

### Supplemental Information

#### **Solventless, Rapid-polymerizable Liquid Resins from Solid Carboxylic Acids through Low-viscosity Acid/Base Complexes**

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**Table of Contents**

1. Experimental Section ..... 3  
    1.1 Materials..... 3  
    1.2 Polymer synthesis ..... 3  
    1.3 Characterization ..... 3  
2. Supplemental Tables ..... 4  
3. Supplemental Figures ..... 5

## 1. Experimental Section

### 1.1 Materials

Carboxylic acids were purchased from various vendors. Phthalic acid (PA), isophthalic acid (iPA), terephthalic acid (tPA), benzoic acid, succinic acid (SA), glutaric acid (GA), adipic acid (AA), oxalic acid, malonic acid, sebacic acid, cyclohexane-1,4-dicarboxylic acid (1,4ChA), citric acid, butylated hydroxytoluene (BHT), and deuterated solvents were purchased from Sigma Aldrich. Azelaic acid, pimelic acid, cis-cyclohexane-1,2-dicarboxylic acid (cChA), trans-cyclohexane-1,2-dicarboxylic acid (tChA), and levulinic acid were purchased Ambeed. Ethyl(2,4,6-trimethylbenzoyl)-phenyl phosphonate (TPO-L) was purchased from TCI Chemicals. Glycerol epoxy (GEX-313) and sorbitol epoxy (GEX-622) were gifted from Nagase Specialty Materials. All chemicals were used as received.

### 1.2 Polymer synthesis

*Synthesis of the acid-base complexes.* To a round bottom flask or a scintillation vial equipped with a magnetic stirrer, DMAEMA and carboxylic acids in a certain acid/base molar ratio were added. The flask was heated at 120 °C under vigorous stirring for several minutes until all solids disappeared. In some cases, free-radical inhibitor BHT (1wt% with respect to the total mass) was added prior to heating to prevent undesired free-radical polymerization reactions.

*Photopolymerization of DMAEMA-acid complexes.* The poly(DMAEMA-acid) specimens were directly polymerized from the resin, without the use of any solvent. To the resin, 1wt% TPO-L was added and was mixed by using a FlackTek Speedmixer. The resin was casted into a silicone mold that has desired shapes such as a rectangular bar or an ASTM D638 type IV “dogbone” specimen. The resin was exposed to 405nm light for 5 minutes by using a commercial light chamber (“Form Cure” sold by Formlabs) at 2.9 mW (4.13 mW/cm<sup>2</sup>) measured by a Thorlabs PM100D energy meter (see the picture below).



*Dual-cure polymerization reactions.* The dual-cure polymer resins were prepared by mixing the DMAEMA-acid complexes with an epoxy monomer, in an stoichiometric acid/epoxy ratio. To the resin, 1wt% TPO-L was added and was mixed by using a FlackTek Speedmixer. The resin was casted into a silicone mold that has desired shapes and thicknesses. The resin was “photo cured” in a Form Cure for 5 minutes, followed by 3 hours of “heat cure” under 130 °C in a convection oven.

### 1.3 Characterization

Dynamic Mechanical Analysis (**DMA**) was conducted on a TA DHR-20 equipped with oscillatory force applied in the axial direction. Rectangular bars were fabricated by curing polymers in a silicone mold with approximate dimensions of 30 mm x 5 mm x 1 mm (LxWxT). The specimens were tested with 0.1% axial strain at a frequency of 1 Hz, ramping from 22 °C to 250 °C at 3 °C/min. Glass transition temperature ( $T_g$ ) was determined by the  $\tan \delta$  peak position. Rubbery modulus was determined by the storage modulus ( $E'$ ) at  $T_g + 40$  °C.

Stress relaxation test was conducted on DMA using rectangular specimen with approximate dimensions of 30 mm x 5 mm x 1 mm (LxWxT). The specimen was kept at various elevated temperatures for 5 mins, followed by applying 1% tensile strain for 15 mins. The relaxation stress was recorded during the isostrain period.

