Supporting Information

1,2-Dithiolanes/Ynes Photopolymerizations to Generate High Refractive Index Polymers

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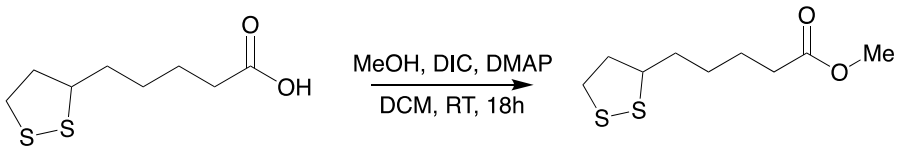
S1. Synthesis of LipOMe



20.00 g (96.9 mmol; 1.0 eq) of DL- a-Lipoic acid was dissolved in anhydrous dichloromethane (300 mL) under a nitrogen atmosphere. Then 5.92 g (48.5 mmol; 0.5 eq) of 4-*N,N'*-dimethylamino) pyridine were added slowly to the solution followed by *N, N*-diisopropyl carbodiimide (DIC) (14.64 g; 116 mmol; 1.2 eq). The reaction mixture was stirred 10 minutes at room temperature and cooled using ice bath. To continue, 31.00 g; 970 mmol, 10 eq) of methanol was added dropwise using an addition funnel. The reaction mixture was stirred at room temperature overnight. The solid by-product was filtered using a celite pad. The organic layer is washed 2 x 1 M solution of HCL and 2 x with brine and dried over $MgSO_4$ and filtered. The organic layer was concentrated; material was purified using flash chromatography 80:20 mixture of hexane: ethyl acetate. After solvent evaporation 20.00 g of a yellow, low-viscosity liquid were obtained (yield: 94%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.67 (s, 3H, OCH_3), 3.61 (m, 1H, (S-C*H*-C), 3.18 (m, 2H, S-C$\underline{H_2}$-CH_2) 2.50 (m, 1H, S-CH_2-C$\underline{H_2}$), 2.34 (t, 2H, *J* = 8Hz, CH_2), 1.94 (m, 1H, S-CH_2-C$\underline{H_2}$), 1.70 (m, 4H, CH_2), 1.49 (m, 2H, CH_2). ^{13}C NMR (101 MHz,

CD_2Cl_2) δ 173.69 (CO), 56.41(S-CH-C), 51.27(CH_3), 40.22, 38.50 (S-C-CH_2), 34.57(S-CH_2-C), 33.72(CH_2), 30.07(CH_2), 28.71(CH_2), 24.66 (CH_2).

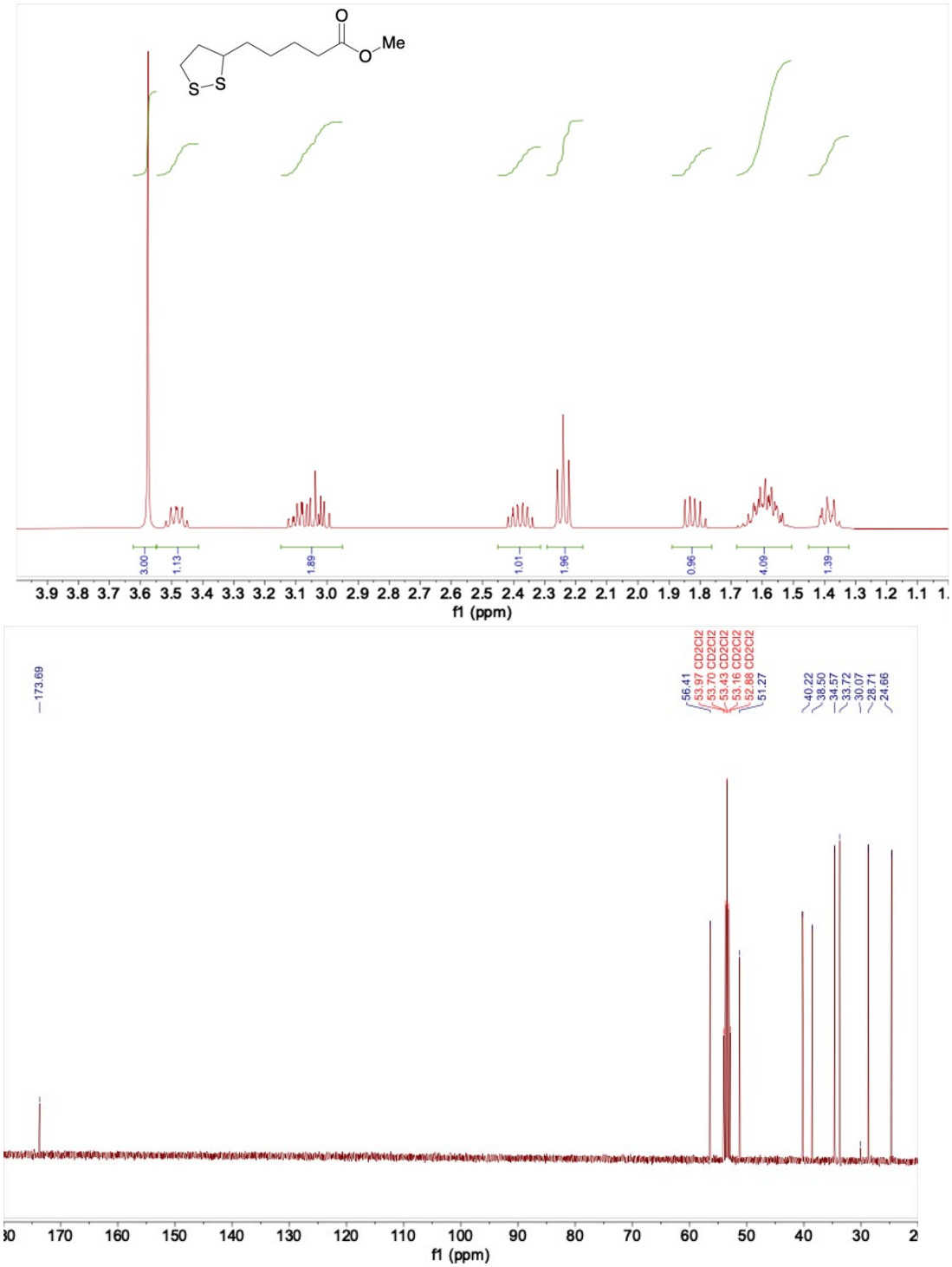
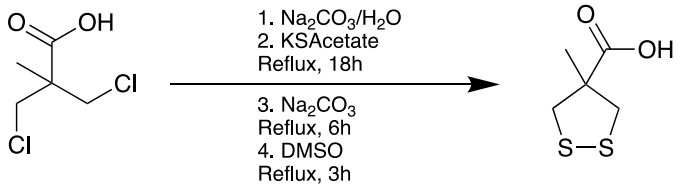


Figure S1. ^{1}H NMR and 13C NMR of LipOMe.

S2. Synthesis of Me-AspAc



13.14 g (0.0768 mol) of 3,3'-dichloropivalic acid and 300 ml of distilled water were placed in a 500 mL round-bottomed flask equipped with a condenser and a dropping funnel. To continue, 8.55 g (0.0868 mol, 1.05 eq) of sodium carbonate was added slowly; once the addition was finished, 17.55 g (0.1536 mol) of potassium thioacetate dissolved in 70 mL of distilled water was added dropwise, and the reaction mixture was brought to reflux for 18 hours. The reaction was allowed to reach room temperature, and 25.62 g (0.2418 mol) of sodium carbonate was added slowly, then it was allowed to reflux for 6 hours. After the disappearance of the starting material, 14 mL of DMSO was added, followed by refluxing for another 3 hours. The reaction mixture was allowed to reach room temperature and acidified with cold HCl (100 mL) in an iced bath. A yellow precipitate is obtained, filtered, washed with iced water, and dried on air. The yellow solid was recrystallized from a methylene chloride/hexane mixture to obtain 8.74 g of a yellow solid. Yield: 57%.^{1}H NMR (400 MHz, CD_3OD): δ 3.66 (d, J = 12 Hz, 2H, CH_2), 2.96 (d, J = 12 Hz, 2H, CH_2), 1.48 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD_3OD): δ 176.58 (CO), 57.22 (C), 47.39 (CH_2), 23.06 (CH_3).

