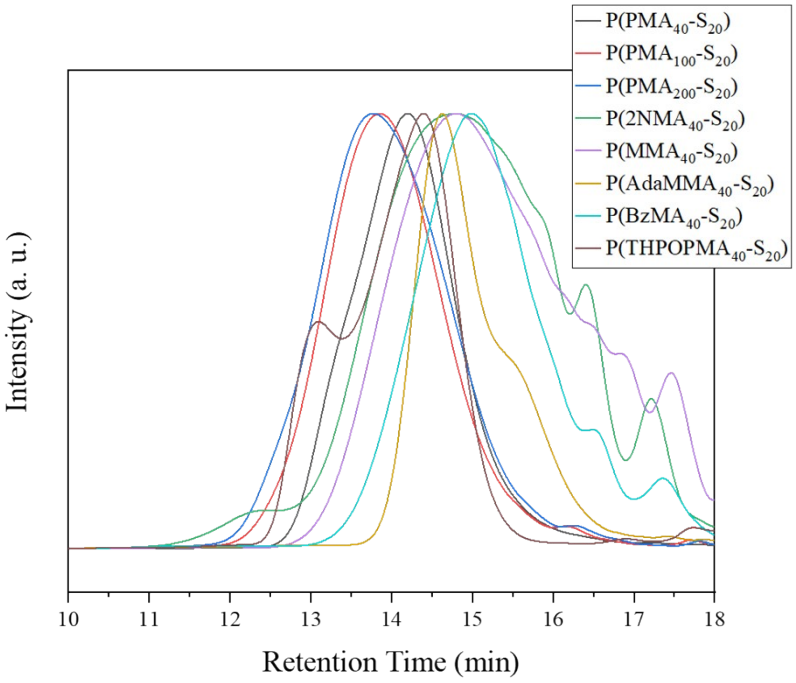


Figure S4. GPC curves of polymers.

Table S3. Abbe number of polymers

Entry	Polymers	Abbe number
1	PPMA	51.6
2	P(PMA_{100}-S_{20})	43.7
3	P(PMA_{40}-S_{20})	42.7
4	P(PMA_{100}-S_{20}) + 20% TiO_2	19.9
5	P(PMA_{40}-S_{20}) + 20% TiO_2	20.1
6	P($THPOPMA_{40}$-S_{20}) + 20% TiO_2	21.8