Differential Scanning Calorimetry (**DSC**) tests were conducted on a TA Instruments DSC 2500 equipped with an autosampler. Samples (~ 5mg) were heated and cooled at 10 °C/min. In a typical experiment, three heat-cool cycles were performed, and the third heating cycle was reported.

Thermogravimetric Analysis (**TGA**) tests were conducted using TA Instruments TGA 550 with autosampler. Samples (~ 5mg) were heated at 5 °C/min under nitrogen environment.

Fourier transform infrared spectroscopy (**FTIR**) spectra were collected on a Nicolet iS50 spectrometer equipped with a horizontal stage. MCT-A was used as the detector, and air was used as the background. Real-time FTIR series were collected by placing samples on a horizontal stage (PIKE Technologies). Repeated single scans were conducted on thin samples that were sandwiched between two NaCl salt plates. 405nm light irradiation was operated by using a Mightex LED light source equipped with a liquid light guide and a collimating lens. The light intensity was measured by a Thorlabs PM100D energy meter.

**Tensile test** was performed on an Instron 5969. Dog bone specimens were prepared according to ASTM D638 type IV with a gauge length of 33 mm. Strain rate varied from 1 to 25 mm/minute, targeting a duration of the test within 1-5 minutes. Five replicates were conducted for each set of polymer specimen.

Viscosity was determined by a TA DHR-20 rheometer equipped with parallel plates (20 mm diameter, aluminum). The gap was set to be 200  $\mu\text{m}$ . Steady strain scan was conducted, and the viscosity was determined at 60  $\text{s}^{-1}$  at 22 °C.

$^1\text{H NMR}$  spectra were collected on a Bruker Avance NEO 500 MHz.



## 2. Supplemental Tables

**Table S1.** Numerical data for Figure 1C. Viscosities of stoichiometric DMAEMA-acid complexes.

| Acid                | Viscosity (cP @ 22 °C) | Standard deviation(cP) |
|---------------------|------------------------|------------------------|
| PA                  | 214                    | 3                      |
| iPA                 | 4351                   | 88                     |
| Glutaric acid (n=3) | 96                     | 2                      |
| Adipic acid (n=4)   | 85                     | 1                      |
| Pimelic acid (n=5)  | 82                     | 1                      |
| Suberic acid (n=6)  | 77                     | 1                      |
| Azelaic acid (n=7)  | 144                    | 1                      |
| Sebacic acid (n=8)  | 80                     | 1                      |
| cChA                | 220                    | 2                      |
| tChA                | 399                    | 6                      |
| 1,4ChA              | 58403                  | 1056                   |

**Table S2.** Numerical data for Figure 3C. Viscosities of off-stoichiometric DMAEMA-acid complexes.

| Acid               | Viscosity (cP @ 22 °C) | Standard deviation (cP) |
|--------------------|------------------------|-------------------------|
| 20 mol% excess PA  | 472                    | 5                       |
| 40 mol% excess PA  | 2026                   | 44                      |
| 60 mol% excess PA  | 7380                   | 183                     |
| 80 mol% excess PA  | 29597                  | 212                     |
| 100 mol% excess PA | 60771                  | 674                     |
| 20 mol% excess AA  | 175                    | 5                       |
| 40 mol% excess AA  | 204                    | 4                       |
| 60 mol% excess AA  | 340                    | 10                      |
| 80 mol% excess AA  | 7905                   | 136                     |
| 100 mol% excess AA | 34637                  | 2526                    |