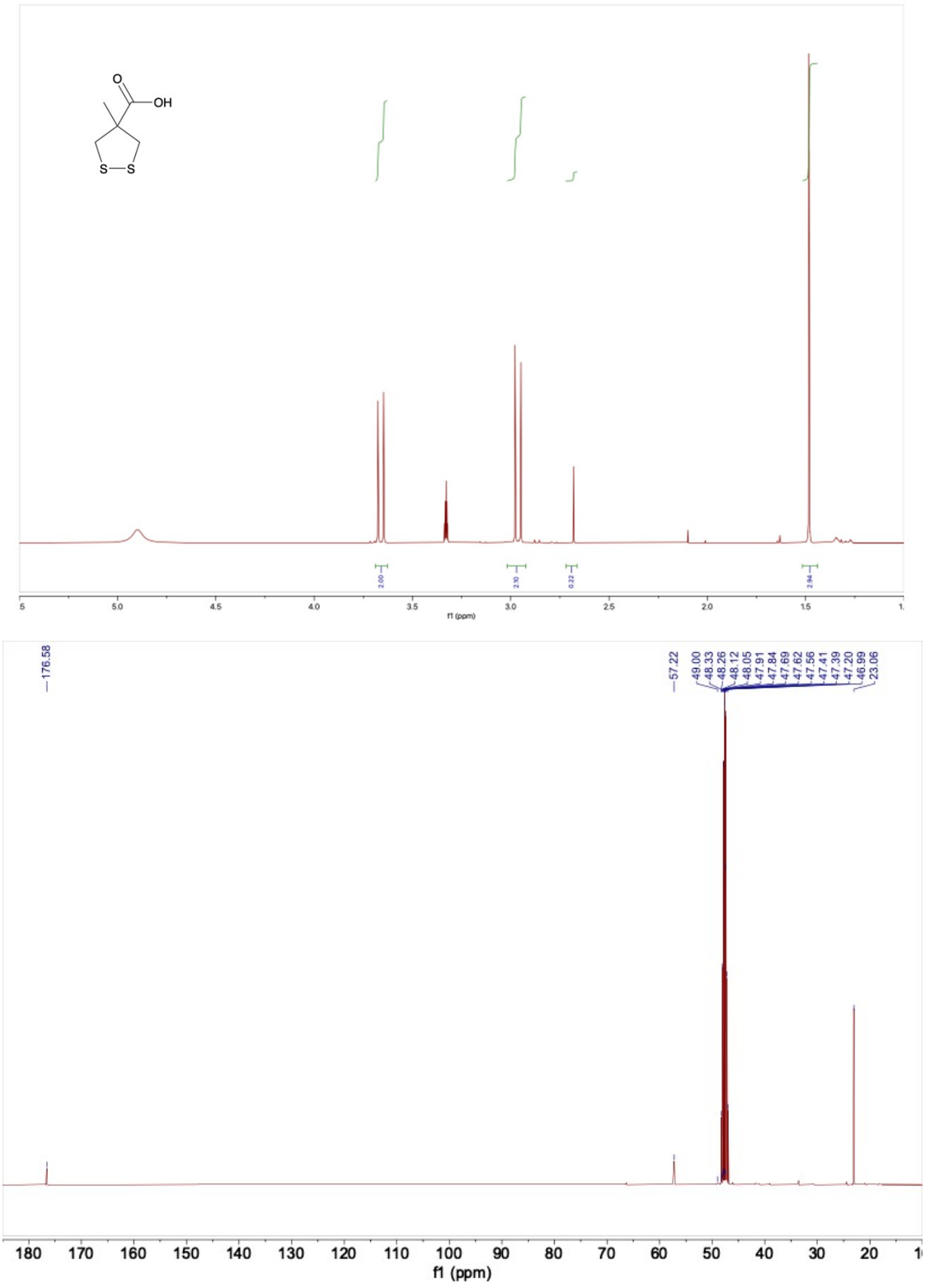
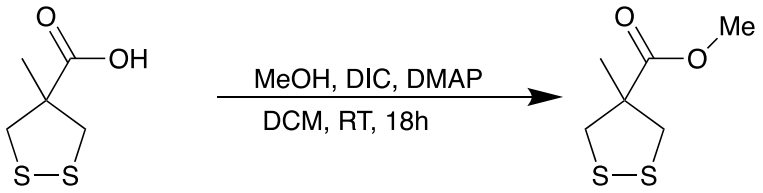


Figure S2. ^{1}H NMR and ^{13}C NMR of Me-AspAc.

S3. Synthesis of Me-AspOMe



10.00 g (60.9 mmol; 1.0 eq) of Methyl Asparagusic acid (synthesis 2) was dissolved in anhydrous dichloromethane (150 mL) under a nitrogen atmosphere. Then 0.372 g (3.0 mmol; 0.05 eq) of 4-*N,N'*- dimethylamino) pyridine were added slowly to the solution followed by *N,N*-diisopropylcarbodiimide (DIC) (9.22 g; 73 mmol; 1.2 eq). The reaction mixture was stirred 10 minutes at room temperature and cooled using an ice bath. To continue, 19.51 g; 608 mmol, 10 eq) of methanol was added dropwise using an addition funnel. The reaction mixture was stirred at room temperature overnight. The solid by-product was filtered using a celite pad. The organic layer is washed with 2 x 1 M solution of HCL and 2 x with brine, dried over $MgSO_4$, and filtered. The organic layer was concentrated; the material was purified using flash chromatography 80:20 mixture of hexane: ethyl acetate. After solvent evaporation 20 g of a yellow, low-viscosity liquid were obtained (yield: 73%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 3.76 (s, 3H, OCH_3), 3.68 (d, J = 10.4 Hz, 2H, SCH_2), 2.96 (d, J = 10.4 Hz, 2H, SCH_2), 1.49 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 174.76 (CO), 57.55 ($(CH_2)_2$-C- CH_3), 51.92 (OCH_3), 47.84($(CH_2)_2$), 24.02 ($(CH_2)_2$-C-CH_3).

