Supporting Information for:

Preparation and characterization of crosslinked poly(vinylimidazolium) anion exchange membranes for artificial photosynthesis

Blaine M. Carter[1], Laura Keller[2], Matthias Wessling[2,3], and Daniel J. Miller[1†]

†Corresponding Author, Tel: +1 (510) 495-2353 E-mail: danieljmiller@lbl.gov

[1]Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, Berkeley, CA 97420, United States

[2]RWTH Aachen University, Chemical Process Engineering, Forckenbeckstr. 51, 52074 Aachen, Germany

[3]DWI – Leibniz Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

Fig. S1. ^{1}H (500 MHz, $CDCl_3$) of compound **ii**

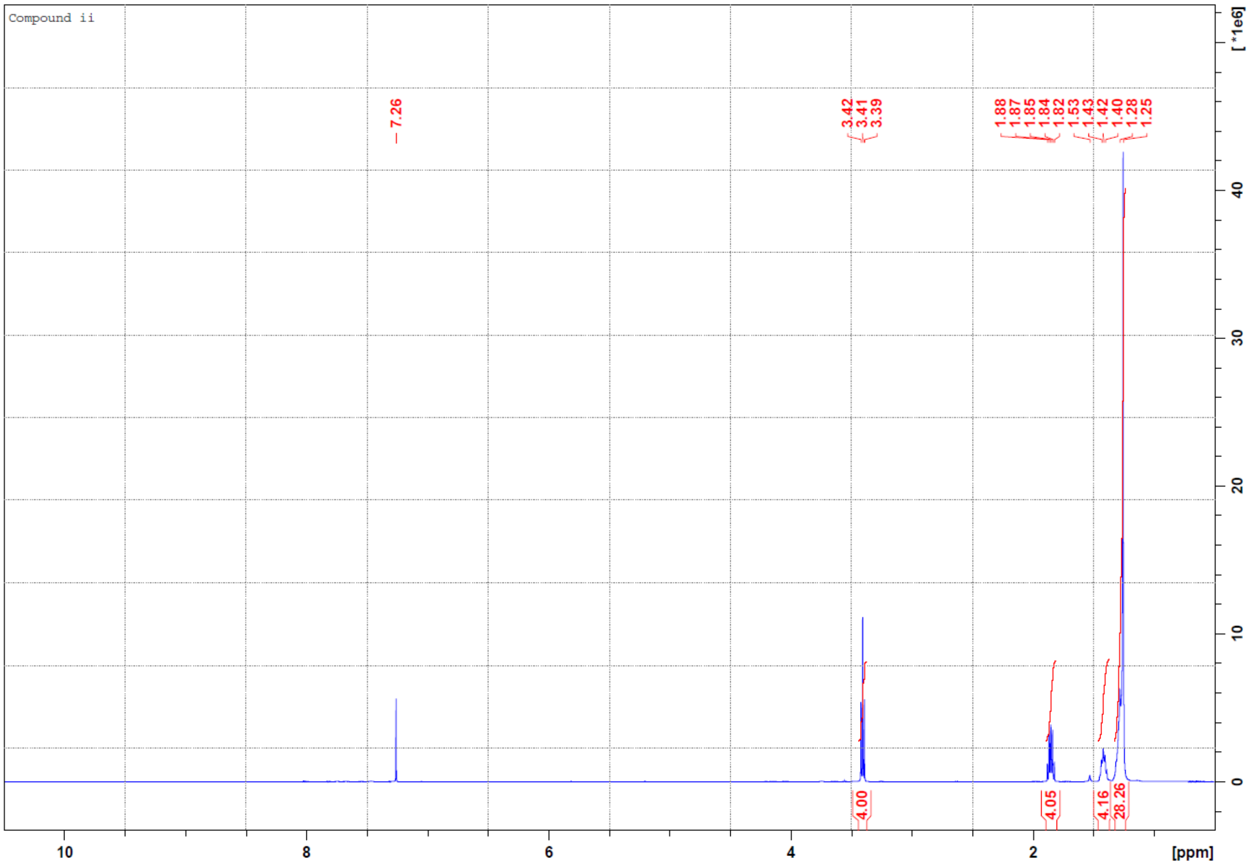


Fig. S2. ^{13}C (500 MHz, CDCl$_3$) of compound **ii**

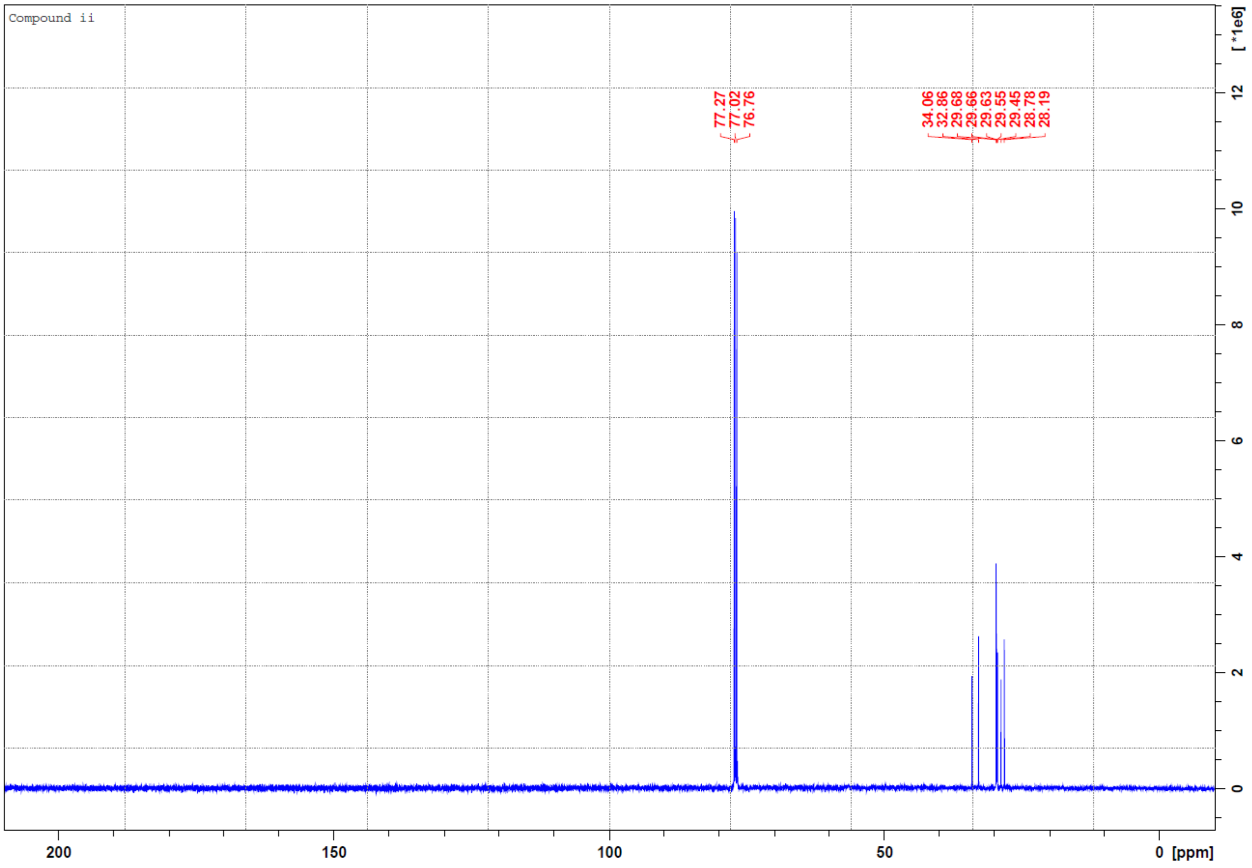


Fig. S3. ^{1}H (500 MHz, DMSO-d_6) of monomer **1**

