

Supporting Information

Title: Photopatternable, Degradable, and Performant Polyimide Network Substrates for E-Waste Mitigation

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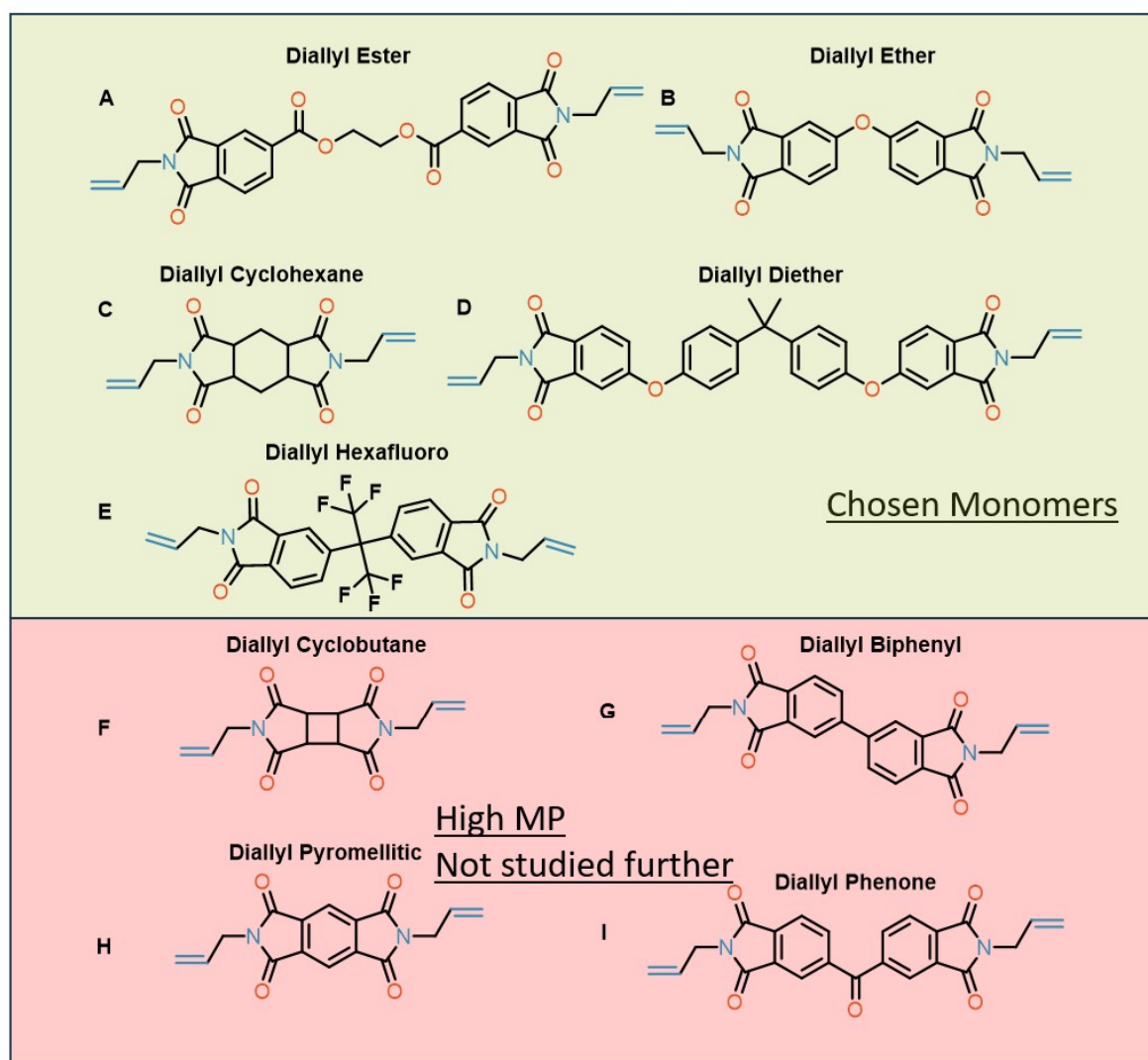
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1. Experimental Section

1.1 Materials

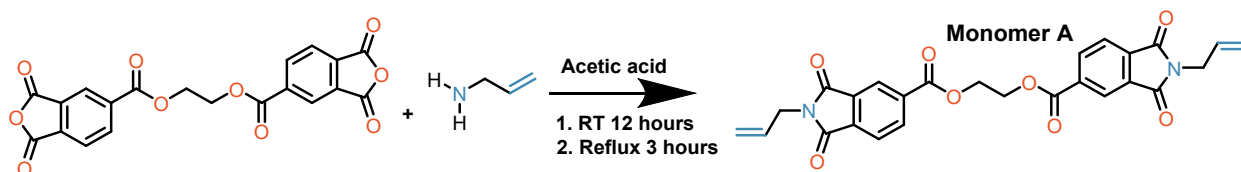
Trimethylolpropane tris(3-mercaptopropionate) (TMPMP), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), 4,4'-oxydiphthalic anhydride, 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride), cyclobutane-1,2,3,4-tetracarboxylic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic dianhydride, and 3,3',4,4'-biphenyltetracarboxylic dianhydride were purchased from Sigma Aldrich. Ethane-1,2-diyl bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) and 1,2,4,5-cyclohexanetetracarboxylic dianhydride were purchased from Ambeed. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride was purchased from Matrix Scientific. Eutectic gallium indium (EGaIn) (75 wt. % Ga, 25 wt. % In) was purchased from Indium Corp. Electrical components including 3V CR2032 battery, battery holder, LED light, and 50 Ohms resistor were purchased from DigiKey.

1.2 Monomer synthesis

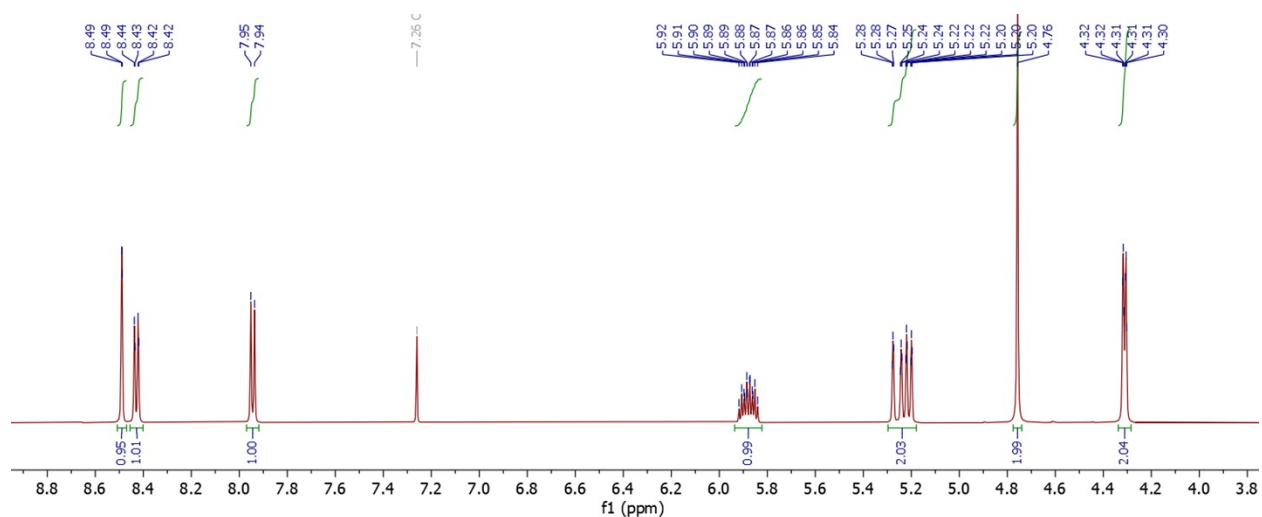


Scheme S1. Structures of the nine different diallyl imide containing monomers synthesized. F-I monomers were found with prohibitively high melting points that were impractical to use as solventless resins.