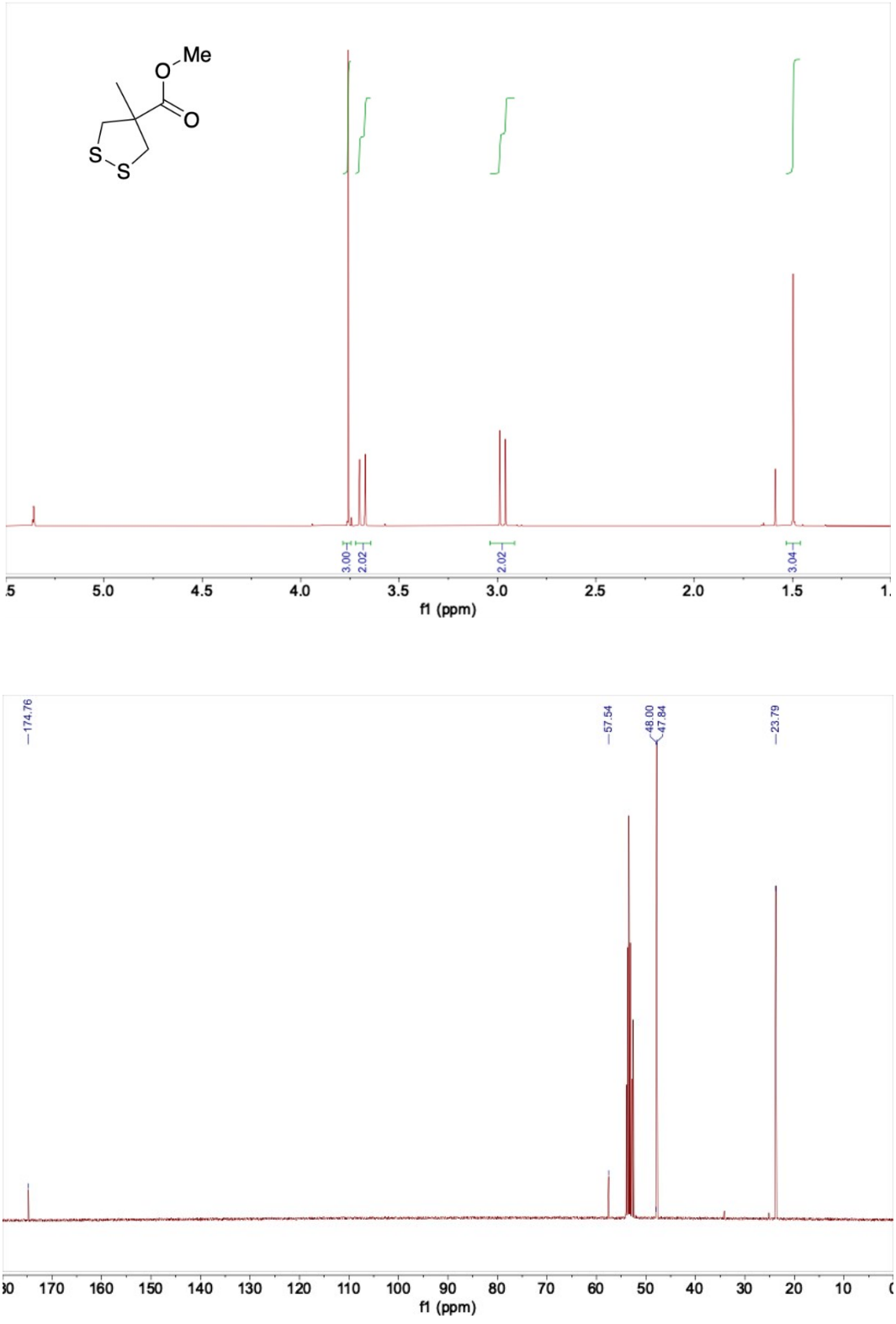


Figure S3. ^{1}H NMR and ^{13}C NMR of Me-AspOMe

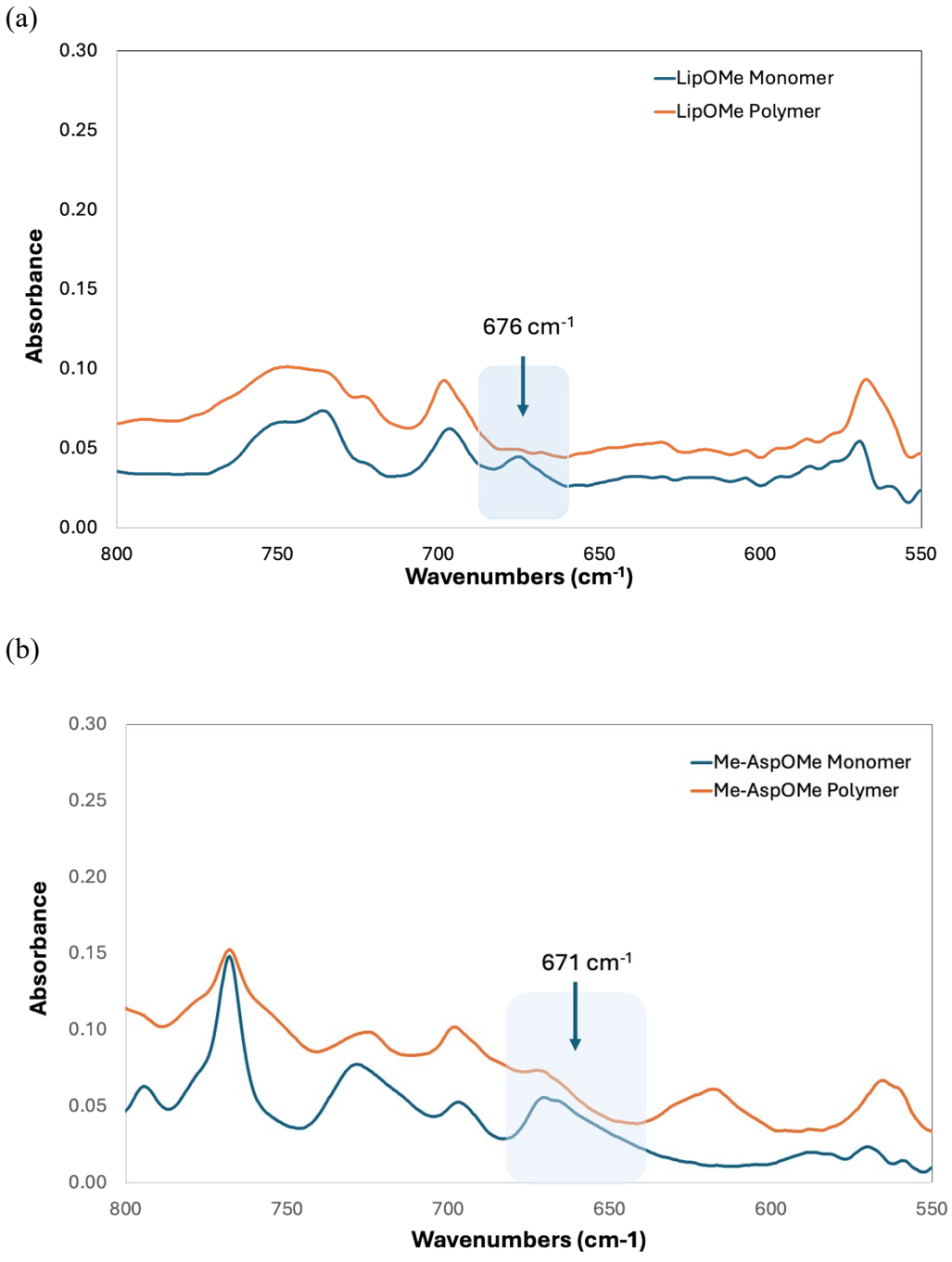


Figure S4. FTIR spectra (region between 800 – 500 cm^{-1}) for LipOMe and Me-AspOMe before and after polymerization.

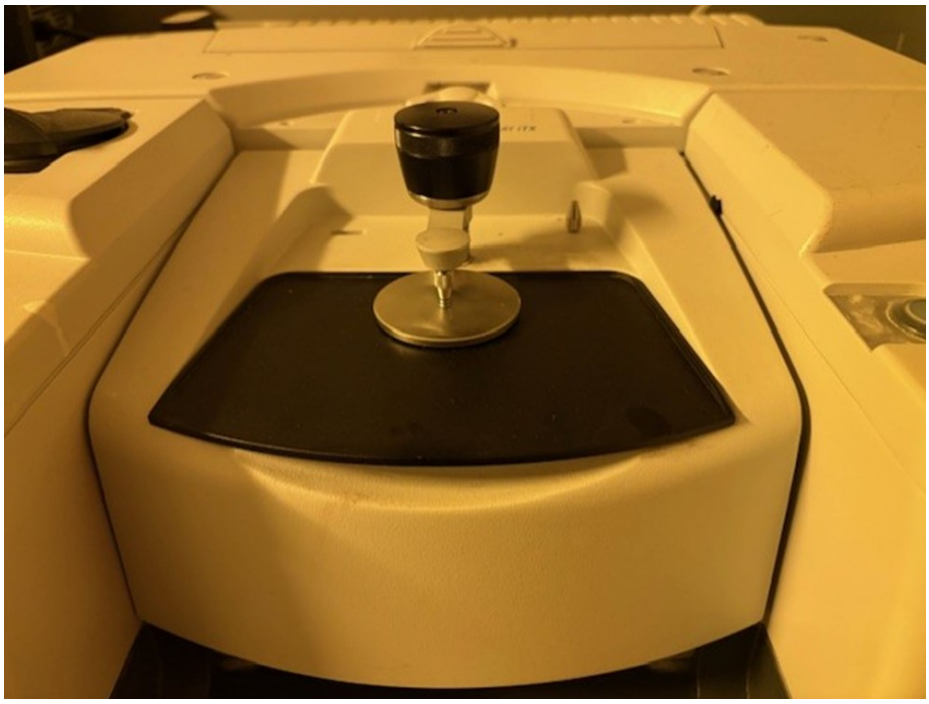
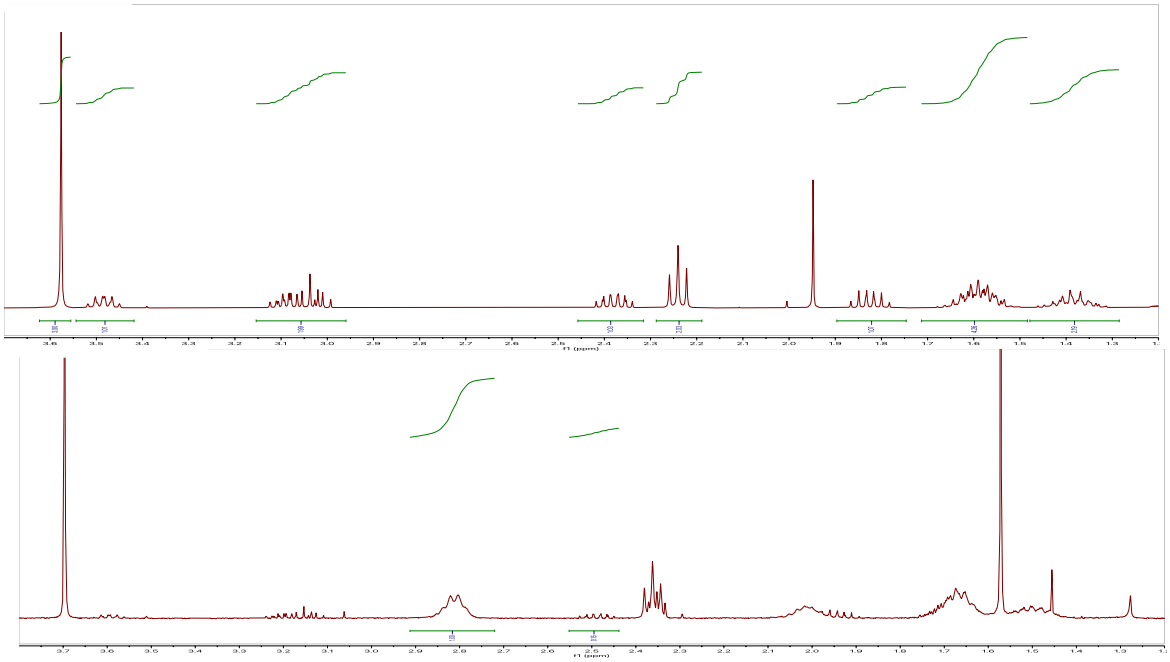


Figure S5. Photography of ATR-FTIR setup used to monitor dithiolanes homopolymerization conversion and thermal reversibility.

(a)



(b)

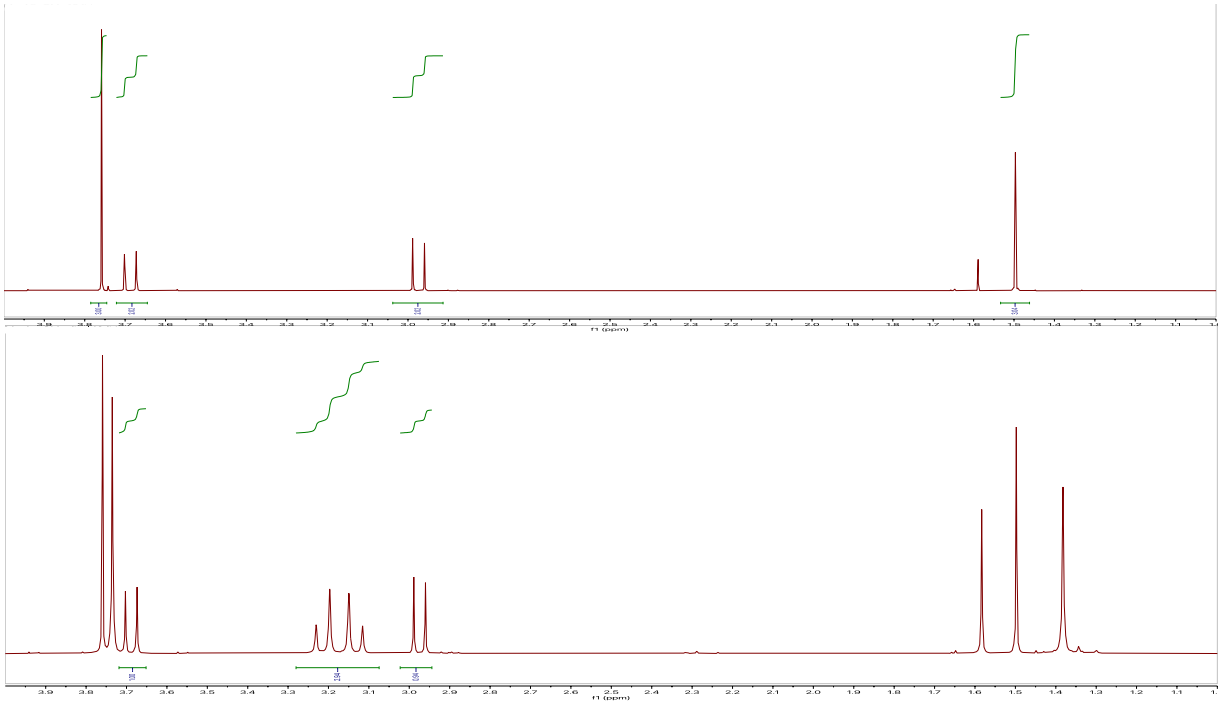
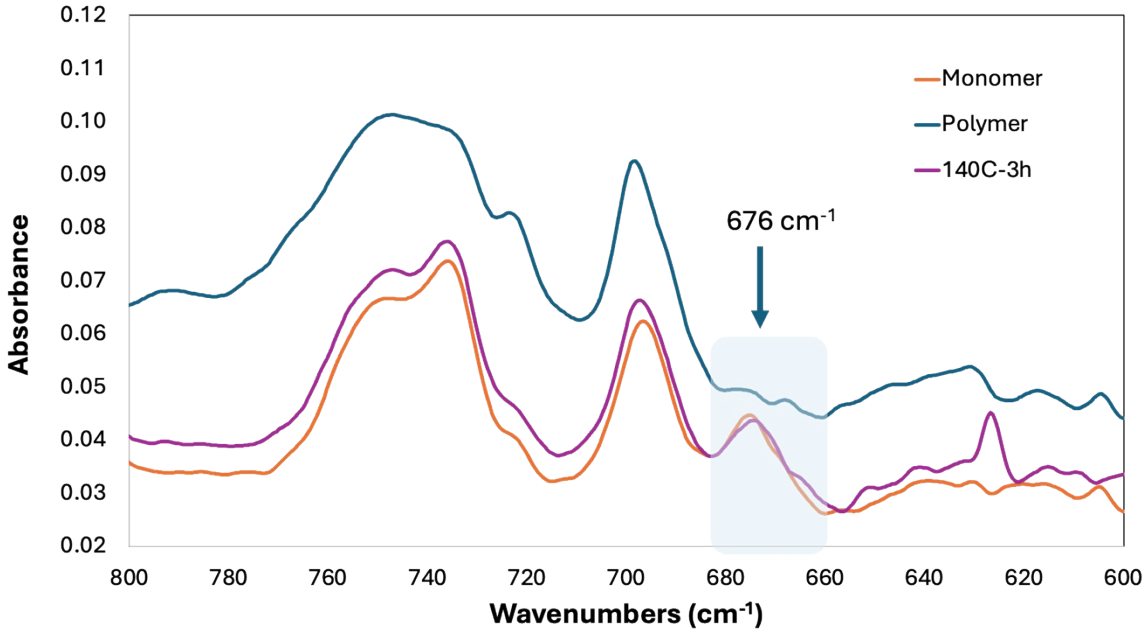