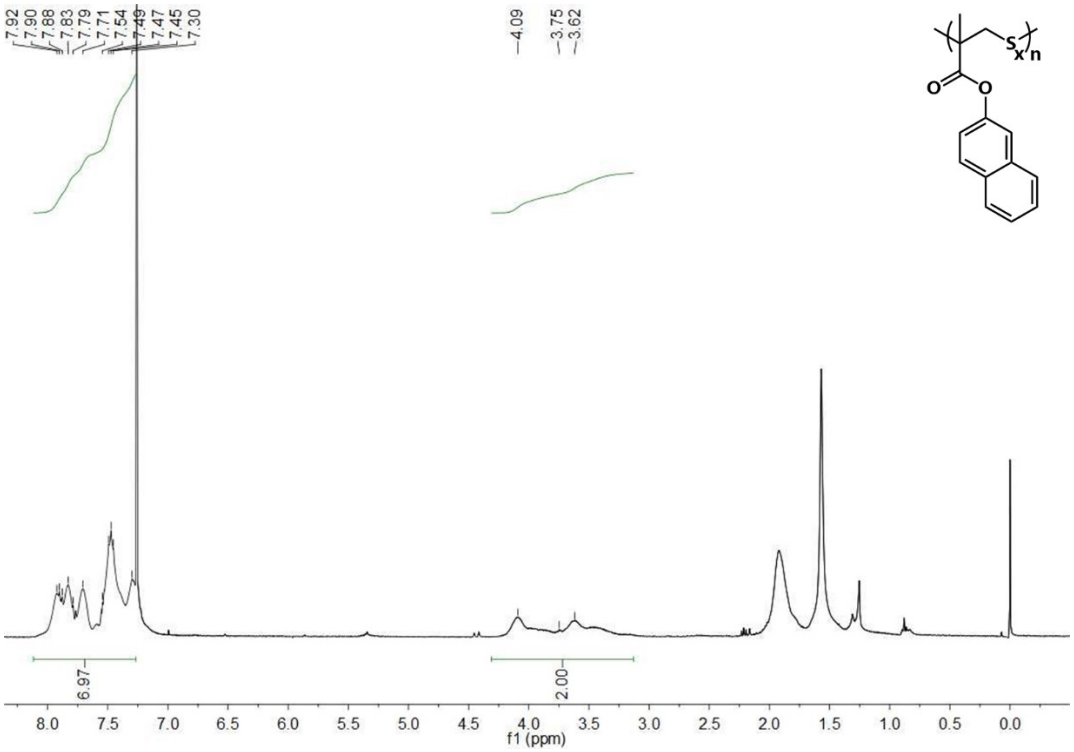


Figure S5. ^{1}H NMR spectrum of P(2NMA$_{40}$-S$_{20}$)

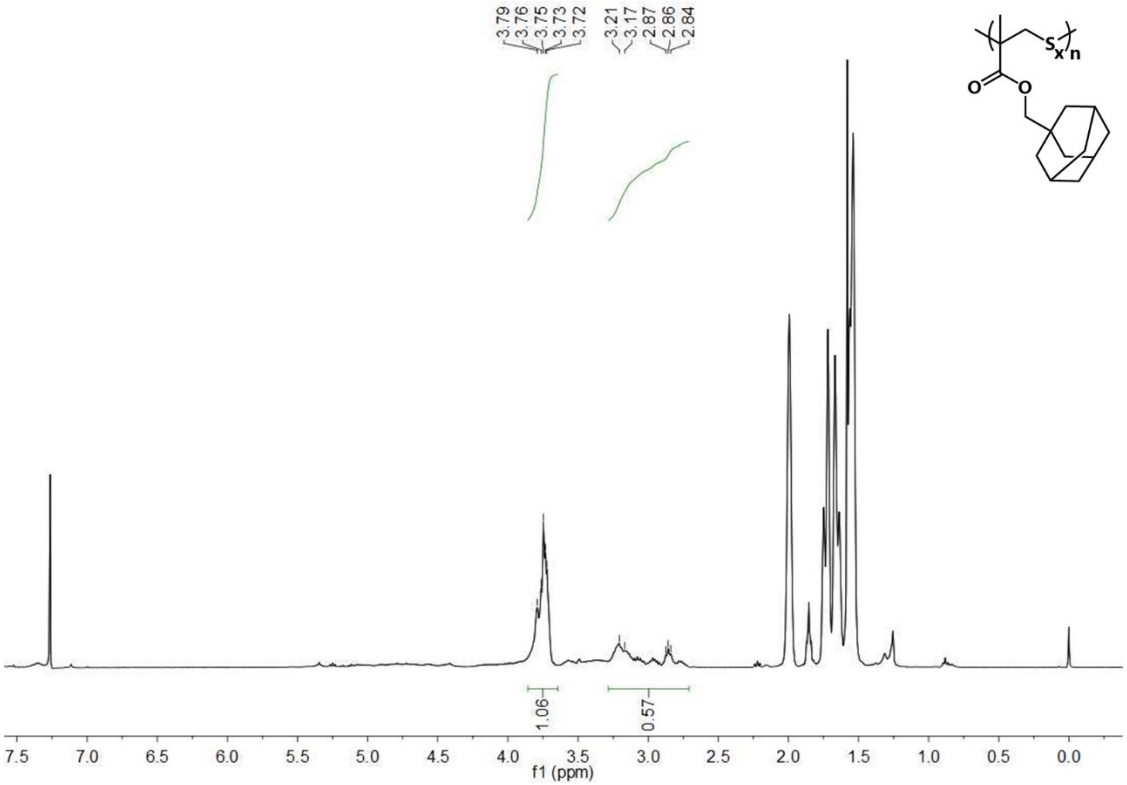


Figure S6. ^{1}H NMR spectrum of P(AdaMMA$_{40}$-S$_{20}$)