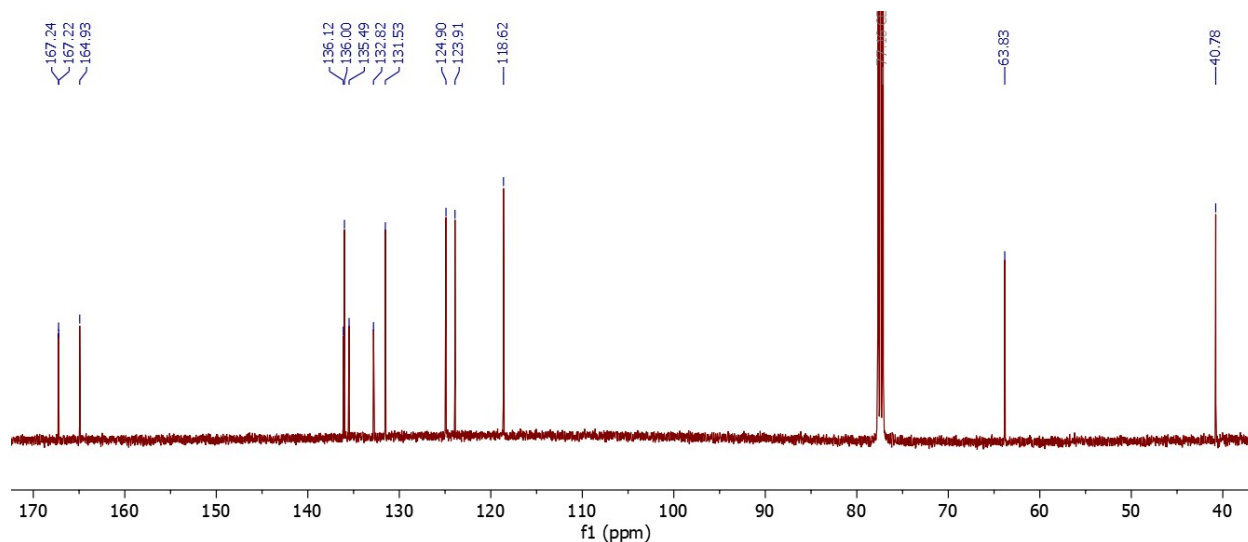
1.2.1 Synthesis of the diallyl imide ester (monomer A)



In a 1L round bottom flask 20 grams (48.7 mmol) of ethane-1,2-diyl bis(1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) was suspended in 250 mL of acetic acid. The mixture was stirred while 7.3 mL (97.5 mmol) of allyl amine was added dropwise to the solution. The flask was stirred for 12 hours with mixture becoming clear. The mixture was then refluxed for 3 hours with any remaining solids dissolved. The flask was then cooled to room temperature and 250 mL of DI water added. The flask was again warmed to reflux or until solids were dissolved. Once the flask was cooled back to room temperature solids were filtered, rinsed with DI water. Solids were recrystallized with 250 mL of acetone and dried under vacuum at 80 °C for 12 hours to give an off-white powder (20.0 g). Yield: 84%. Melting Point (M.P.) 112 °C. Fourier transform infrared (FTIR) (ATR): $\nu = 3078, 2982, 2914$ (C-H), 1778, 1722, 1700 (C=O), 1626 (C=C), 1480, 1423, 1393, 1335, 1271 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 2H), 8.43 (d, $J = 7.7$ Hz, 2H), 7.94 (d, $J = 7.7$ Hz, 2H), 5.88 (m, 2H), 5.30 – 5.18 (m, 4H), 4.76 (s, 4H), 4.31 (d, $J = 5.8$ Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.99, 164.68, 135.89, 135.75, 135.25, 132.58, 131.28, 124.66, 123.67, 118.38, 63.59, 40.54.