Figure S6. ^{1}H NMR for LipOMe (a) and Me-AspOMe (b) before and after polymerization.

(a)



(b)

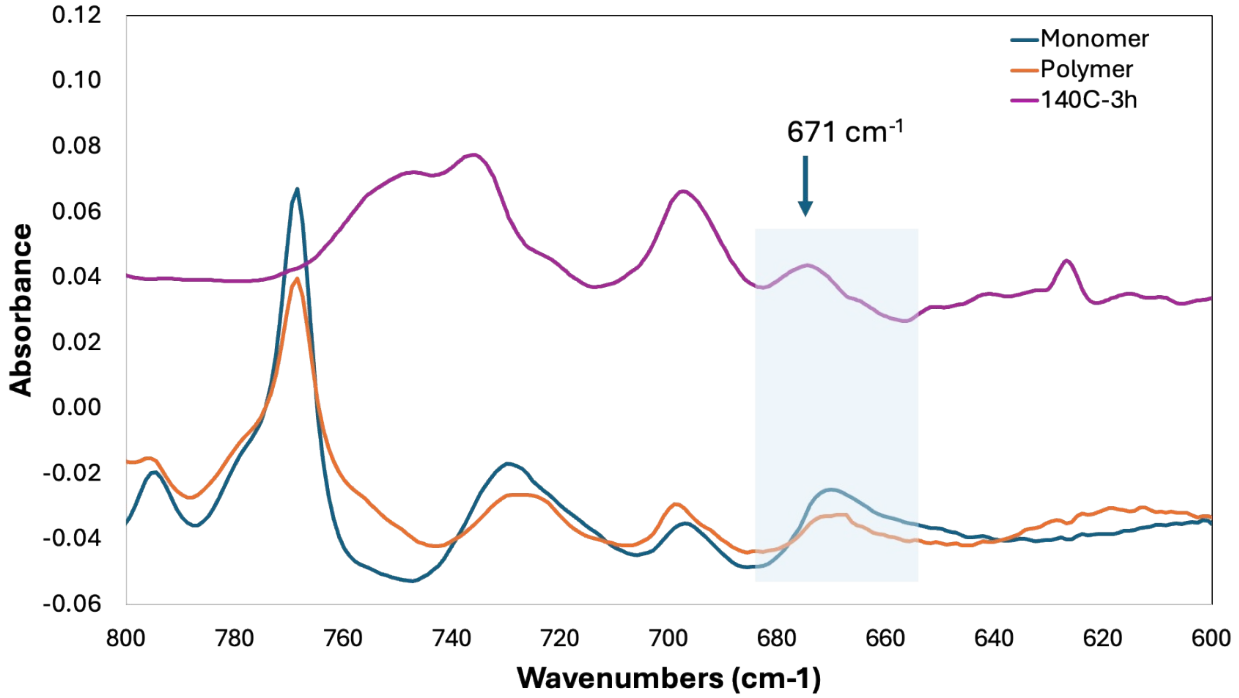


Figure S7. FTIR spectra region between 800-500 cm^{-1} for LipOMe (a) and Me-AspOMe (b) before, after polymerization, and after heating 140 ^{o}C for 3 h.

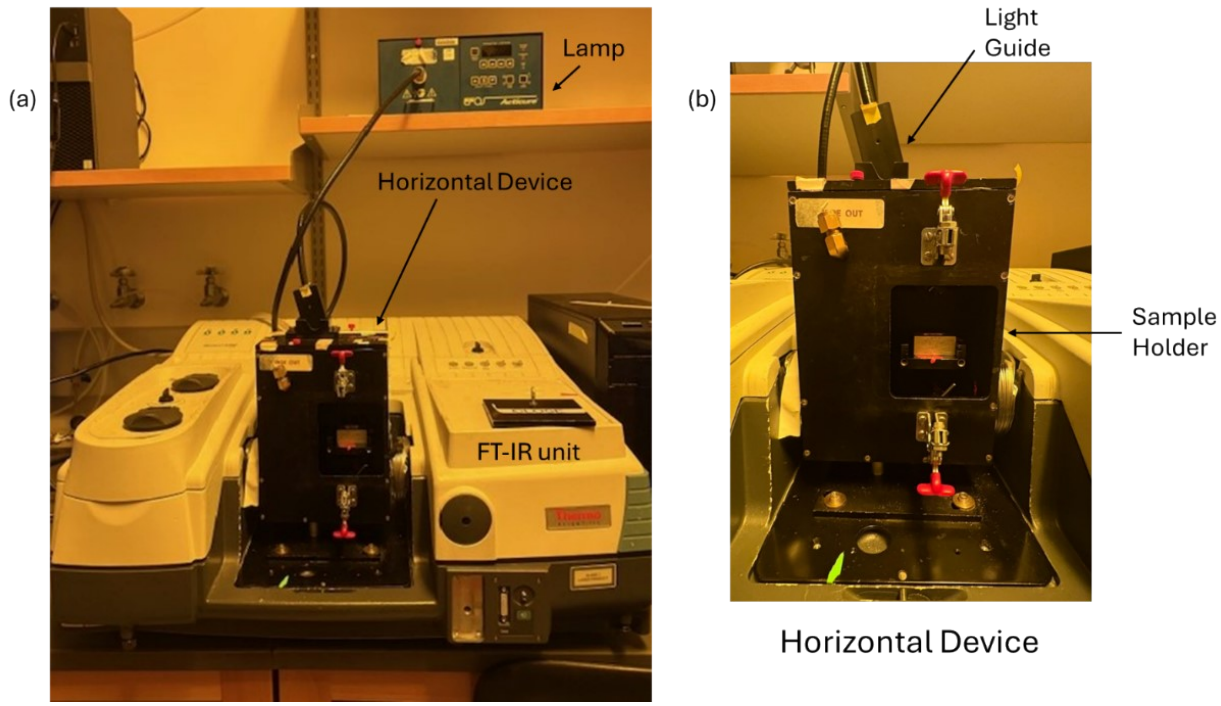
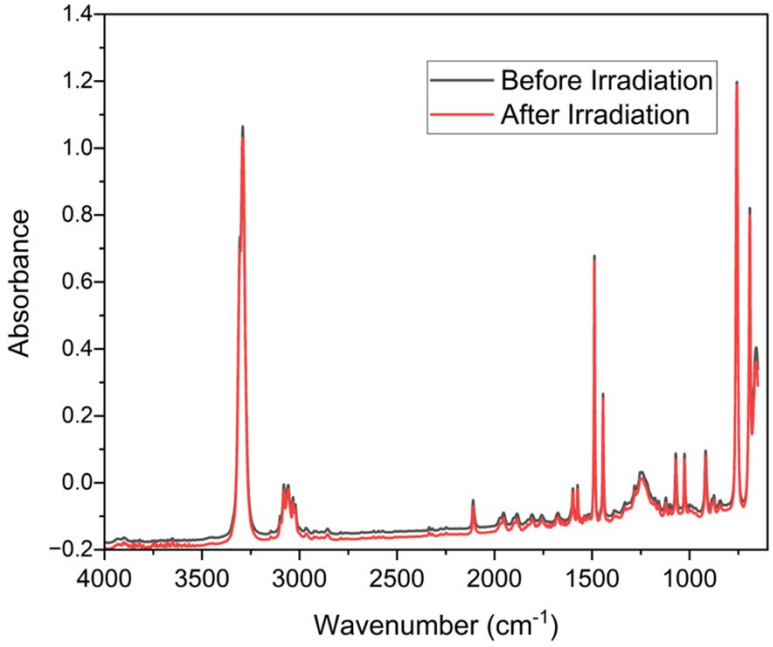
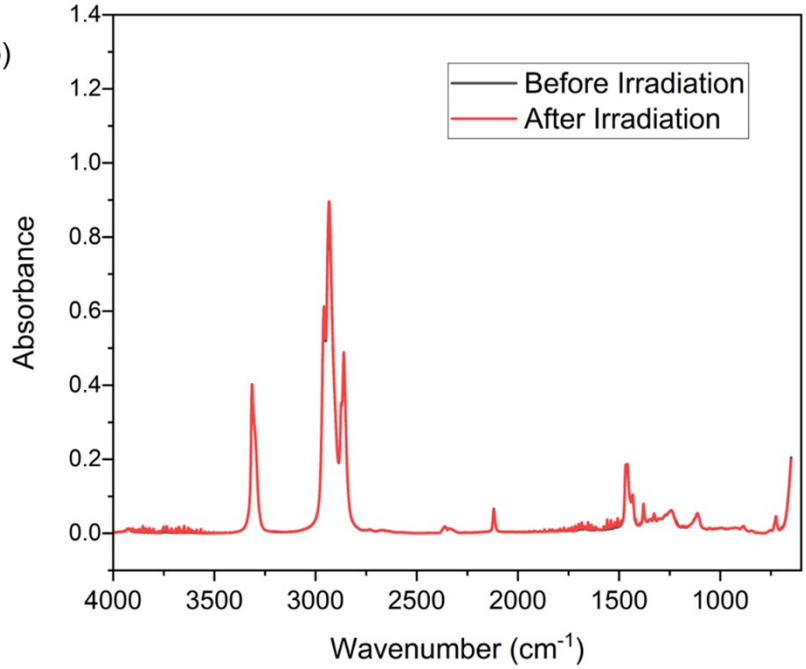