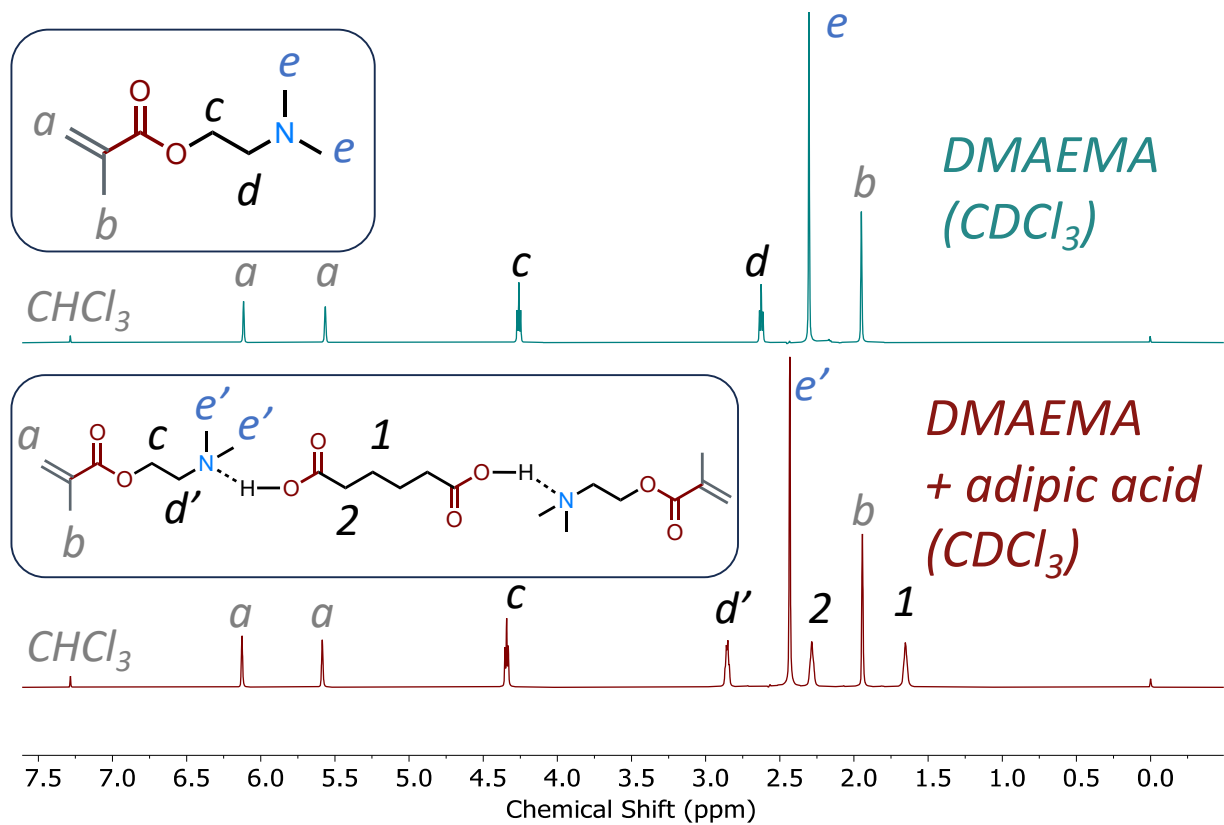
**Table S3.** Entailed formulation sheet of polymer samples used in this work.

| Sample name              | DMAEMA (g) | Acid (g)   | Epoxy (g)       | Inhibitor (g)/Initiator (g) |
|--------------------------|------------|------------|-----------------|-----------------------------|
| Poly(DMAEMA-AA)          | 1.57       | AA, 0.73 g | n/a             | BHT, 0.02 g/TPO-L, 0.02g    |
| Poly(DMAEMA-PA)          | 1.57       | PA, 0.83 g | n/a             | BHT, 0.02 g/TPO-L, 0.02g    |
| DMAEMA-AA/glycerol epoxy | 1.57       | AA, 0.73 g | GEX-313, 1.41 g | BHT, 0.02 g/TPO-L, 0.03g    |
| DMAEMA-PA/glycerol epoxy | 1.57       | PA, 0.83 g | GEX-313, 1.41 g | BHT, 0.02 g/TPO-L, 0.03g    |
| DMAEMA-AA/sorbitol epoxy | 1.57       | AA, 0.73 g | GEX-622, 1.91 g | BHT, 0.02 g/TPO-L, 0.03g    |
| DMAEMA-PA/sorbitol epoxy | 1.57       | PA, 0.83 g | GEX-622, 1.91 g | BHT, 0.02 g/TPO-L, 0.03g    |