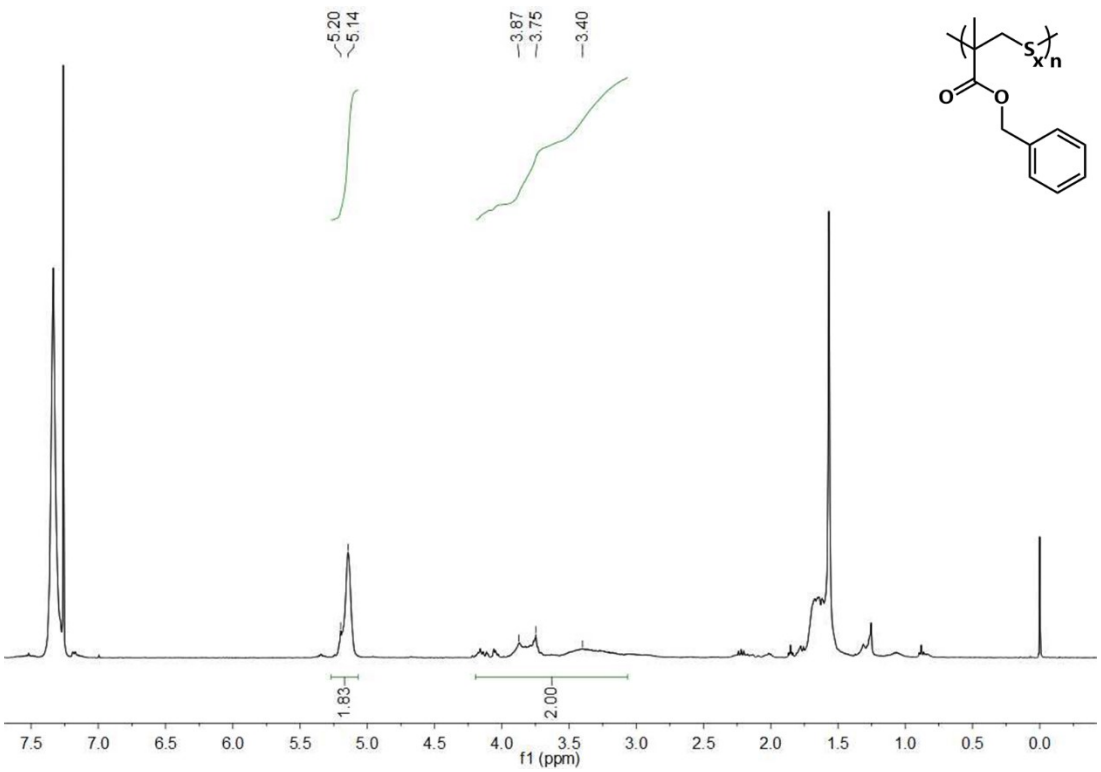


Figure S7. ^{1}H NMR spectrum of P(BzMA$_{40}$-S$_{20}$)