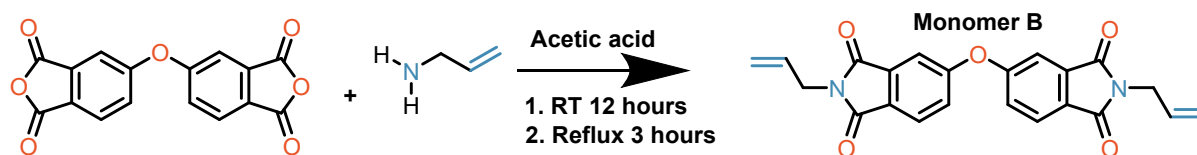


^1H NMR (500 MHz, CDCl_3 -d) spectrum of ester monomer A

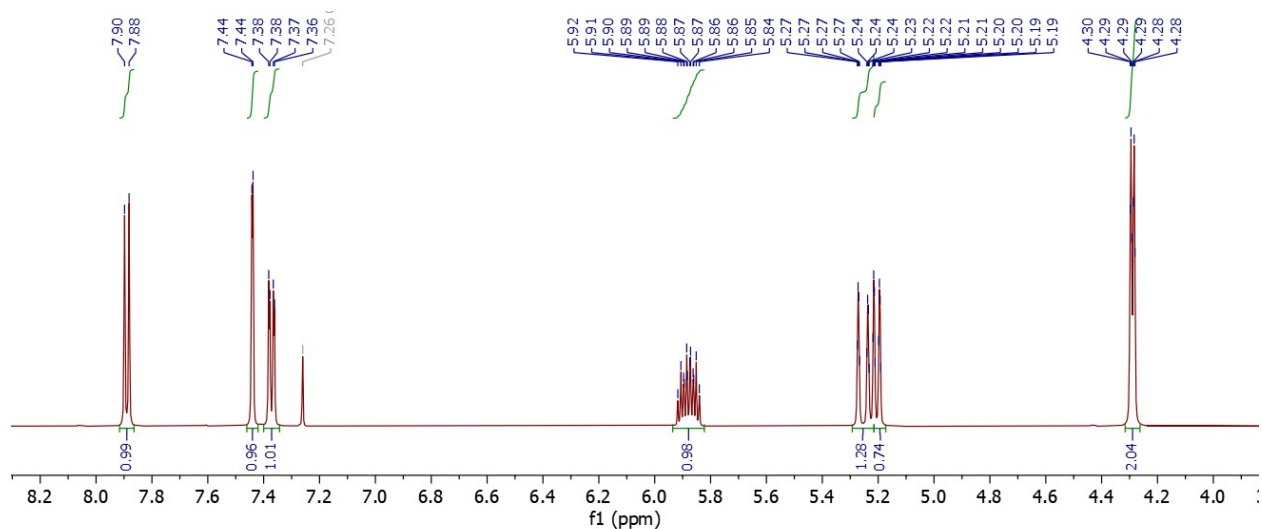


^{13}C NMR (126 MHz, $\text{CDCl}_3\text{-d}$) spectrum of ester monomer A

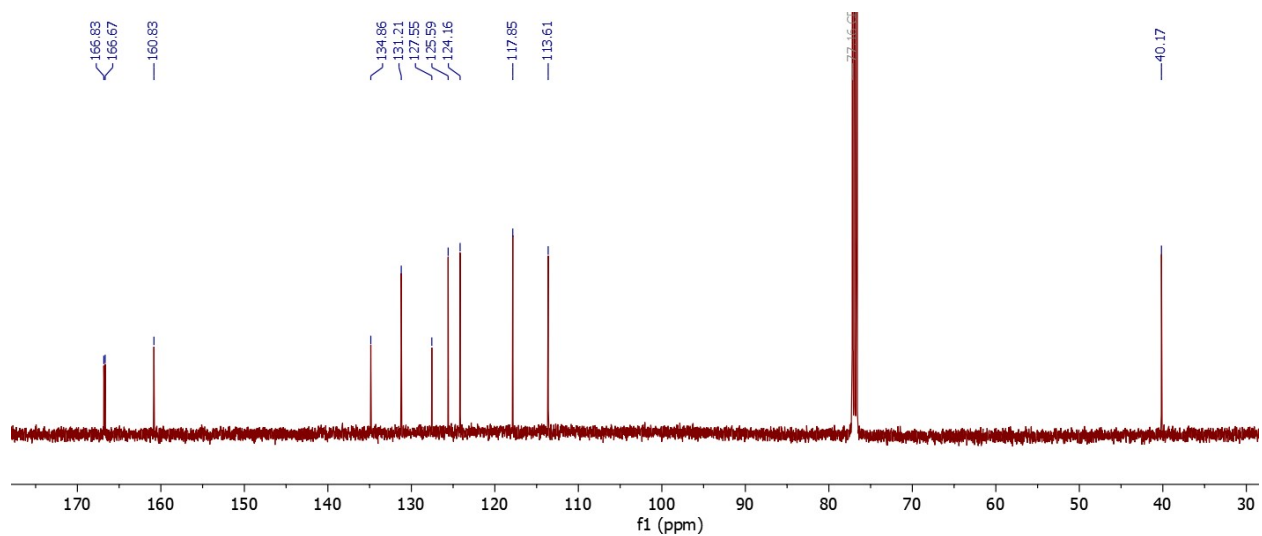
1.2.2 Synthesis of the diallyl imide ether (monomer B)



In a 1L round bottom flask 20 grams (64.5 mmol) of 4,4'-Oxydiphthalic anhydride was suspended in 250 mL of acetic acid. The mixture was stirred while 9.65 mL (129 mmol) of allyl amine was added dropwise to the solution. The flask was stirred for 12 hours with mixture becoming clear. The mixture was then refluxed for 3 hours with any remaining solids dissolved. The flask was then cooled to room temperature and 250 mL of DI water added. The flask was again warmed to reflux or until solids were dissolved. Once the flask was cooled back to room temperature solids were filtered, rinsed with DI water. Solid was recrystallized in 150 mL of acetone and dried under vacuum at 80 °C for 12 hours to give a white powder (19.8 g). Yield: 91%. M.P. 150 °C. Fourier transform infrared (FTIR) (ATR): $\nu = 3079, 3031, 2987, 2924$ (C-H), 1768, 1700, (C=O), 1605 (C=C), 1475, 1422, 1384, 1360, 1270 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.1$ Hz, 2H), 7.44 (s, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 5.88 (m, 2H), 5.25 – 5.20 (m, 4H), 4.29 (d, $J = 5.6$ Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.34, 167.18, 161.34, 135.37, 131.72, 128.06, 126.10, 124.67, 118.36, 114.12, 40.67.

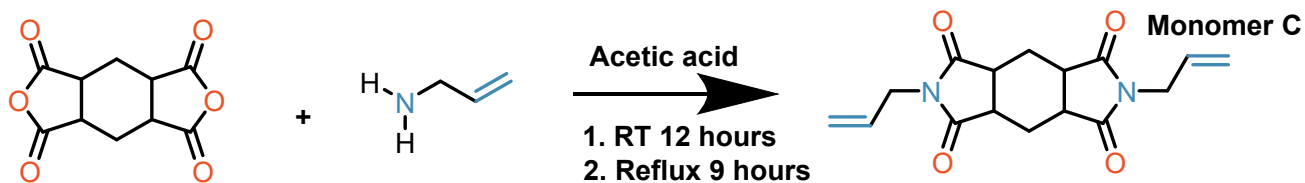


¹H NMR (500 MHz, CDCl₃-d) spectrum of ether monomer B



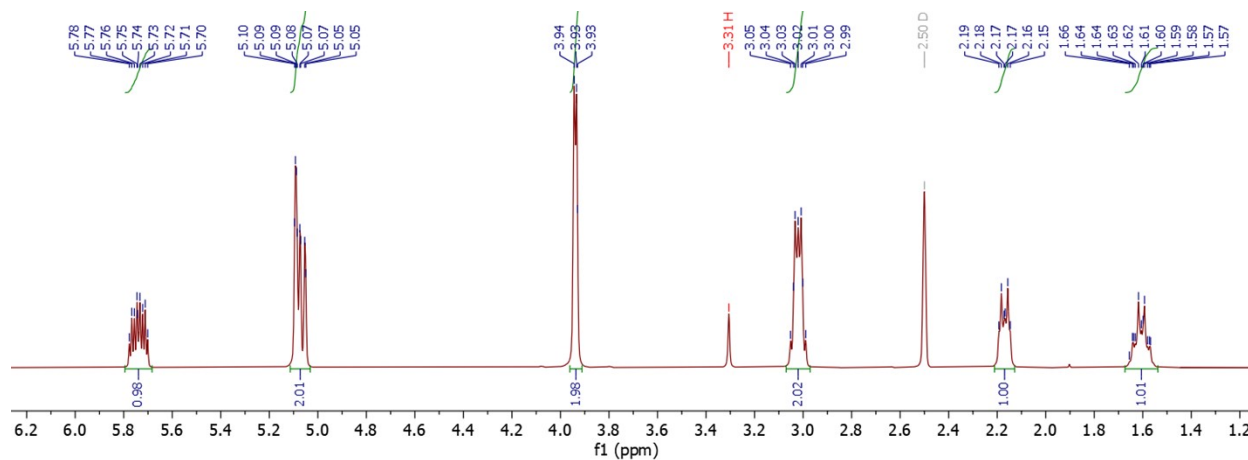
¹³C NMR (126 MHz, CDCl₃-d) spectrum of ether monomer B

1.2.3 Synthesis of diallyl imide cyclohexane (monomer C)

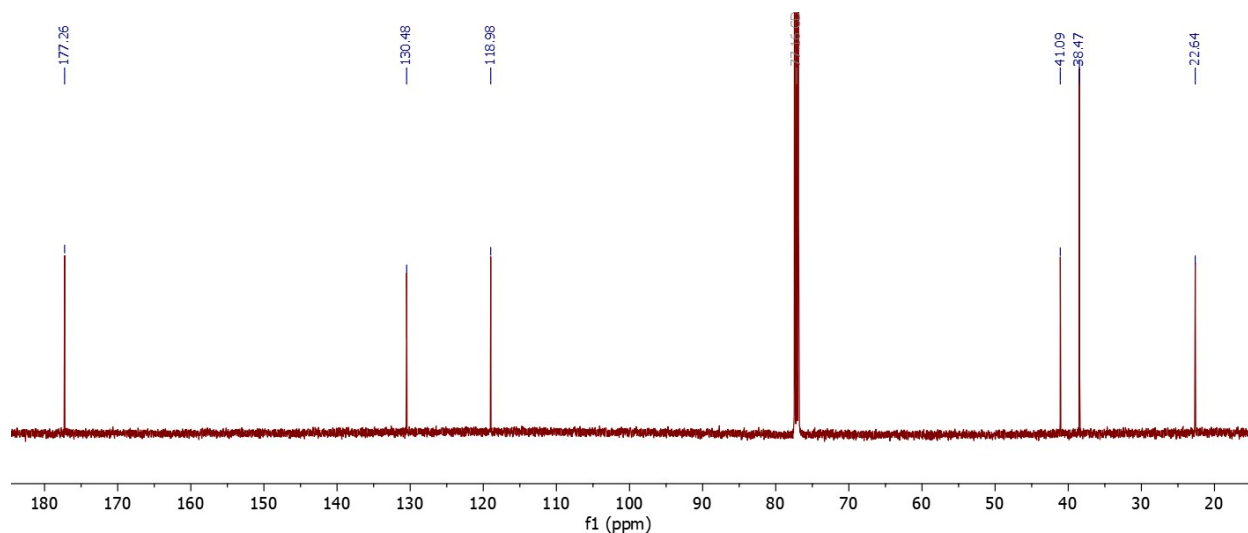


In a 1L round bottom flask 20 grams (102 mmol) of 1,2,4,5-Cyclohexanetetracarboxylic dianhydride was suspended in 200 mL of DMF. The mixture was stirred while 15.65 mL (204 mmol) of allyl amine was added dropwise to the solution. The flask was stirred for 12 hours with mixture becoming clear. 200 mL of toluene was added to the mixture. The mixture was then refluxed for 9 hours with any remaining solids dissolved and water and toluene removed using Dean-Stark trap. The remaining toluene and DMF

were removed using rotary evaporation. Viscous oil was dissolved in 150 mL of methanol and crystallized. Crystals were filtered and dried under vacuum at 80 °C for 12 hours to yield white crystals (19.0 g). Yield: 70%. M.P. 148 °C. Fourier transform infrared (FTIR) (ATR): $\nu = 3090, 2977, 2932, 2880$ (C-H), 1762, 1683, 1645 (C=O), 1424, 1388, 1334, 1192 cm^{-1} . ^1H NMR (500 MHz, DMSO- d_6) δ 5.81 – 5.70 (m, 2H), 5.24 – 5.15 (m, 4H), 4.07 (d, $J = 6.1$ Hz, 4H), 2.93 (m, 4H), 2.69 – 2.60 (m, 2H), 1.55 – 1.41 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.01, 130.23, 118.73, 40.84, 38.22, 22.39.