Figure S8. (a) Photographs of the equipment and experimental setup (in-house fabricated horizontal attachment) used to monitor the copolymerization of dithiolane-ynes in real time. (b) View of the horizontal device with the front door removed allows the sample to be placed in the horizontal position on top of the sample holder (silver block). [1]

(a)


Before Irradiation
After Irradiation
Absorbance
Wavenumber (cm-1)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
−0.2
4000
3500
3000
2500
2000
1500
1000

(b)


Before Irradiation
After Irradiation
Absorbance
Wavenumber (cm-1)
1.4
1.2
1.0
0.8
0.6
0.4
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0.0
4000
3500
3000
2500
2000
1500
1000

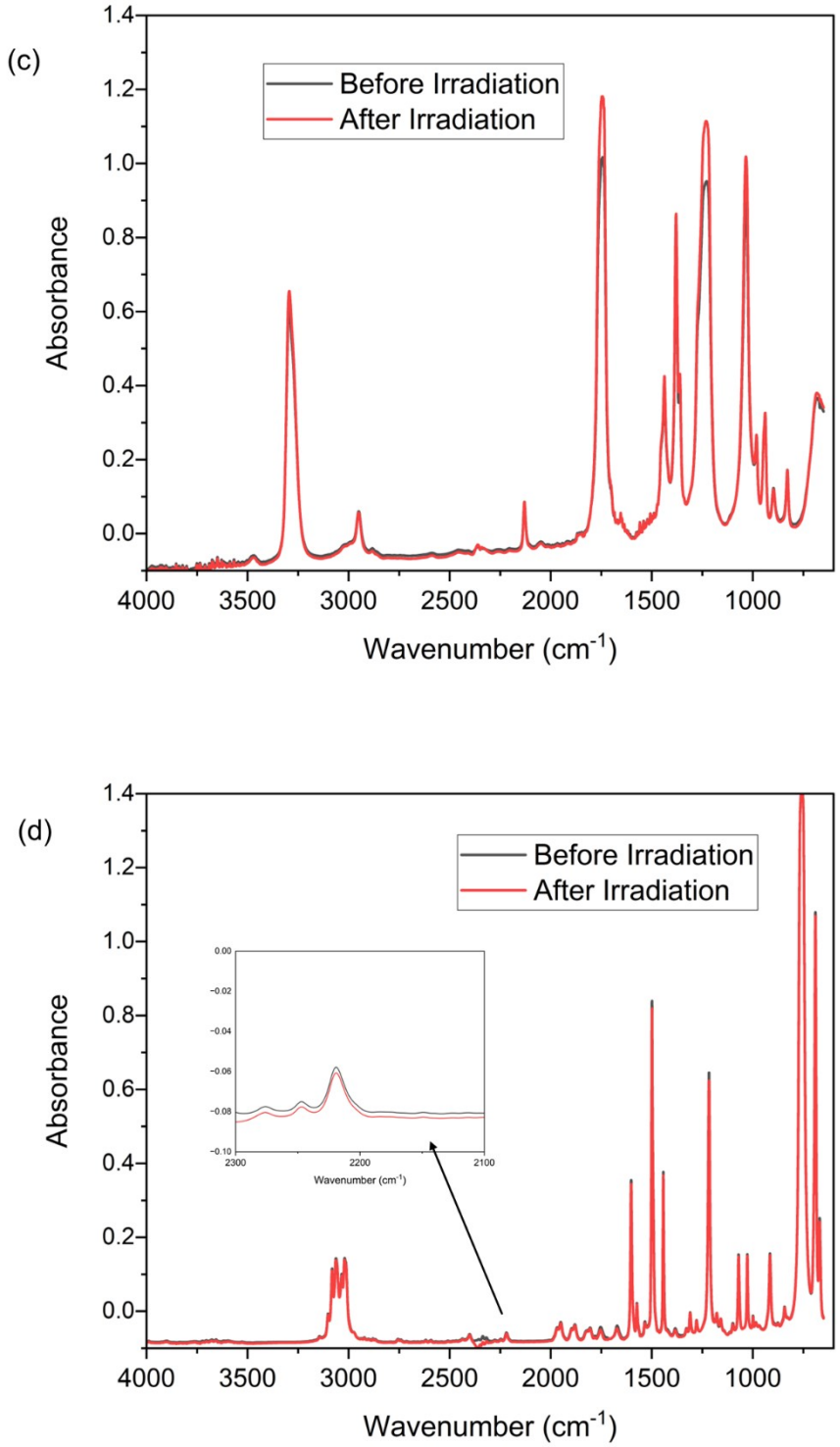
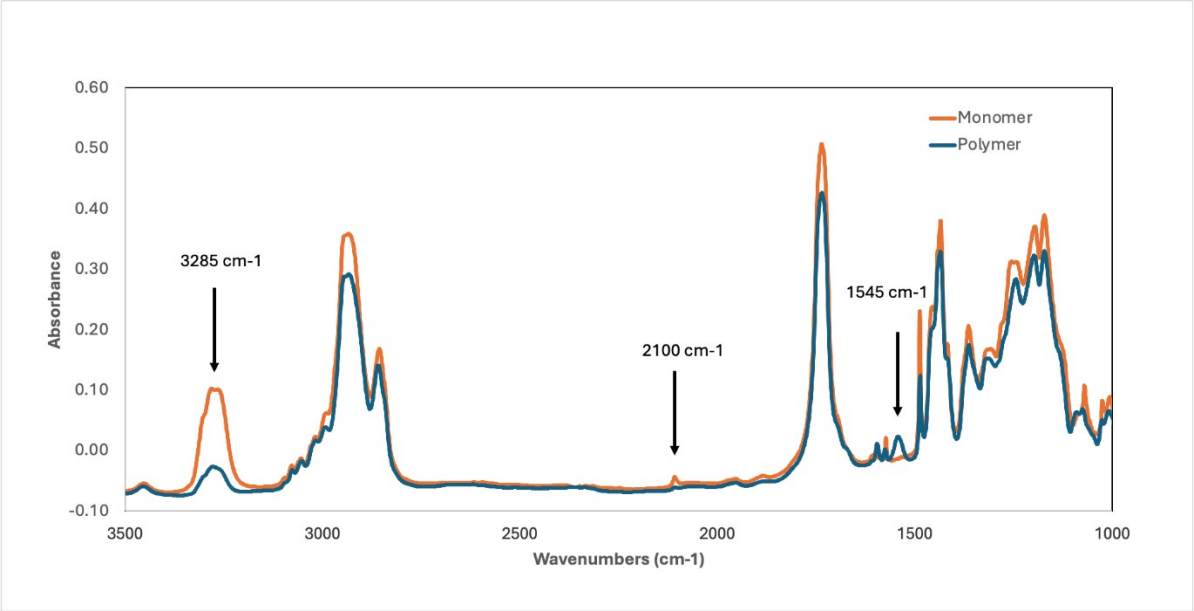


Figure S9. FTIR spectra before and after photopolymerization for (a) phenylacetylene, (b) 1-octyne, (c) propargyl acetate, and (d) diphenylacetylene. Photopolymerization reactions were carried out with filtered light (400-500 nm) for 600 s at 40 mW/cm^2 light intensity.