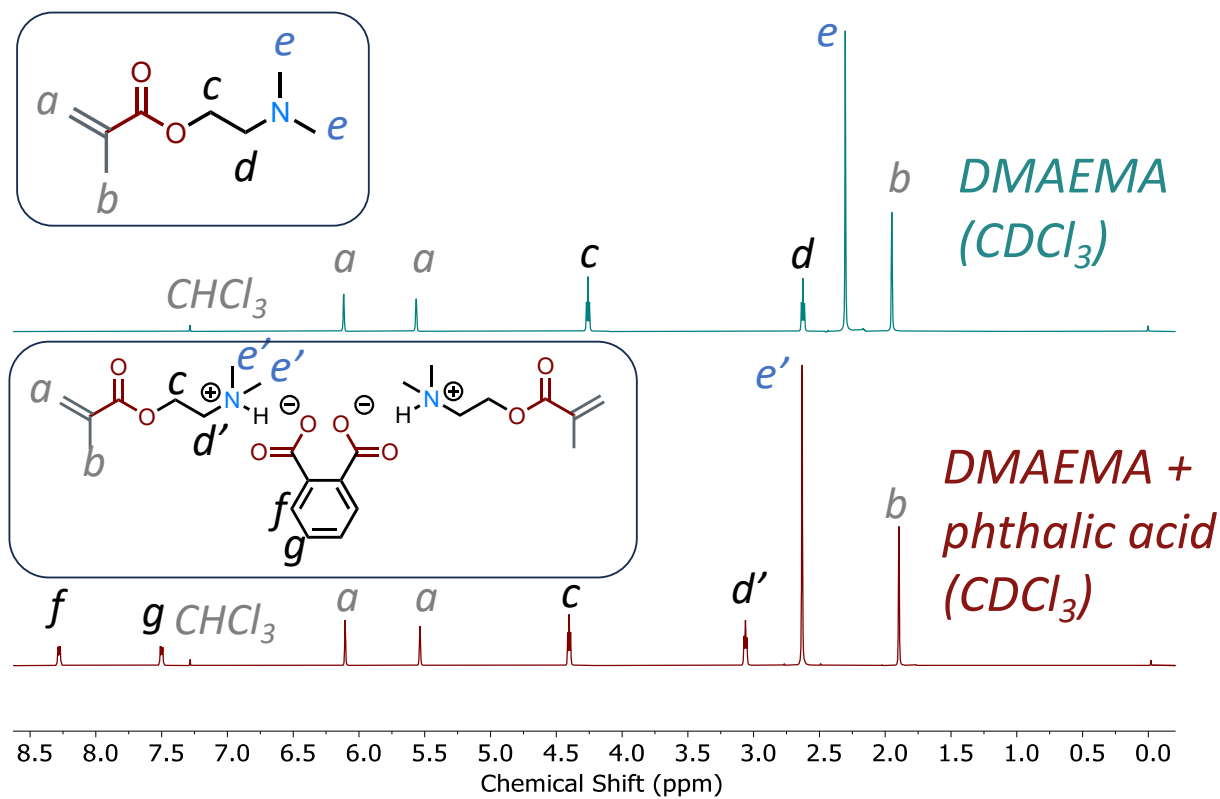
**Table S4.** Numerical data of tensile properties shown in Figure 5C and Figure 6E-F