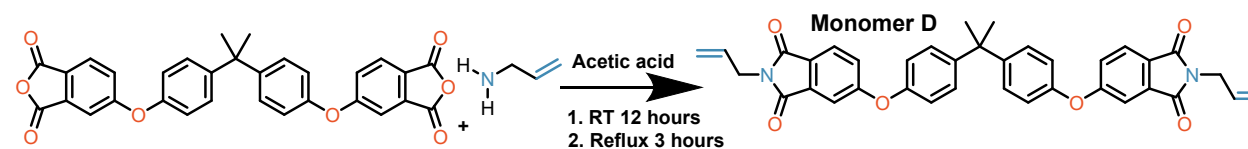


^1H NMR (500 MHz, CDCl_3 - d) spectrum of cyclohexane monomer C

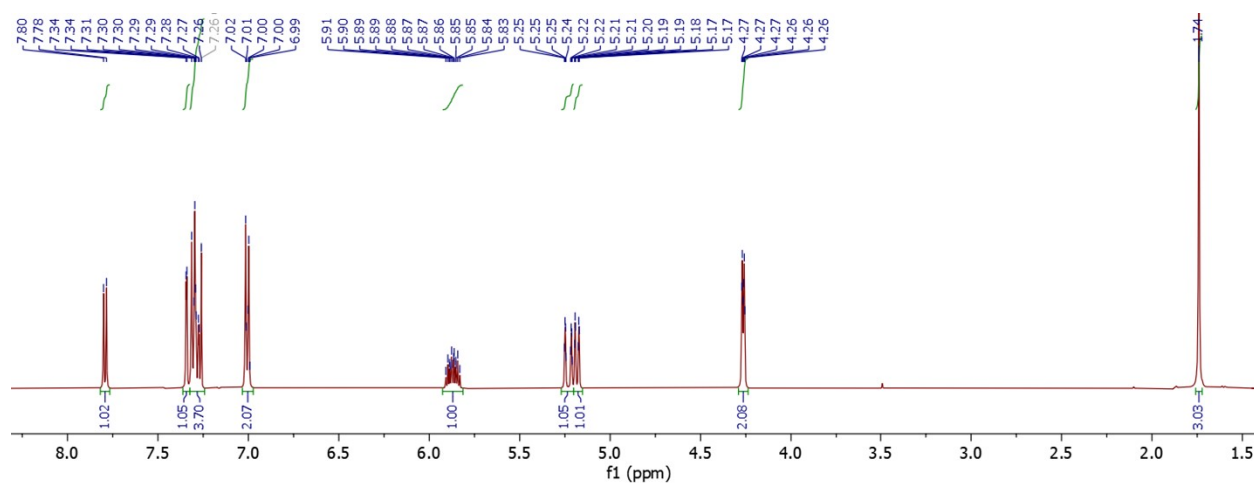


^{13}C NMR (126 MHz, CDCl_3 - d) spectrum of cyclohexane monomer C

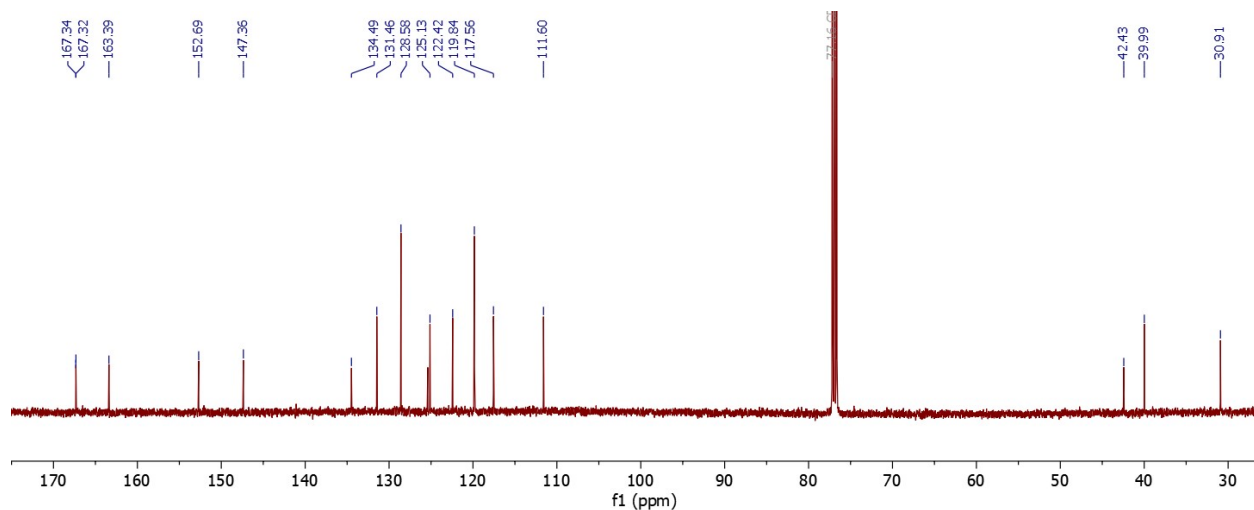
1.2.4 Synthesis of diallyl imide diether (monomer D)



In a 1L round bottom flask 20 grams (38.4 mmol) of 4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride) was suspended in 250 mL of acetic acid. The mixture was stirred while 5.75 mL (76.9 mmol) of allyl amine was added dropwise to the solution. The flask was stirred for 12 hours with mixture becoming clear. The mixture was then refluxed for 3 hours with any remaining solids dissolved. The flask was then cooled to room temperature and 250 mL of DI water added. Solids formed from adding water were filtered, rinsed with DI water. Solid was then recrystallized using 250 mL 1:1 mixture of methanol and acetone mixture and dried under vacuum at 70 °C for 12 hours to yield a off white powder (19.5 g). Yield: 85%. M.P. 94 °C. Fourier transform infrared (FTIR) (ATR): $\nu = 3062, 2965, 2929, 2874$ (C-H), 1770, 1704 (C=O), 1601 (C=C), 1509, 1474, 1433, 1386, 1333 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.79 (d, $J = 8.2$ Hz, 2H), 7.34 – 7.24 (m, 8H), 7.01 (d, $J = 8.3$ Hz, 4H), 5.93 – 5.81 (m, 2H), 5.23 – 5.18 (m, 4H), 4.27 (d, $J = 5.6$ Hz, 4H), 1.74 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 167.59, 163.64, 152.94, 147.62, 134.74, 131.71, 128.83, 125.64, 125.38, 122.67, 120.09, 117.81, 111.85, 42.69, 40.24, 31.16.