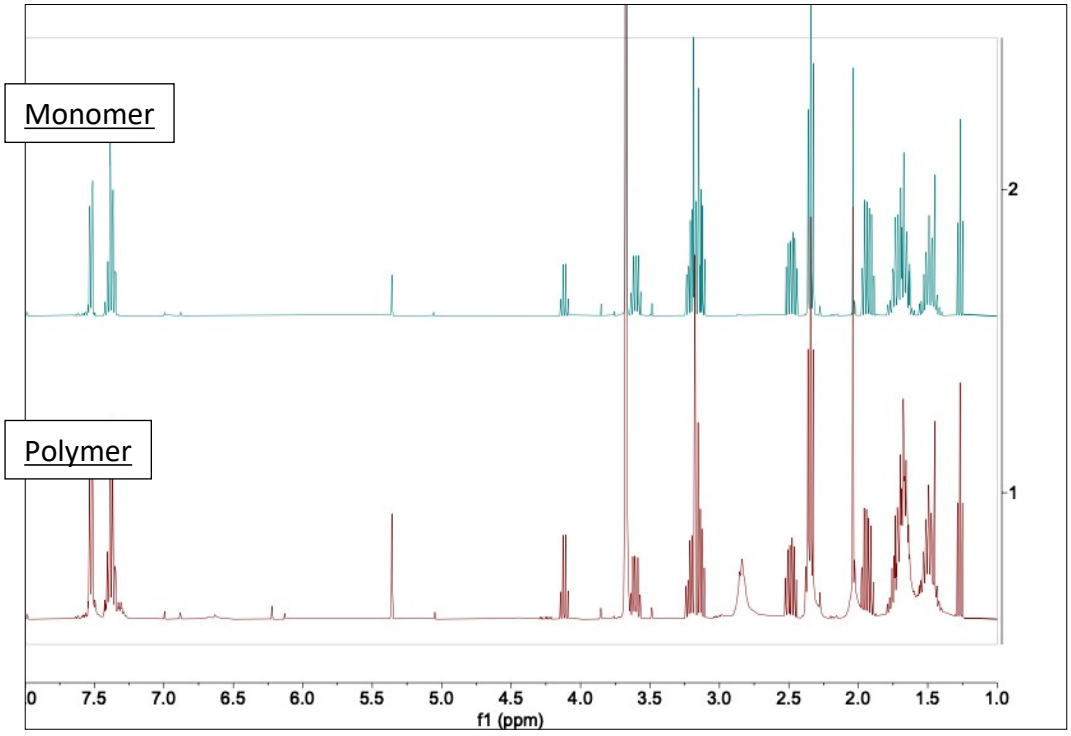


Figure S10. FTIR and ^{1}H NMR for LipOMe:Phenylacetylene 2:1 ratio before and after polymerization

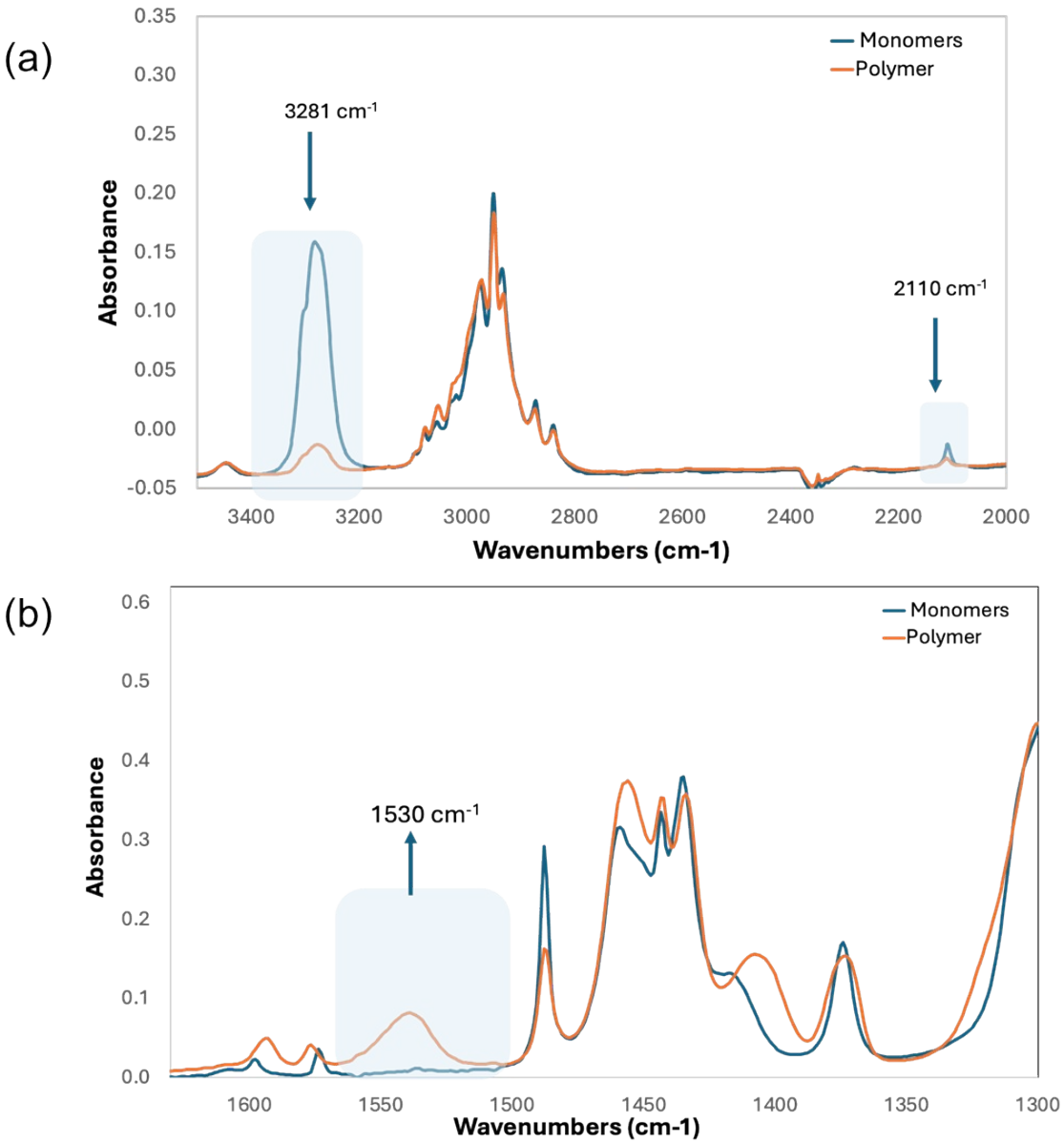


Figure S11. FTIR spectra for copolymerization of Me-AspOMe: phenylacetylene (2:1 ratio) before and after polymerization (a) Region 3500-2000 cm^{-1} and (b) Region 1650-1300 cm^{-1} (400-500 nm filtered light, 40 mW/cm^2, 600 s).

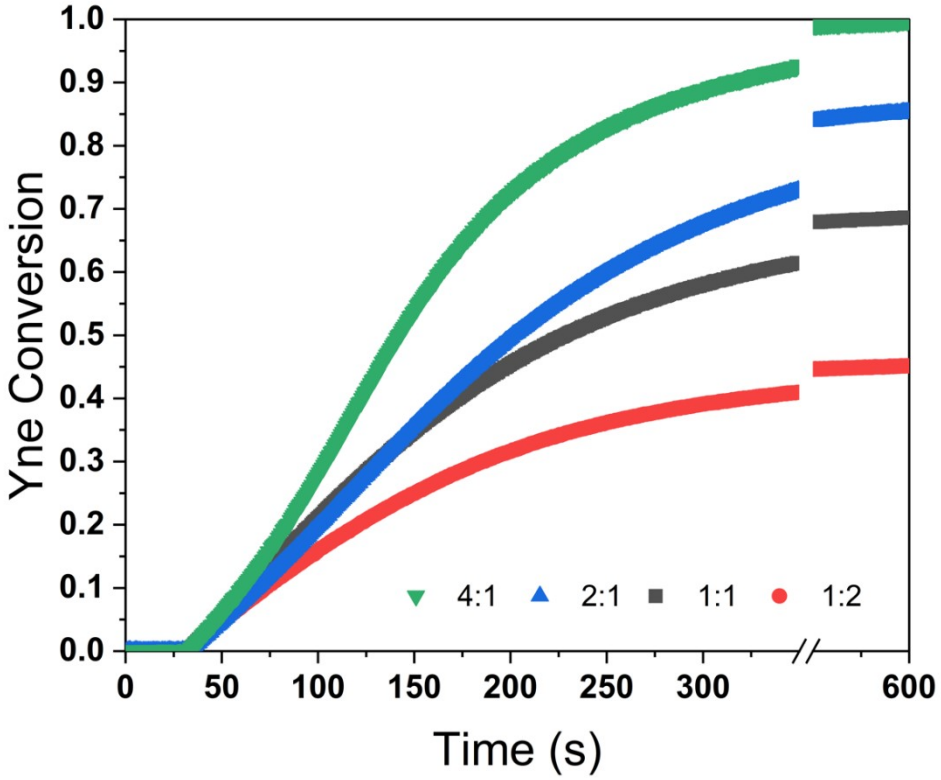


Figure S12. FTIR conversion versus time plots for alkyne reactive groups. a) Me-AspOMe:phenylacetylene, for molar ratios dithiolane:yne = 1:1 (**black squares**), dithiolane:yne = 1:2 (**red circle**), dithiolane:yne = 2:1 (**blue triangles**), dithiolane:yne = 4:1 (**green triangles**). Photopolymerization conditions: 405-500 nm filtered light, 40 mW/cm^2, 600s.