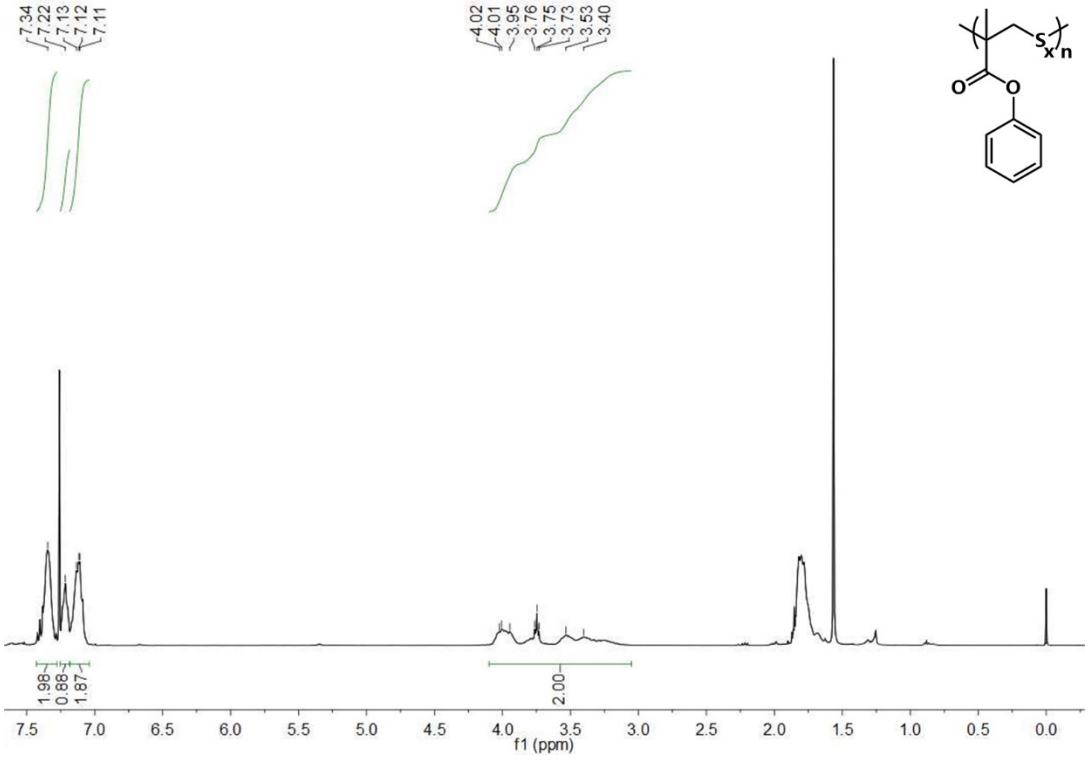


Figure S8. ^{1}H NMR spectrum of P(PMA$_{40}$-S$_{20}$)

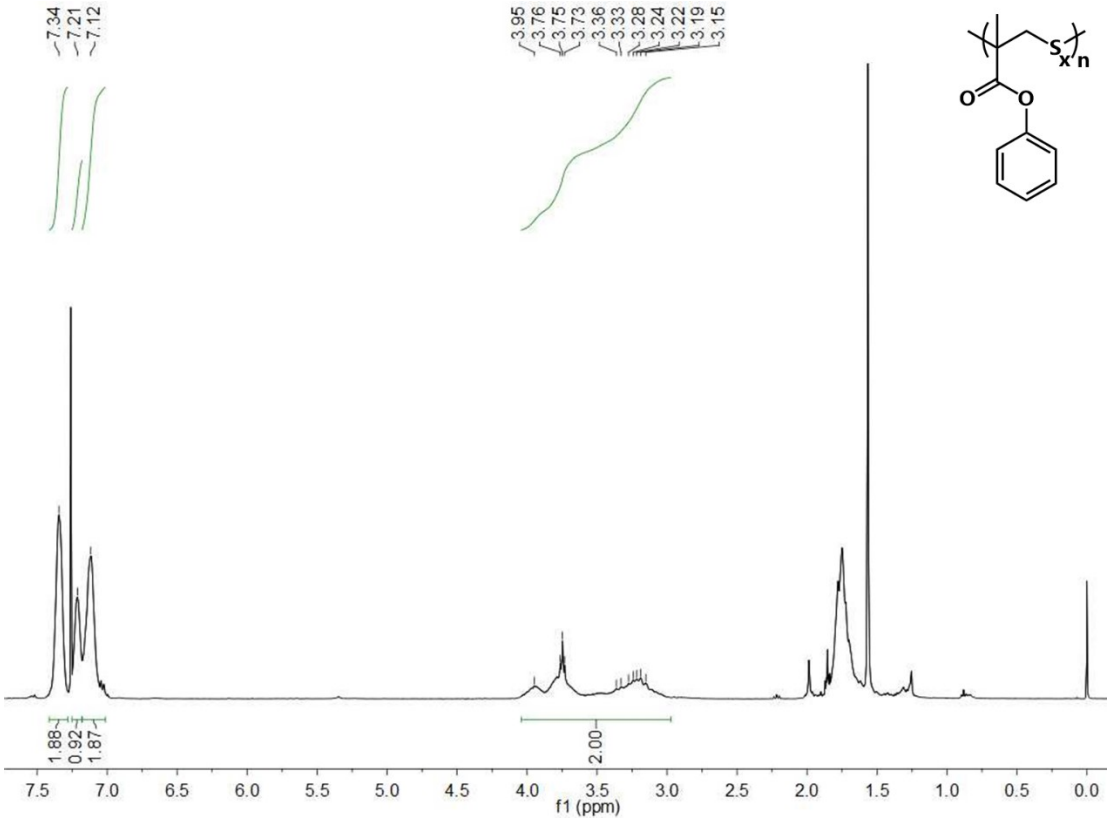


Figure S9. ^{1}H NMR spectrum of P(PMA$_{100}$-S$_{20}$)