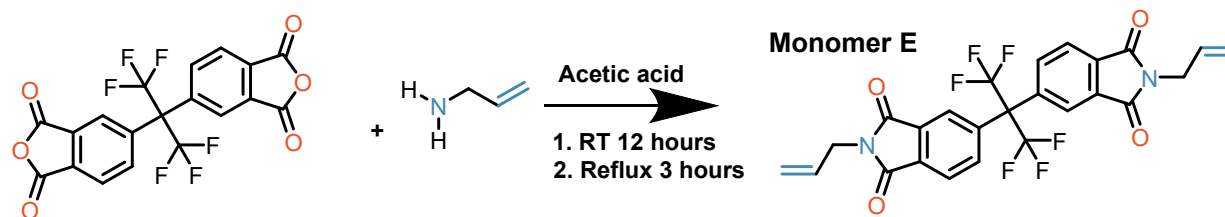


^1H NMR (500 MHz, CDCl_3 -d) spectrum of diether monomer D

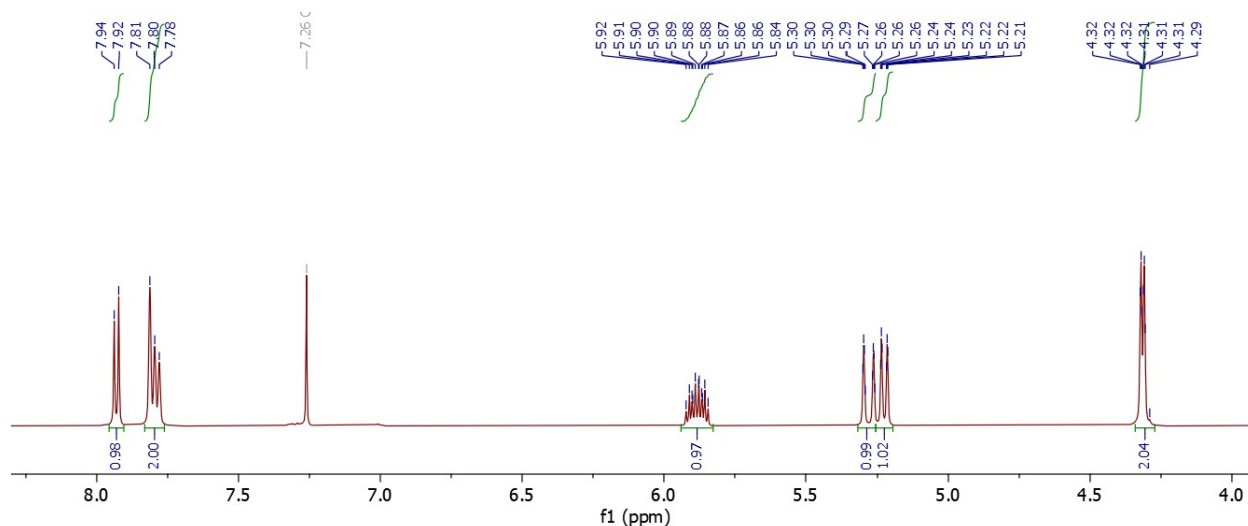


^{13}C NMR (126 MHz, CDCl_3 -d) spectrum of diether monomer D

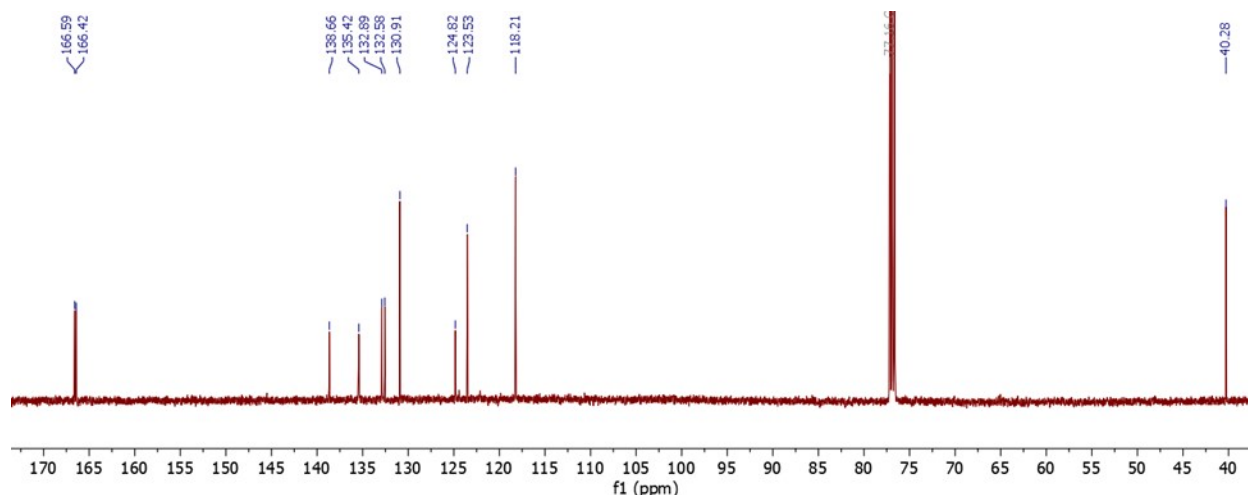
1.2.5 Synthesis of diallyl imide hexafluoro (monomer E)



In a 1L round bottom flask 20 grams (45 mmol) of 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride was suspended in 250 mL of acetic acid. The mixture was stirred while 6.74 mL (90 mmol) of allyl amine was added dropwise to the solution. The flask was stirred for 12 hours with mixture becoming clear. The mixture was then refluxed for 3 hours with any remaining solids dissolved. The flask was then cooled to room temperature and 250 mL of DI water added. The flask was again warmed to reflux or until solids were dissolved. Once the flask was cooled back to room temperature solids were filtered, rinsed with DI water. Solid was then recrystallized using 250 mL 1:1 mixture of methanol and acetone mixture and dried at 80 C for 12 hours to yield a white powder (19.4 g). Yield: 82.4%. M.P. 157 °C. Fourier transform infrared (FTIR) (ATR): $\nu = 3090, 2930$ (C-H), 1780, 1710 (C=O), 1620 (C=C), 1440, 1390, 1300, 1250 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ 7.93 (d, $J = 7.9$ Hz, 2H), δ 7.81 (s, 2H), 7.79 (d, $J = 8.0$ Hz, 2H), 5.88 (m, 2H), 5.285 – 23 (m, 4H), 4.32 (d, $J = 5.7$ Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 166.59, 138.66, 135.42, 132.89, 132.58, 130.91, 124.82, 123.53, 118.21, 40.28.