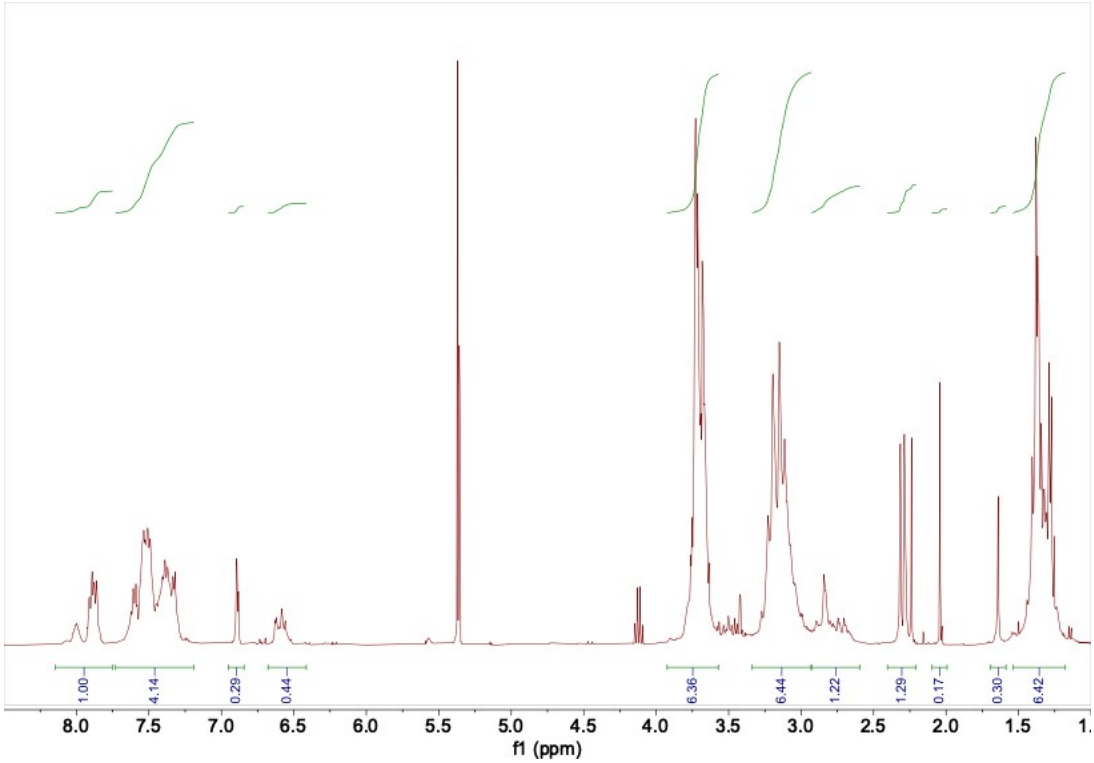


Figure S13. ^{1}H NMR for fraction 2 isolated from photopolymerization of Me-AspOMe: phenylacetylene (2:1) corresponding to the polymer formed. Here, peaks found between 8.0–7.5 ppm corroborated the presence of phenyl rings, while signals at 3.7–3.5 ppm, 3.3–3.0 ppm, and 1.5–1.2 ppm ranges correspond to CH_2 and CH_3 groups associated with the opening of the dithiolane ring. It is noteworthy to mention the peak around 6.5 ppm, which is attributed to the presence of a vinyl sulfide unit within the polymer chain, can also be identified.

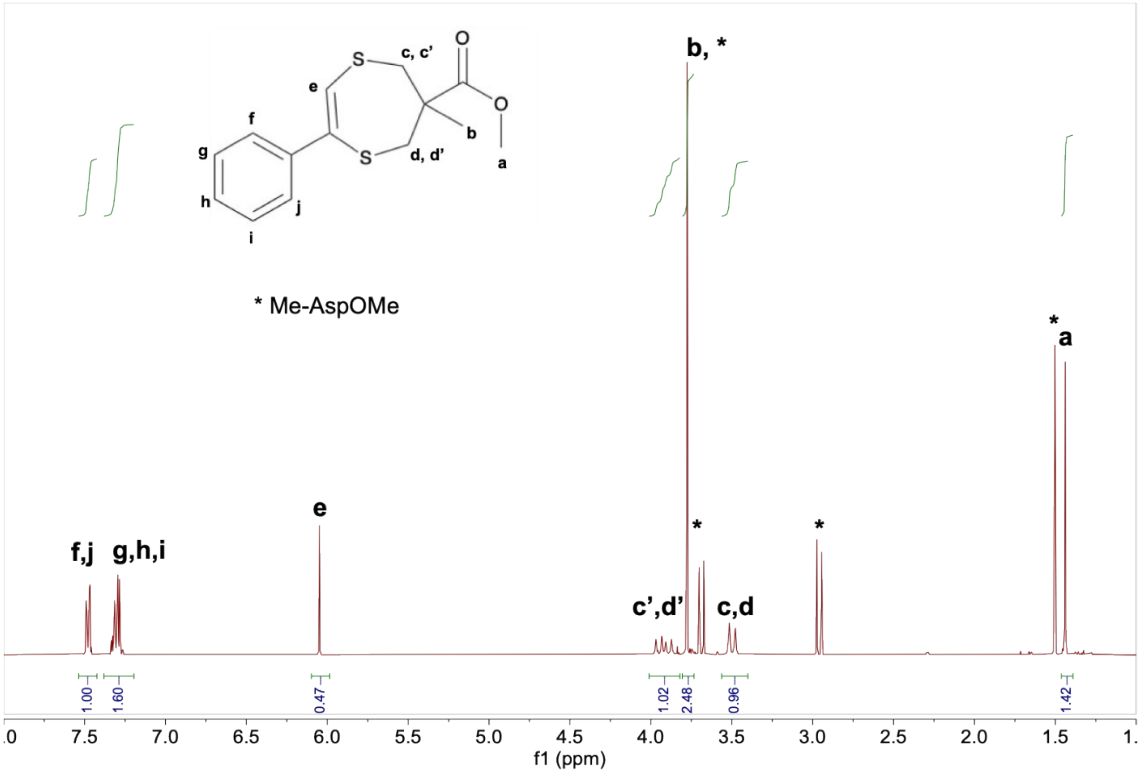


Figure S14. ^{1}H NMR for fraction 1 isolated from photopolymerization of Me-AspOMe:phenylacetylene (2:1) showing a peak at δ = 6.09 ppm corresponding to vinyl sulfide intermediate.

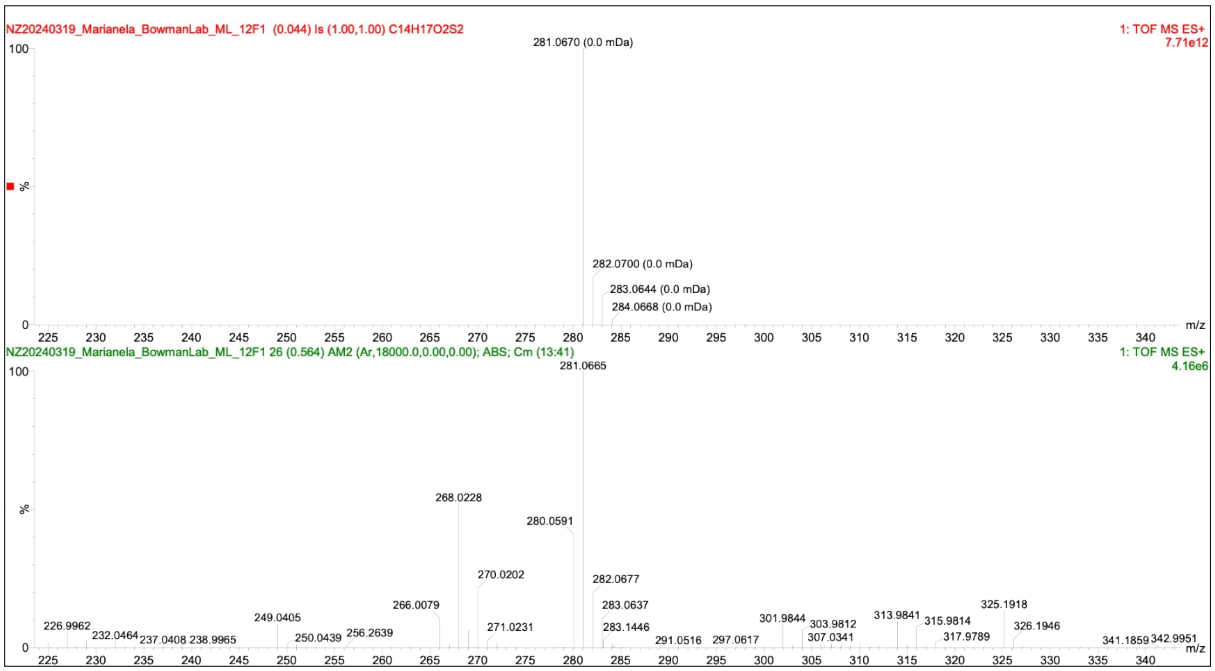
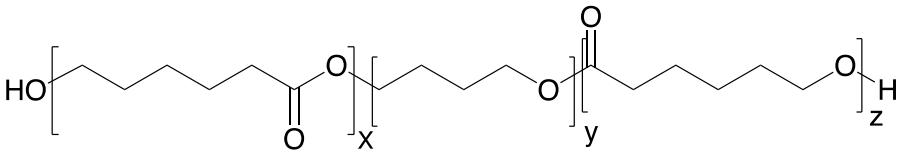
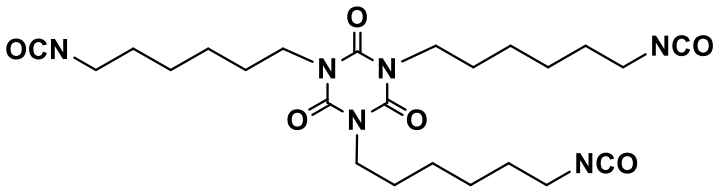


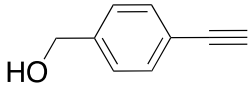
Figure S15. LC-MS results for fraction 1 isolated from photopolymerization of Me-AspOMe:phenylacetylene (2:1).



PCL-b-PTHF-b-PCL 2000



TNCO



4-Ethynylbenzyl alcohol

Figure S16. Components of matrix used for holography films.