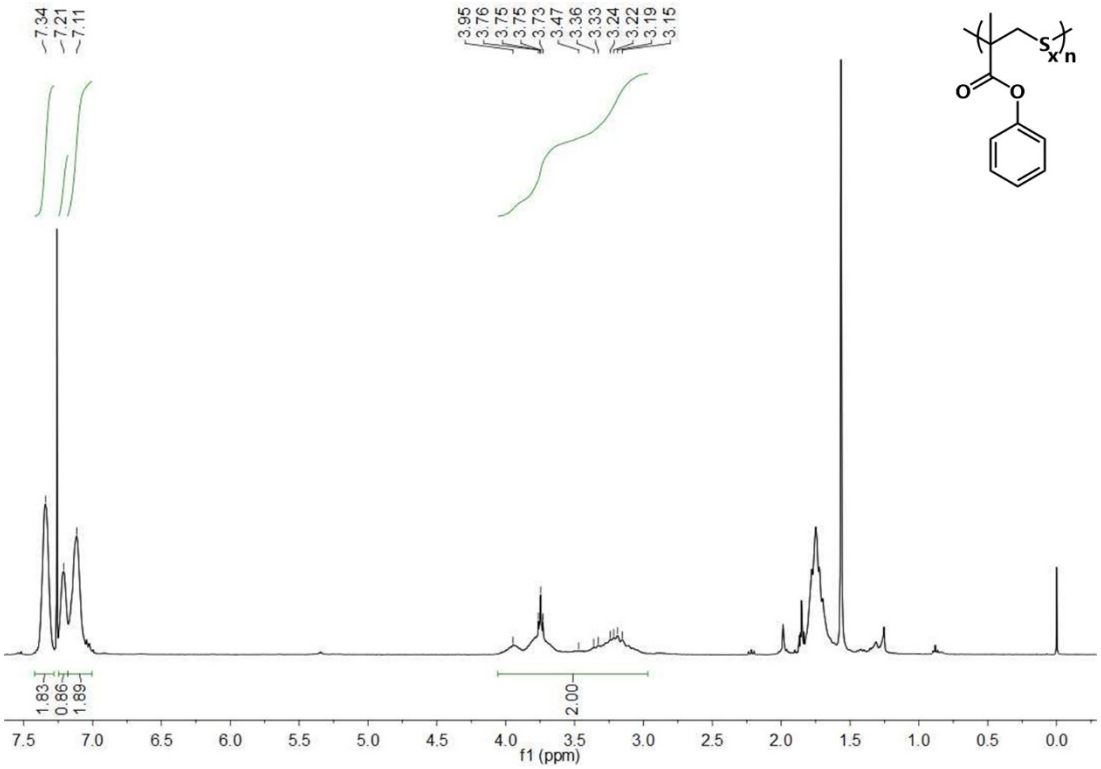


Figure S10. ^{1}H NMR spectrum of P(PMA$_{200}$-S$_{20}$)