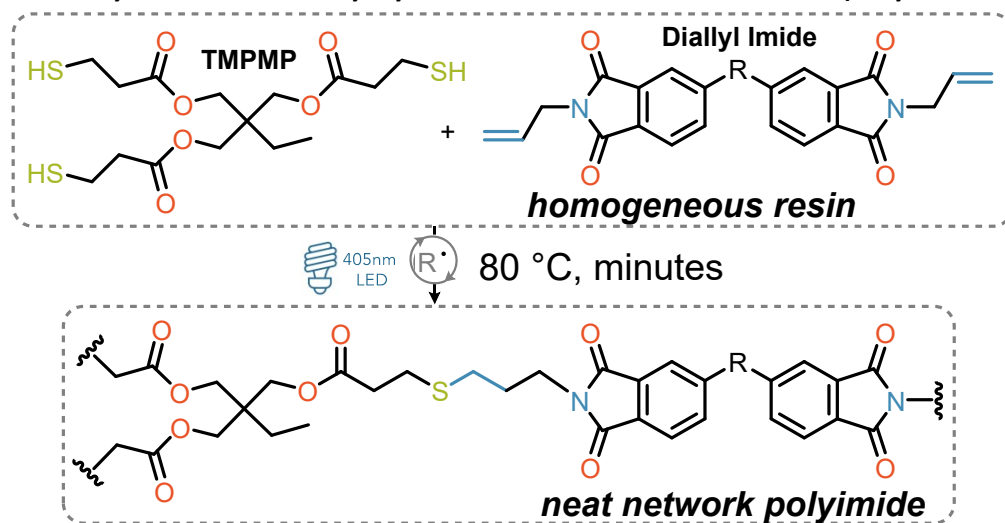


^1H NMR (500 MHz, $\text{CDCl}_3\text{-d}$) spectrum of hexafluoro monomer E



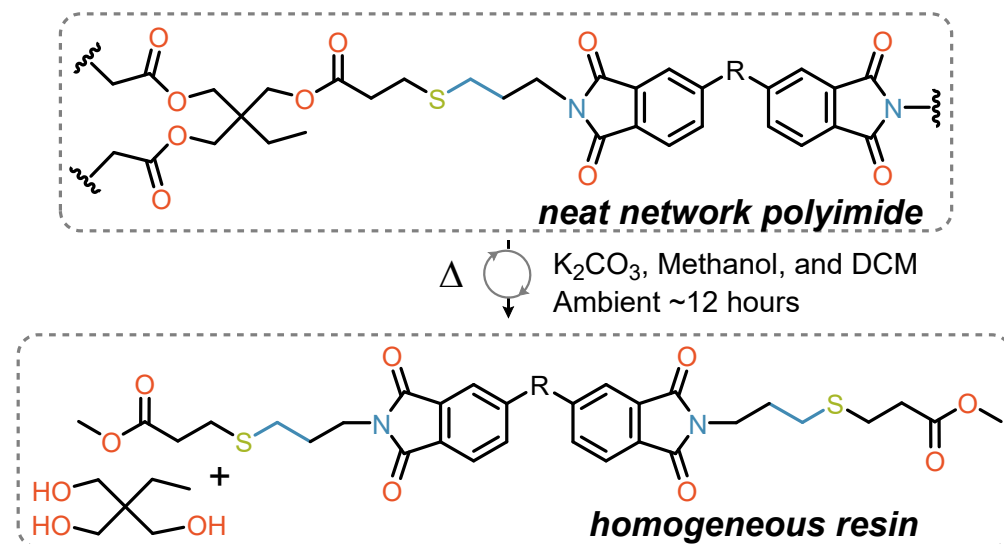
^{13}C NMR (126 MHz, $\text{CDCl}_3\text{-d}$) spectrum of hexafluoro monomer E

1.2.6 Polymerization of Diallyl Cyclohexane monomers with TMPMP (PI cyclohexane)



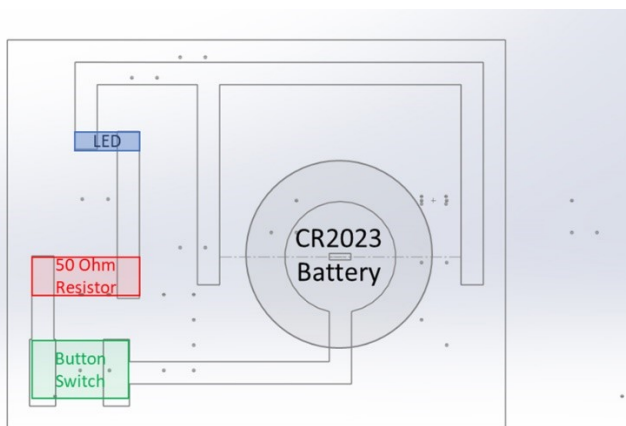
All polymerizations were carried out in a similar manner. 1 gram (3.3 mmol) of cyclohexane monomer, 0.834 grams (2.1 mmol) of trimethylolpropane tris(3-mercaptopropionate) (TMPMP), and 0.018 grams (0.052 mmol) of TPO were added to cantillation vial. The vial was warmed slowly to melt the cyclohexane monomer and mixed. Melted resin was then added to preheated molds in 80 °C Form Cure UV curing oven. The samples were cured for 10 minutes at 405 nm wavelength with 5 mW/cm^2 light intensity (measured by Thorlabs PM100D optical power meter equipped with a standard photodiode S120VC sensor).

1.2.7 Degradation of network polymers



All polymer degradations were performed using the same procedure. Polymer discs with a diameter of 10 mm and a thickness of 2 mm (~0.18 g) were added to scintillation vials. A bulk solution of 1:1 by volume dichloromethane (DCM):methanol with 0.01 gram of potassium carbonate (K₂CO₃) per mL of solvent (0.07 M) was mixed overnight to saturate solution. 10 mL of the solution was then added to polymer discs. Polymer discs were weighed throughout degradation to monitor. At each time point, samples were taken out of the solution and were weighed after physically drying the surface with a Kim wipe.

1.2.8 Demo



10 mm

1 gram of TMPMP, diallyl ester, and TPO resin was prepared according to above polymerization procedure and was melted and poured onto glass slide warmed to 80 °C. A second slide with two 100 um spacers was slowly placed on top of the first slide. Both glass slides were treated with Rain-X® to allow

easy removal of film. Both slides were then clamped together and the resin cured at 80 °C with UV light. Glass slides were allowed to cool before removing the PI ester film.

Liquid metal circuit patterning was adapted from Ozutemiz et al.¹ Single sided dicing tape was laser cut to the circuit dimensions and masked over the substrate. Thermal evaporation was used to deposit 20 nm Cr and 200 nm Cu onto the surface (Kurt J Lesker). Once deposited, the mask was removed. The sample was then dip-coated by hand into an EGaIn bath with a 0.5 M HCl layer on the surface to aid in removal of excess EGaIn. Dip-coating was repeated until LM had wetted the entire surface of the copper. Excess EGaIn was sprayed off using IPA along with being removed by a syringe.

1.3 Characterization

Dynamic Mechanical Analysis (**DMA**) tests were conducted on a TA DHR-20 with oscillatory force applied in the axial direction. Rectangular bars of 30 mm x 5 mm x 1 mm (LxWxT) were fabricated by curing in a silicone mold. The samples were tested with 0.1% axial strain at a frequency of 1 Hz, ramping from 40 °C to 200 °C at 3 °C/min. An axial gap limit of 3 mm was set. Glass transition temperature (T_g) was determined by the highest point on the $\tan \delta$ curve. Rubbery modulus was determined by the storage modulus (E') at $T_g + 40$ °C. Crosslinking density (M_c) was calculated using the following equation where R is the universal gas constant, T is T_g plus 40 °C, d is the density of the polymer, and G' is the rubbery modulus at T_g plus 40 °C.

$$M_c = \frac{3RTd}{E'}$$

Differential Scanning Calorimetry (**DSC**) tests were collected using TA instruments DSC 2500 with ramp rate of 10 C/minute starting at 0 °C and going to 150 °C.

Thermogravimetric Analysis (**TGA**) tests were conducted using TA Instruments SDT 650 with autosampler. Samples were heated from 40 °C to 800 °C at 20 °C/min heating rate.

Fourier transform infrared spectroscopy (**FT-IR**) spectra were collected on a Nicolet iS50 spectrometer equipped with a single-bounce Smart iTR Attenuated Total Reflectance (ATR) setup. DTGS-KBr was used as the detector, and the air was used as the background. Spectra were collected from 4000 cm^{-1} to 600 cm^{-1} . Polymer samples were made into a thin film to achieve sufficient contact with the ATR window.

Tensile testing was performed using an Instron 5969 dual column tabletop testing system. Dog bones with 34 mm were used with a pull rate ranging from 1 mm/minute to 5 mm/minute for PI ether. Samples were tested 48 hours after being cured. Five of each polymer sample was tested. Tensile modulus was calculated by using the slope from 0.1% to 0.2% strain.

¹H and ¹³C **NMR** spectra were collected on a Bruker Avance NEO 500 MHz. CDCl₃ was used as the solvent for all spectra collected.

Thermal conductivity was measured using the Hot Disk TPS 500 S Thermal Constants Analyzer. Briefly, we prepared disk shaped samples with around 1 inch (2.54mm) of diameter and 1 mm of thickness. To perform the measurements, the Hot Disk sensor, which is Nickel conducting spiral encapsulated in Kapton, was fitted between two disks of samples. The sandwiched sample set was electrically heated until the temperature of the sensor was raised by a few tenths of degrees to several degrees. Under the Bulk

(Type I) Isotropic mode, the temperature change was recorded as a function of time for determining thermal conductivity. We performed N=5 runs for each sample.