| Sample name              | Young's modulus | Ultimate tensile strength | Elongation at break (%) |
|--------------------------|-----------------|---------------------------|-------------------------|
| Poly(DMAEMA-AA)          | 264 ± 57 MPa    | 3.9 ± 0.8 MPa             | 560±250                 |
| Poly(DMAEMA-PA)          | 1371 ± 86 MPa   | 10.0 ± 3.3 MPa            | 2.0 ± 0.6               |
| DMAEMA-AA/glycerol epoxy | 1050 ± 230 MPa  | 45.8 ± 7.2 MPa            | 7.6 ± 2.3               |
| DMAEMA-PA/glycerol epoxy | 2400 ± 140 MPa  | 37.9 ± 0.6 MPa            | 2.1 ± 0.3               |
| DMAEMA-AA/sorbitol epoxy | 2720 ± 200 MPa  | 46.2 ± 5.0 MPa            | 2.4 ± 0.7               |
| DMAEMA-PA/sorbitol epoxy | 2250 ± 60 MPa   | 37.7 ± 6.3 MPa            | 2.1 ± 0.4               |

### 3. Supplemental Figures

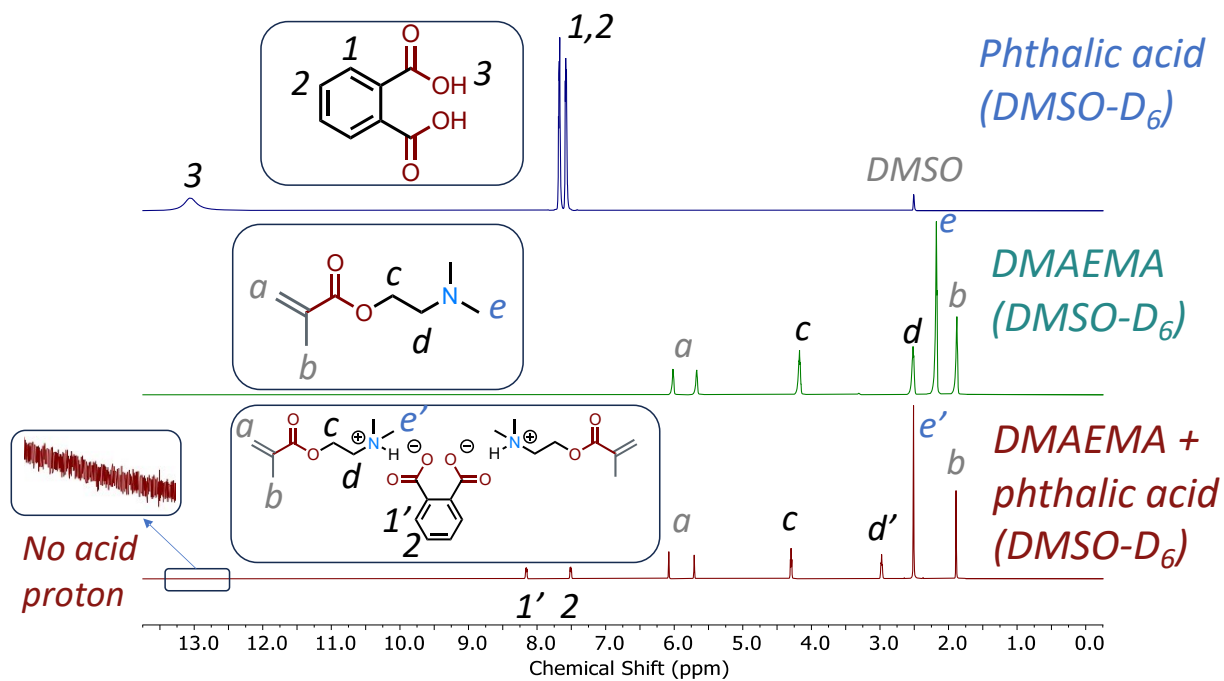


**Figure S1.** <sup>1</sup>H NMR of stoichiometric DMAEMA-adipic acid complex in CDCl<sub>3</sub>.

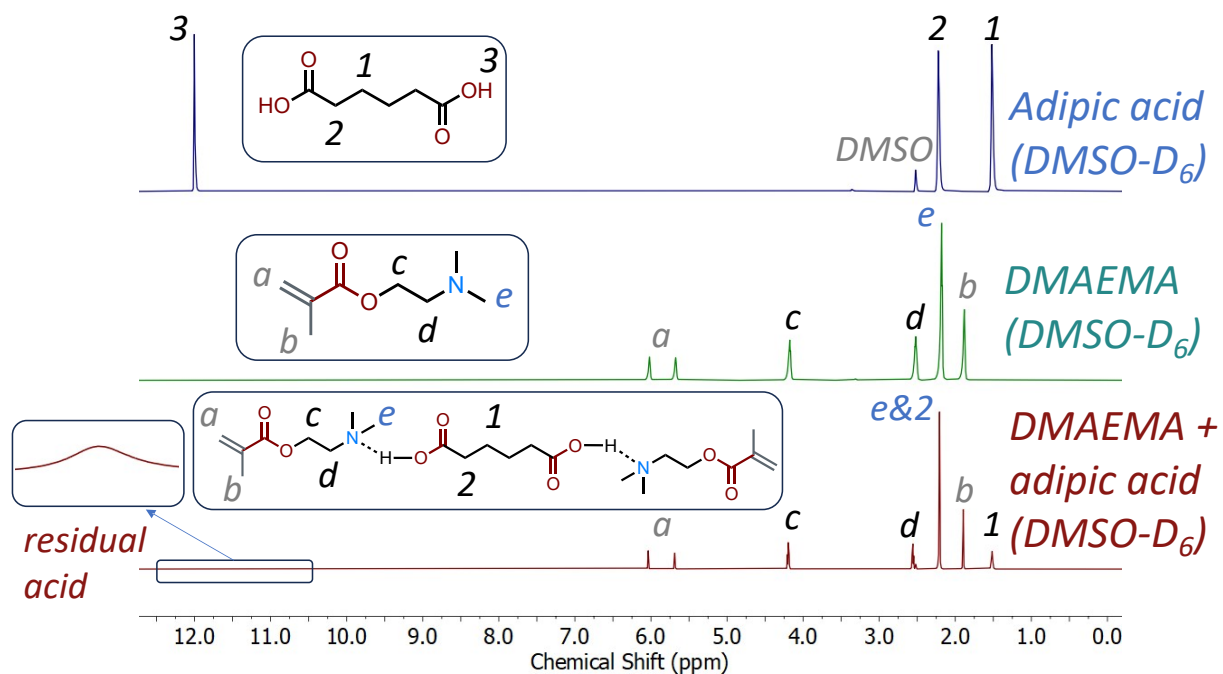