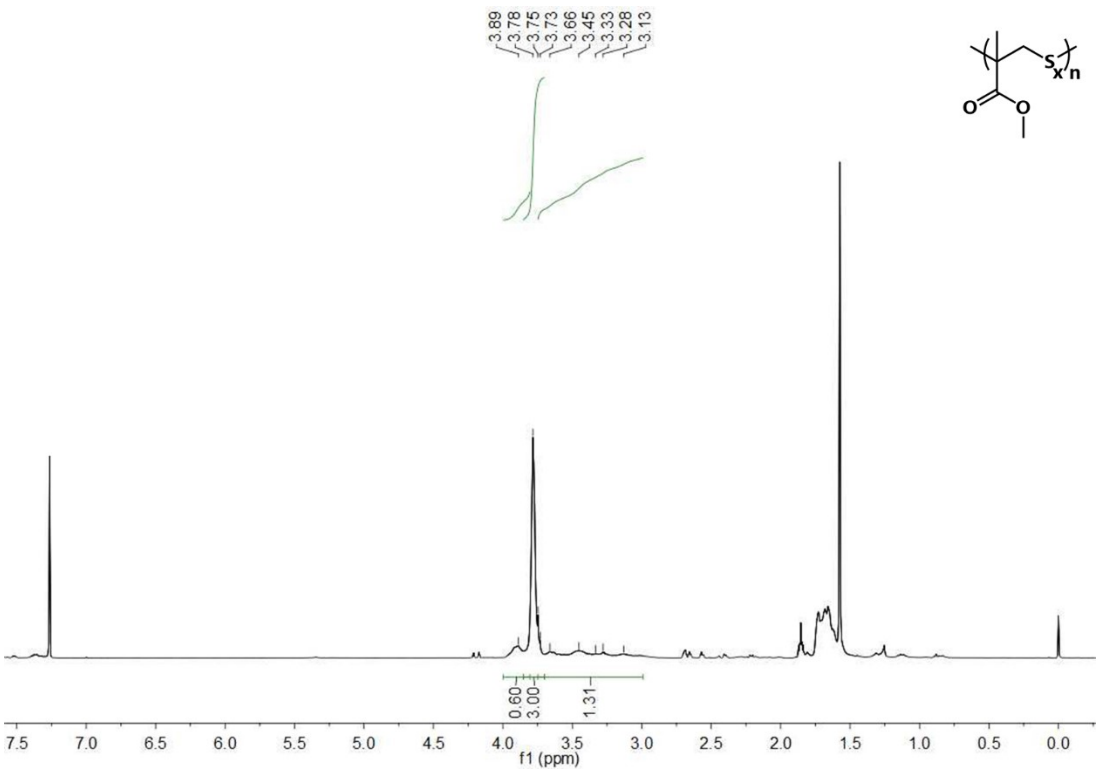


Figure S11. ^{1}H NMR spectrum of P(MMA$_{40}$-S$_{20}$)

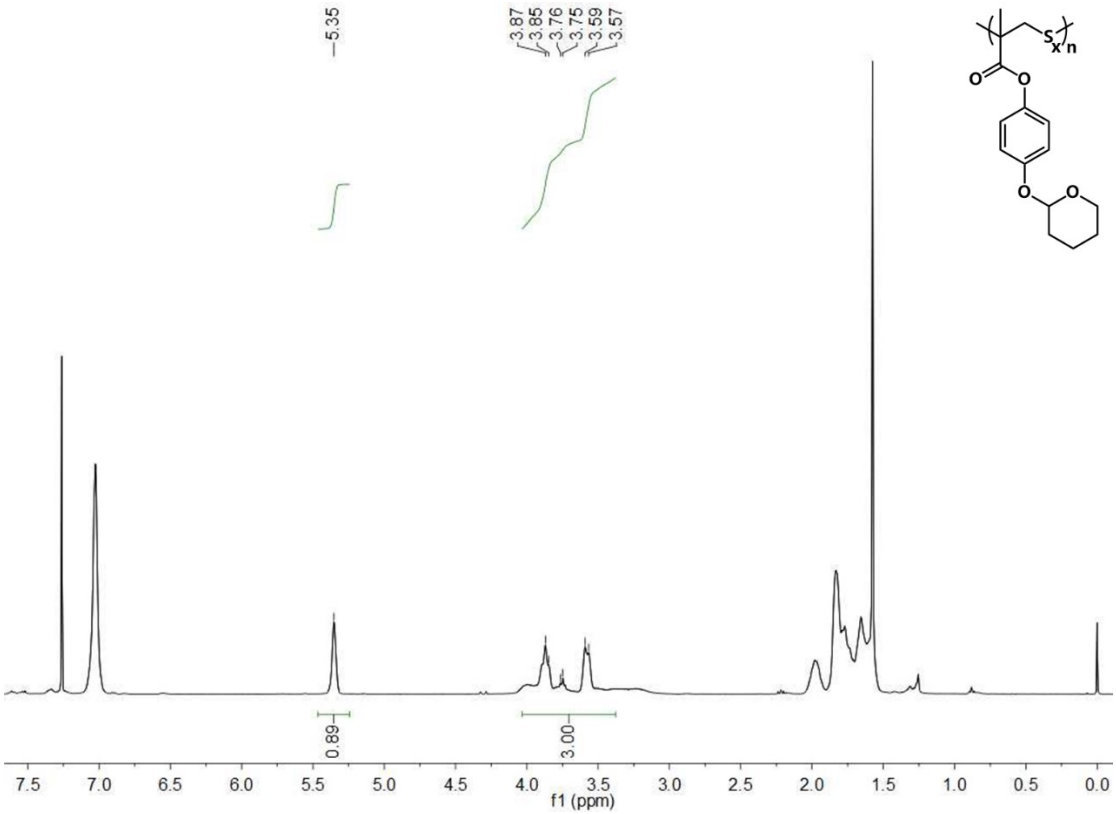


Figure S12. ^{1}H NMR spectrum of P(THPOPMA$_{40}$-S$_{20}$)