Thermal expansion was via thermo-mechanical analysis using a TA Instruments TMA 450. Samples were prepared in a square disk geometry. Each sample was subjected to a cool-heat-cool-heat-cool cycle (-70°C → 300°C → -70°C → 300°C → 30°C) at a rate of at 5°C min⁻¹. Coefficient of thermal expansion is calculated as the slope in the Dimension Change v. Temperature plot in the linear regime above the glass transition temperature (generally 100°C to 230°C).

Vector network analysis was performed on all the candidate electronic substrate materials. Briefly, circular films (d = 25mm) were loaded on to an Anritsu Shockline MS46122B Compact USB Vector Network Analyzer and held in place on concentric electrodes with a vacuum. **Dielectric constant** and **dielectric loss** were recorded at discrete frequencies from 0.8 GHz to 8 GHz corresponding to relevant regimes in wireless communication. For each material, N=5 runs were conducted and the samples were removed and reloaded between runs.

Electrical Conductivity measurements were collected using a Handskit 830LN digital multimeter.

2. Supplemental Tables

Property	Ester	Ether	Cyclohexane	Diether	Hexafluoro	Kapton HN®
T _g (DSC)(°C)	48	49	66	67	72	>300
CTE 100 °C (um/m°C)	199	193	183	199	203	30
T _d 50% (TGA)(°C)	419	428	428	477	425	~600

Table S1. Additional physical, thermal, and electrical properties of five thiol-ene poly(imide ester) networks compared to Kapton, including T_g from DSC, 50 wt% degradation temperature from TGA.

Polymer Degradation (weight %)	1h	2h	3h	4h	5h	6h	7h	8h	9h	12h	24h
Ester (0% DCM)	100	100	100	100	100	100	100	100	100	100	99
Ester (25% DCM)	104	105	103	102	99	97	95	92	89	83	53
Ester (50% DCM)	105	88	75	63	50	-	35	-	15	0	0
Ester (75% DCM)	-	-	-	-	0	0	0	0	0	0	0
Ether (50% DCM)	124	133	141	144	149	-	136	-	-	-	0
Cyclohexane (50% DCM)	123	131	134	138	-	-	-	-	-	-	0
Diether (50% DCM)	139	156	168	166	162	-	141	-	-	-	0
Hexafluoro (50%DCM)	134	137	126	-	-	-	-	-	-	-	0

Table S2. Degradation weight % values of the studied polymer kinetics. Dashes represent data points that could not be collected due to polymer breaking apart.

3. Supplemental Figures

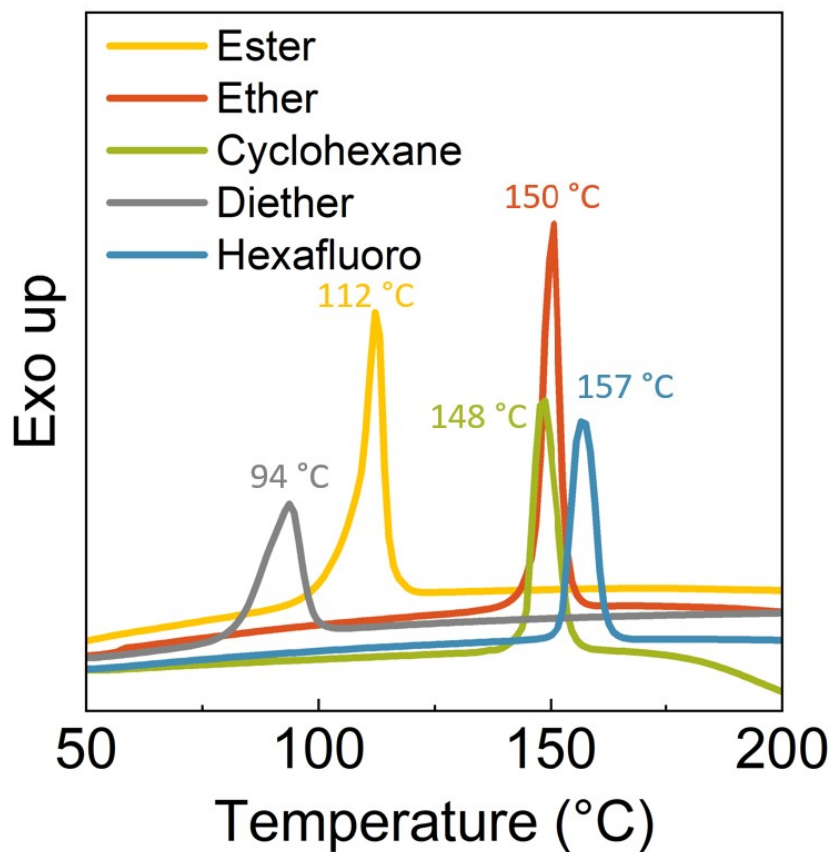


Figure S1. DSC melting points of each of the monomers examined in this study.

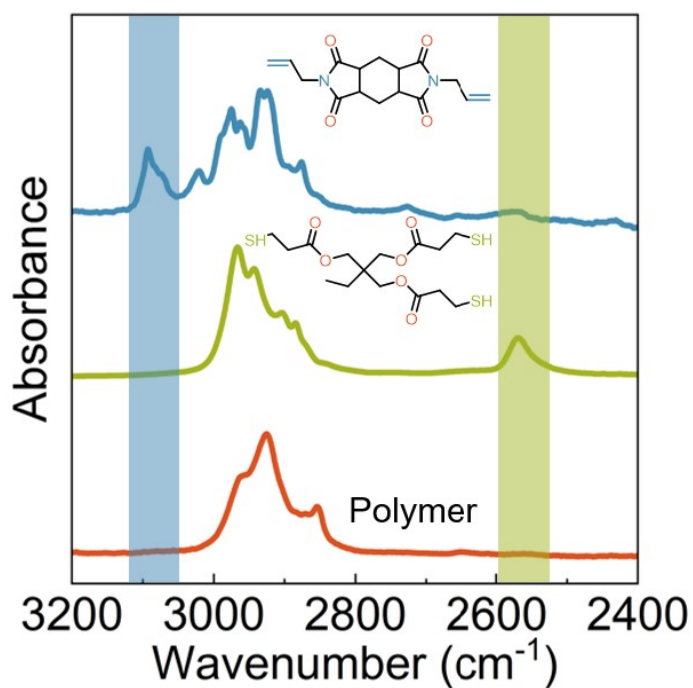


Figure S2. FTIR of diallyl cyclohexane monomer (top), TMPMP thiol monomer (middle) and final cured resin (bottom). Thiol peak ($\sim 2570\text{ cm}^{-1}$) and alkene peak ($\sim 3090\text{ cm}^{-1}$) can be seen to disappear in fully cured polymer showing high conversion.

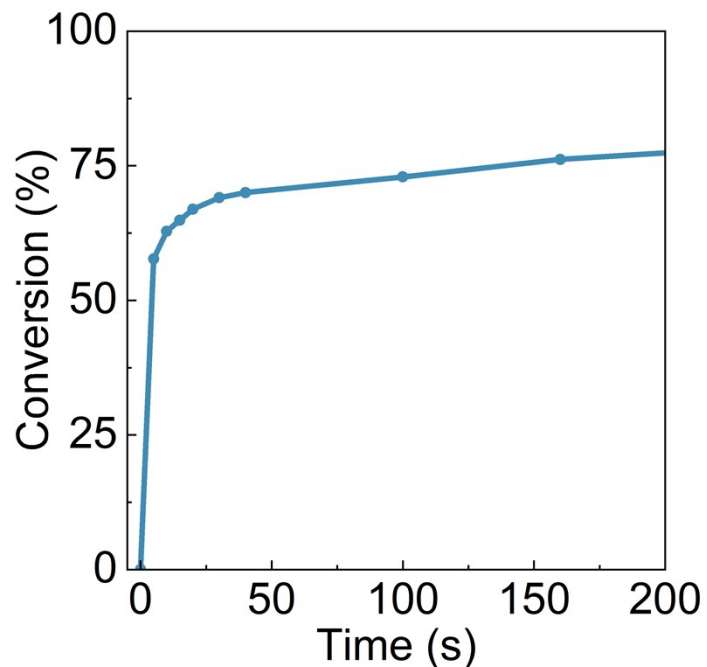


Figure S3. Conversion with time of cyclohexane and TMPMP monitored with FTIR. Conversion levels off around 80% due to vitrification. Near 100% conversion is obtained when polymer is cured at $80\text{ }^{\circ}\text{C}$.