**Figure S2.**  $^1\text{H}$  NMR of stoichiometric DMAEMA-phthalic acid complex in  $\text{CDCl}_3$ .





**Figure S3.**  $^1\text{H}$  NMR of stoichiometric DMAEMA-phthalic acid complex in  $\text{DMSO-}D_6$ .



**Figure S4.**  $^1\text{H}$  NMR of stoichiometric DMAEMA-adipic acid complex in  $\text{DMSO-D}_6$ .

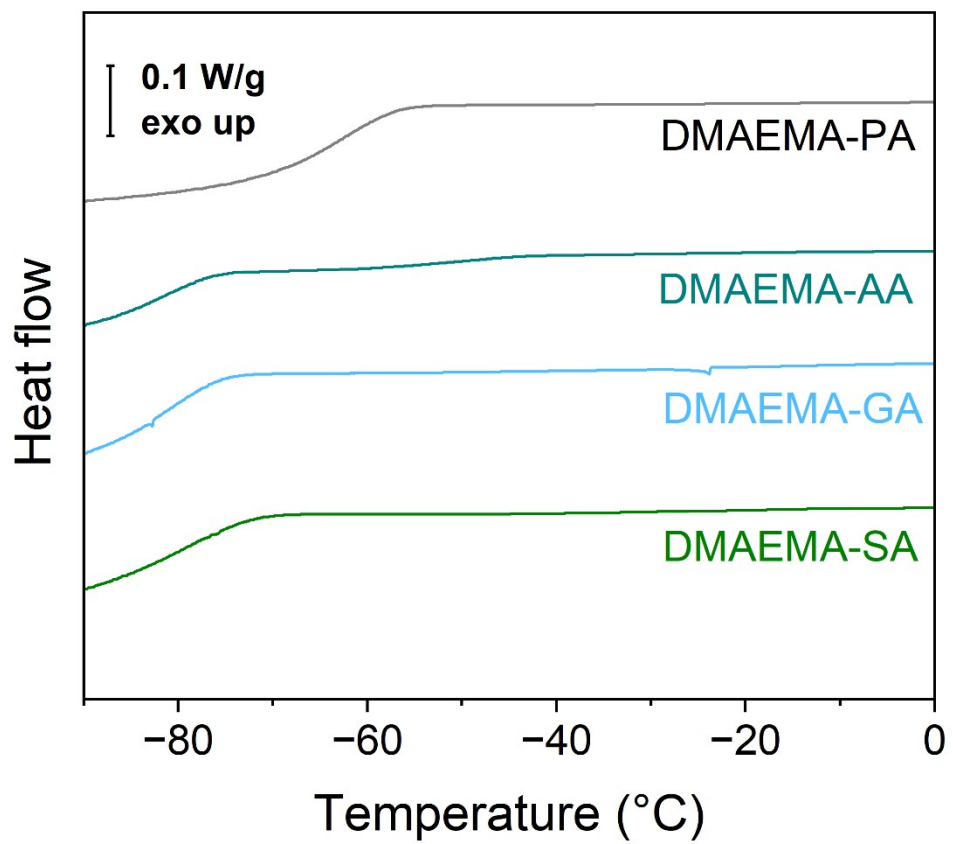
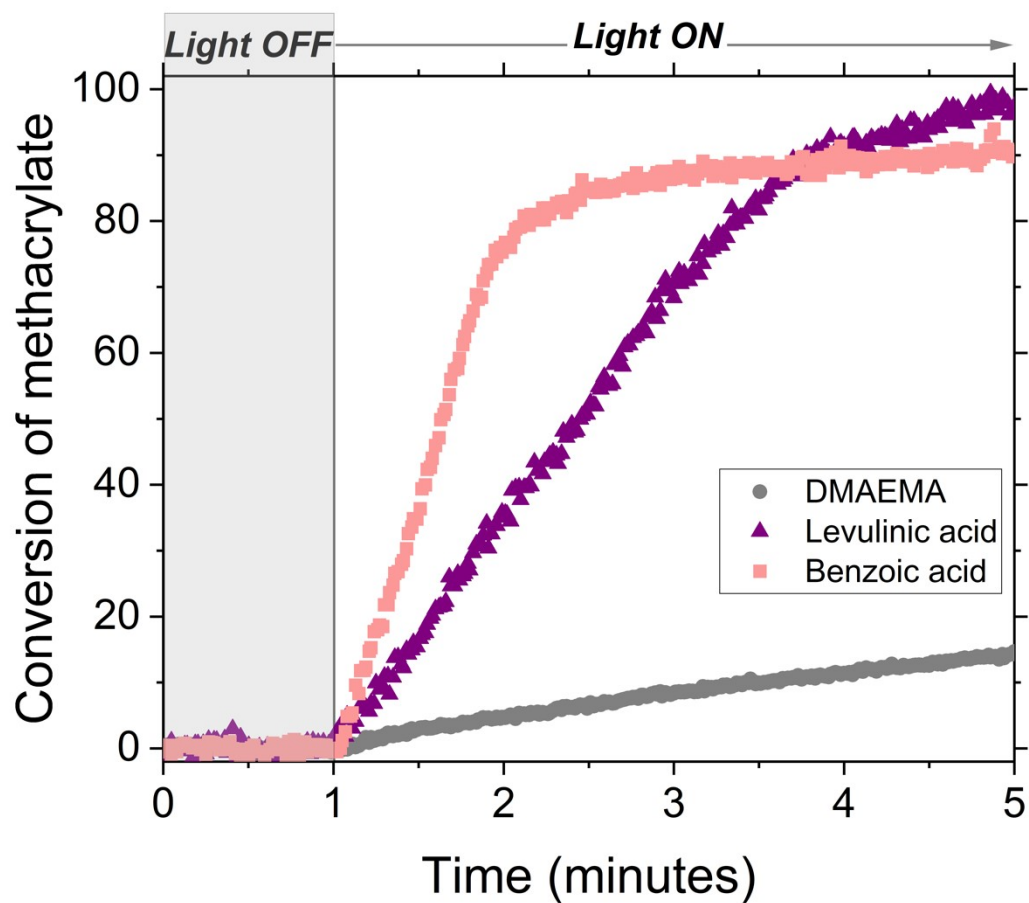
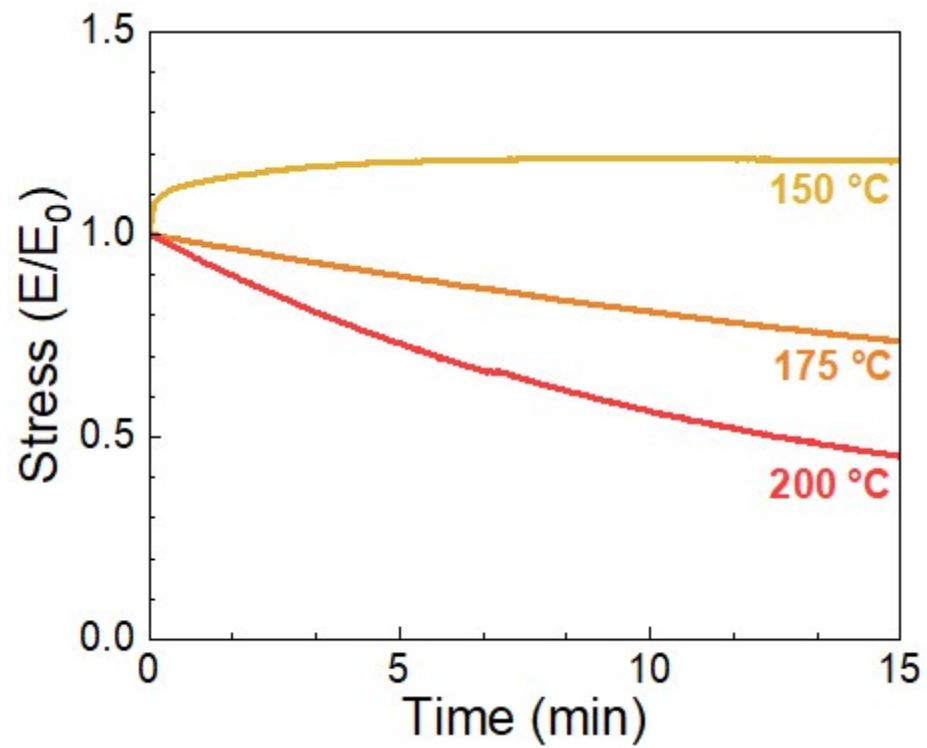


Figure S5. Cooling cycles of DMAEMA-acids complexes at 10 °C /min.



**Figure S6.** Polymerization reaction kinetics of DMAEMA complexes with monofunctional acids, in comparison with the neat DMAEMA resin. Curing conditions: 5 mW/cm<sup>2</sup> 405 nm light from a LED source; light turned on after one min. In all cases, 1wt% TPO-L was used as the photoinitiator.



**Figure S7.** Stress relaxation of DMAEMA-PA-sorbitol epoxy polymer. Test conditions: 1% tensile strain on a rectangular specimen.