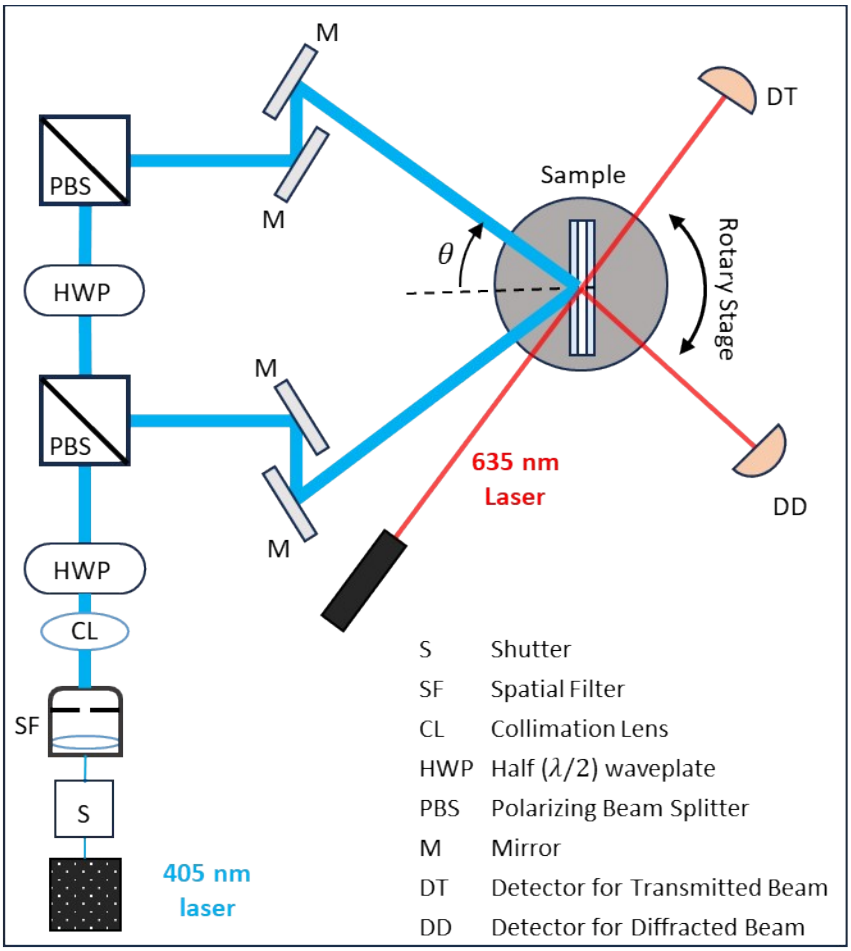


Figure S17. Schematic representation of the holographic optical setup.

Table S1. Conversion for LipOMe and Me-AspOMe was obtained from FTIR and 1H NMR, and the percentage of monomers recovered after heating at 140°C for 3 hours. GPC for poly(LipOMe) and poly(Me-AspOMe). Refractive indices for the dithiolanes monomers and their homopolymers and Δn values. Samples were polymerized in bulk, 40 Mw/cm^2 light, filtered 400-500nm for 600s.

Property	LipOMe	Me-AspOMe
Conversion (ATR FT-IR)	92±2%	75±2%
Conversion (^{1}H NMR)	87±3%	75±3%
% Monomer recovered after heating	84%	10%
Mn (KDa)	14.7	12.0
Mw (KDa)	17.8	14.7
Đ	1.21	1.23
n_D (589nm, 20°C) Monomer	1.512	1.523
n_D (589nm, 20°C) Polymer	1.530	1.566
Δn	0.02	0.04

Table S2. Values of area peak obtained by FT-IR for LipOMe and Me-AspOMe before, after polymerization, and after heating the polymers. Percentages of conversion and monomer recovered. Photopolymerization reactions were initiated with 40 mW/cm^2 light, filtered at 400 – 500 nm. Samples were photoactivated with 1 wt% TPO photoinitiator.

Compound	Initial Area	Final Area	Conversion	Area of Monomer Recovered	% Monomer Recovered
LipOMe	0.1226	0.0126	90%	0.1054	84%
Me-AspOMe	0.0650	0.0160	75%	0.0210	10%

Table S3. Compositions, monomer ratios, alkynes final conversions by FTIR (verified by ^{1}H NMR for terminal alkynes), polymerization rates from Conversion versus time plots obtained by FTIR, and LipOMe conversion obtained by ^{1}H NMR (representative samples). All samples were irradiated between KBr discs with a light intensity of 40mW/cm^2, with 450 ± 500 nm filtered light for 600 s.

Composition	Ratio	% Yne Conversion (FTIR)	Reaction Rate (s^{-1}) x 10^{-3}	% Dithiolane Conversion (^{1}H NMR)
LipOMe:phenylacetylene	4:1	95 ± 1	11	91 ± 2
LipOMe:phenylacetylene	2:1	77 ± 1	09	90 ± 2
LipOMe:phenylacetylene	1:1	55 ± 1	06	89± 2
LipOMe:phenylacetylene	1:2	32 ± 1	03	92 ± 2
LipOMe:1-octyne	4:1	71 ± 1	08	/
LipOMe:1-octyne	2:1	62 ± 1	05	91 ± 2
LipOMe:1-octyne	1:1	36 ± 1	04	/
LipOMe:1-octyne	1:2	24 ± 1	03	/
LipOMe:propargyl acetate	4:1	46 ± 3	05	/
LipOMe:propargyl acetate	2:1	40 ± 1	04	77
LipOMe:propargyl acetate	1:1	21 ± 3	03	/
LipOMe:propargyl acetate	1:2	17 ± 3	02	/
LipOMe:diphenylacetylene	4:1	56 ± 2	13	/
LipOMe:diphenylacetylene	2:1	38 ± 1	10	85
LipOMe:diphenylacetylene	1:1	53 ± 3	50	/
LipOMe:diphenylacetylene	1:2	52 ± 2	61	/

Table S4. Formulation composition for LipOMe and ynes, monomer ratios, polymer number average molecular weight (Mn), dispersity (Đ), indices of refraction for unreacted monomer formulations and the resulting copolymers, and the difference between those indices. Mn and Đ obtained via GPC. Refractive index measurements were taken at the wavelength (λ) of 589 nm using an Abbe refractometer.

Composition	Ratio	Mn (kDa)	Đ	n_D Unreacted	n_D Polymer	Δn
LipOMe:phenylacetylene	4:1	16.4	1.28	1.508	1.559	0.05
LipOMe:phenylacetylene	2:1	18.7	1.33	1.506	1.547	0.04
LipOMe:phenylacetylene	1:1	20.0	1.40	1.505	1.545	0.04
LipOMe:phenylacetylene	1:2	15.3	1.30	1.502	1.519	0.02
LipOMe:1-octyne	4:1	10.5	1.29	1.517	1.528	0.01
LipOMe:1-octyne	2:1	15.3	1.23	1.501	1.517	0.01
LipOMe:1-octyne	1:1	11.2	1.27	1.491	1.505	0.01
LipOMe:1-octyne	1:2	10.5	1.27	1.466	1.477	0.01
LipOMe:propargyl acetate	4:1	16.7	1.28	1.495	1.511	0.02
LipOMe:propargyl acetate	2:1	19.6	1.29	1.506	1.534	0.02
LipOMe:propargyl acetate	1:1	16.8	1.39	1.515	1.542	0.03
LipOMe:propargyl acetate	1:2	14.1	1.31	1.508	1.540	0.03
LipOMe:diphenylacetylene	4:1	7.5	1.44	1.530	1.600	0.07
LipOMe:diphenylacetylene	2:1	10.6	1.48	1.514	1.584	0.07
LipOMe:diphenylacetylene	1:1	8.1	1.52	1.596*	/	/
LipOMe:diphenylacetylene	1:2	6.3	1.65	1.612*	/	/

*Waxy/Crystalline Material

Table S5. Formulation composition for Me-AspOMe and alkynes, monomer ratios, polymer number average molecular weight (Mn), dispersity (Đ), indices of refraction for unreacted monomer formulations and the resulting copolymers, and the difference between those indices. Mn and Đ obtained by GPC. Refractive index measurements were taken at the wavelength (λ) of 589 nm using an Abbe refractometer.

Composition	Ratio	Mn (KDa)	Đ	n_D Unreacted	n_D Polymer	Δn
Me-AspOMe:phenylacetylene	4:1	9.9	1.32	1.528	1.583	0.06
Me-AspOMe:phenylacetylene	2:1	13.0	1.43	1.532	1.588	0.06
Me-AspOMe:phenylacetylene	1:1	9.0	1.23	1.502	1.560	0.06
Me-AspOMe:phenylacetylene	1:2	9.0	1.19	1.506	1.557	0.05
Me-AspOMe:1-octyne	2:1	8.0	1.15	1.500	1.513	0.01
Me-AspOMe:propargyl acetate	2:1	8.0	1.15	1.505	1.518	0.01
Me-AspOMe:diphenylacetylene	2:1	8.0	1.19	1.548	1.598	0.05

Table S6. Compositions, monomer ratios, alkynes final conversions by FTIR (verified by ^{1}H NMR for terminal alkynes), polymerization rates from conversion versus time plots obtained by FTIR, and Me-AspOMe conversion obtained by ^{1}H NMR (representative samples). All samples were irradiated between KBr discs with a light intensity of 40mW/cm^2, with 450 ± 500 nm filtered light for 600 s.

Composition	**Ratio**	**% Yne Conversion by FT-IR**	**Reaction Rate (s^{-1}) x 10^{-3}**	**% Dithiolane Conversion by ^{1}H NMR**
Me-AspOMe:phenylacetylene	4:1	> 99 ± 1	5	65
Me-AspOMe:phenylacetylene	2:1	86 ± 1	4	58
Me-AspOMe:phenylacetylene	1:1	65± 1	3	61
Me-AspOMe:phenylacetylene	1:2	58 ± 1	1	78
Me-AspOMe:1-octyne	2:1	79± 1	3	76
Me-AspOMe:propargyl acetate	2:1	14 ± 3	2	49
Me-AspOMe:diphenylacetylene	2:1	10 ± 1	5	2