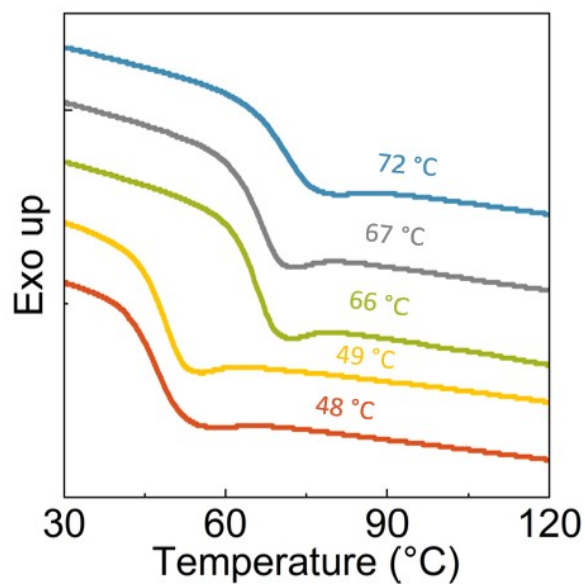


Figure S4. T_g measured by DSC showing a similar trend compared to the T_g measured by DMA.

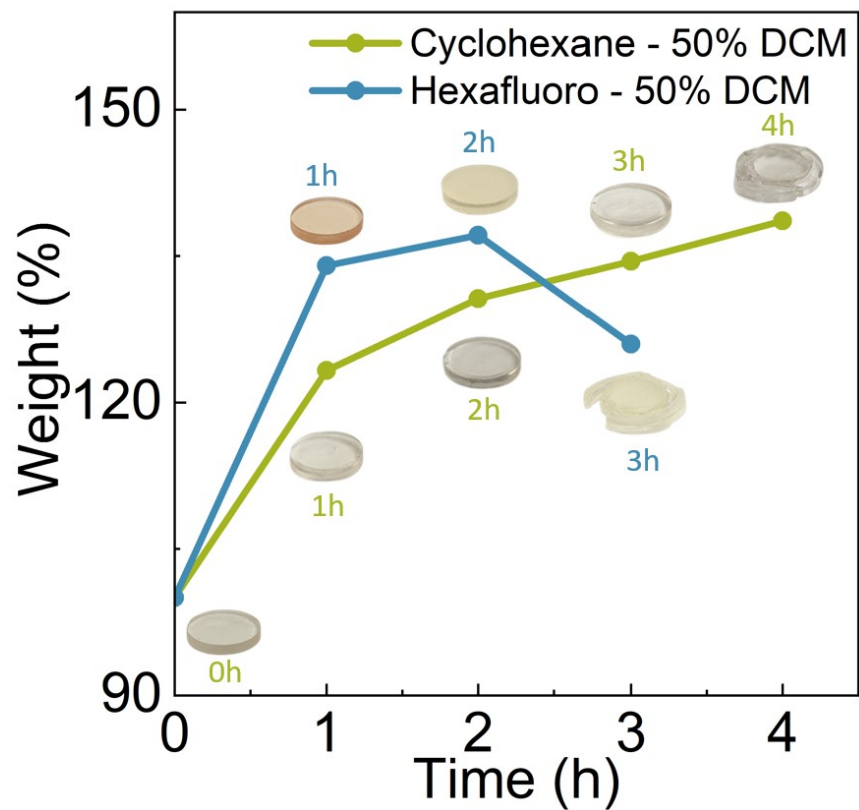


Figure S5. Degradation kinetics of PI-cyclohexane and PI-hexafluoro polymers with different 50% DCM and 50% methanol using constant K_2CO_3 concentration. Both PI's can be seen to swell gaining weight until discs fall apart. Complete degradation was seen within 24 hours.

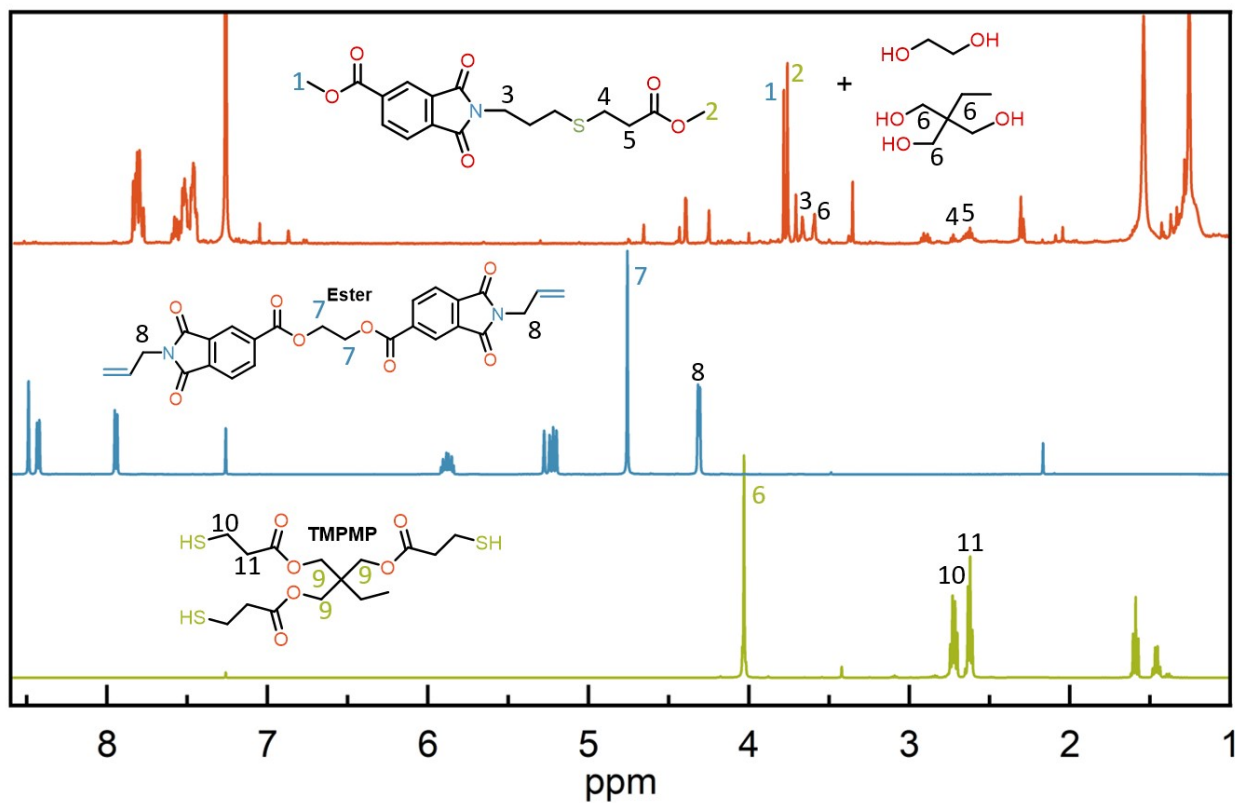


Figure S6. NMR comparing the ester monomer and TMPMP with degraded resin. The methyl ester peaks can be seen for both the aromatic and alkyl adjacent esters.