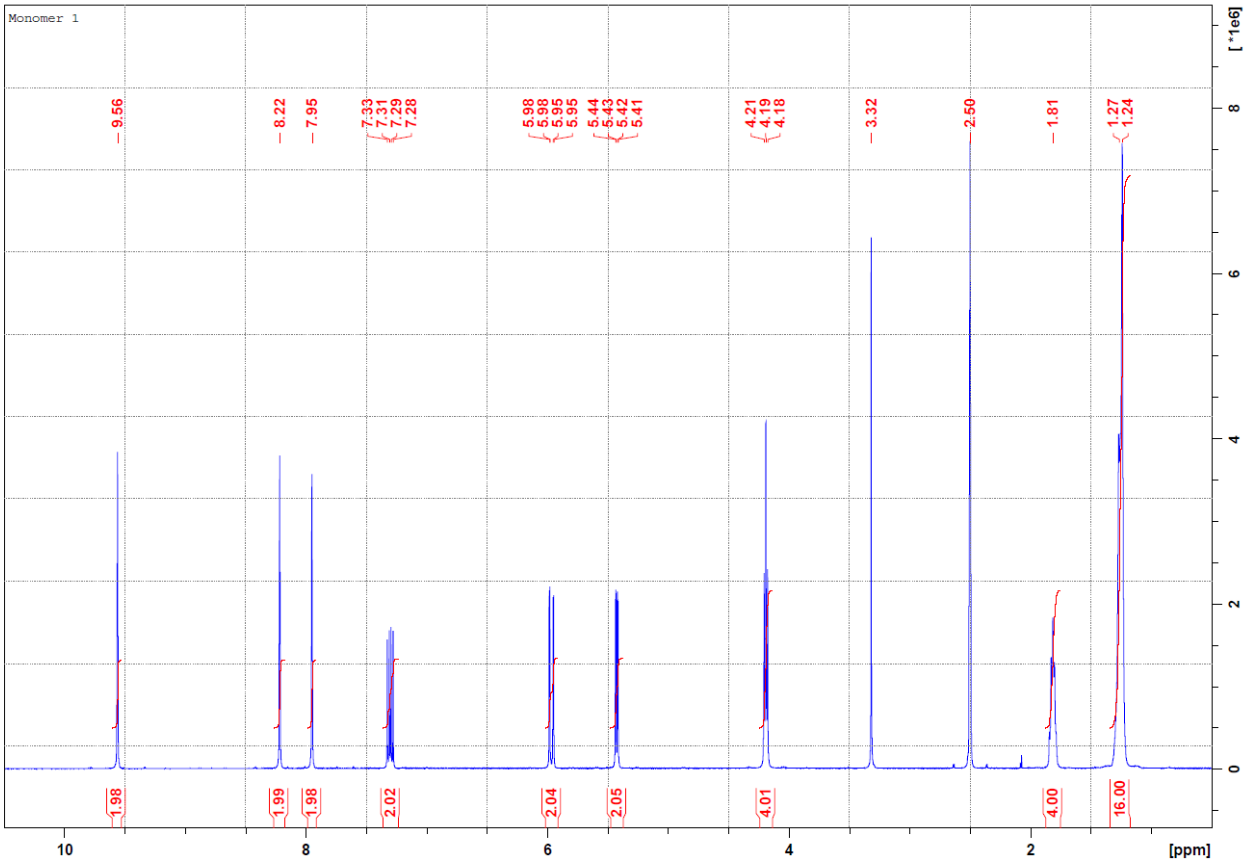


Fig. S4. ^{13}C (500 MHz, DMSO-d_6) of monomer **1**

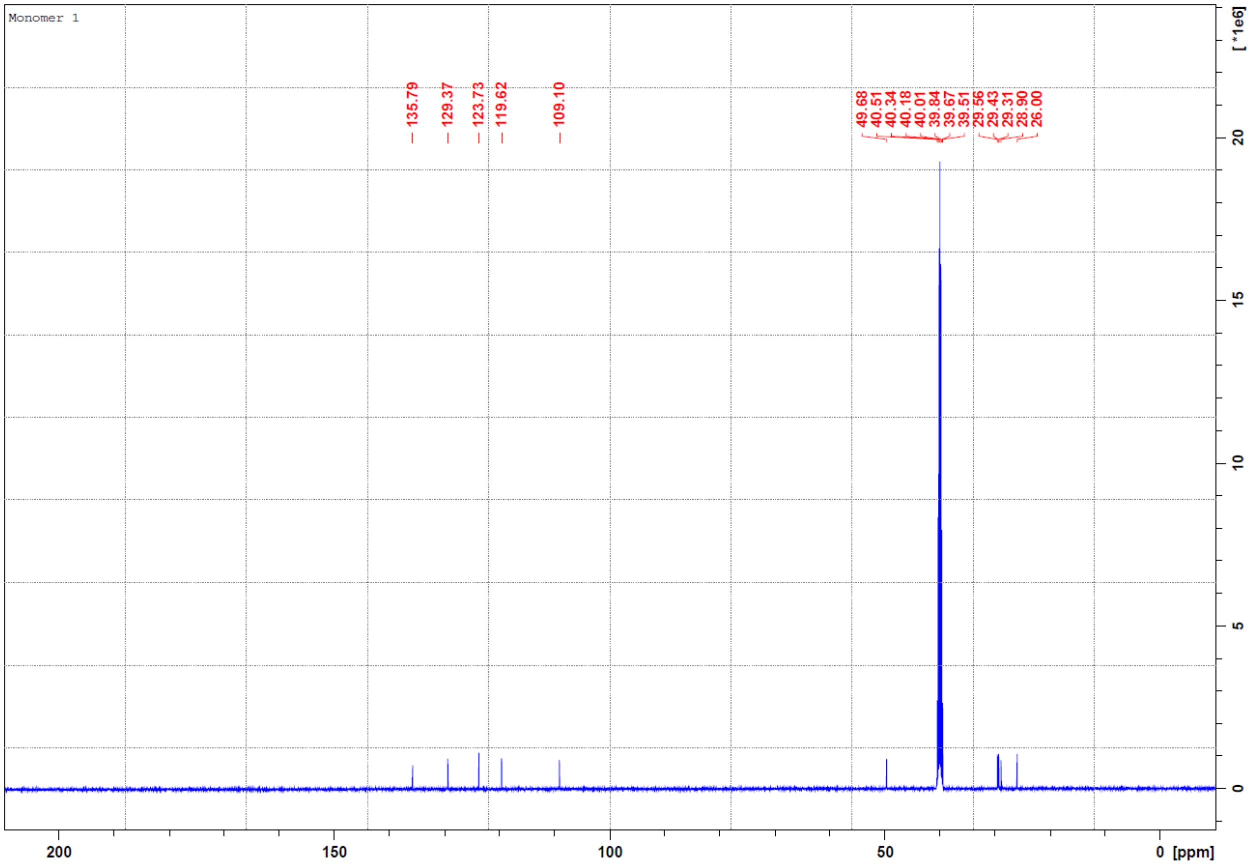


Fig. S5. ^{1}H (500 MHz, DMSO-d_6) of monomer **2**

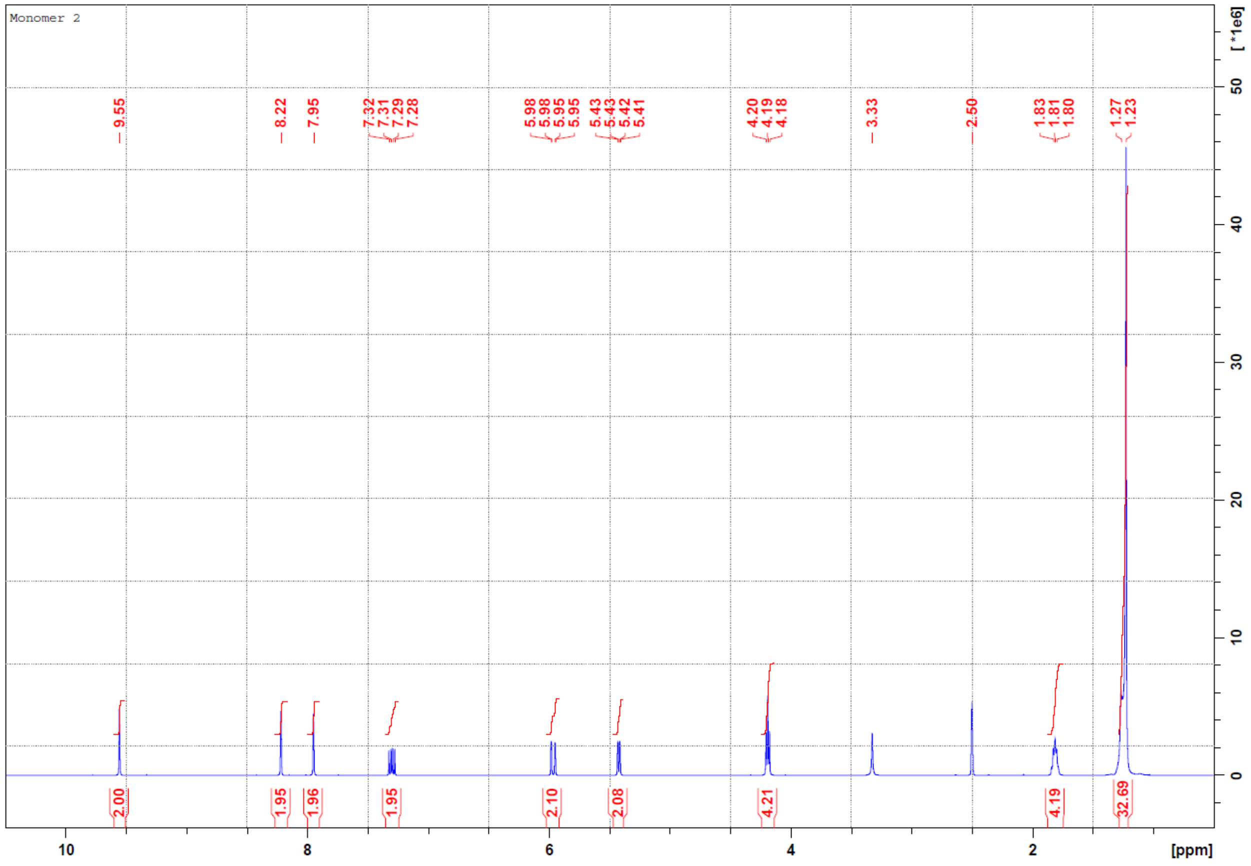


Fig. S6. ^{13}C (500 MHz, DMSO-d_6) of monomer **2**

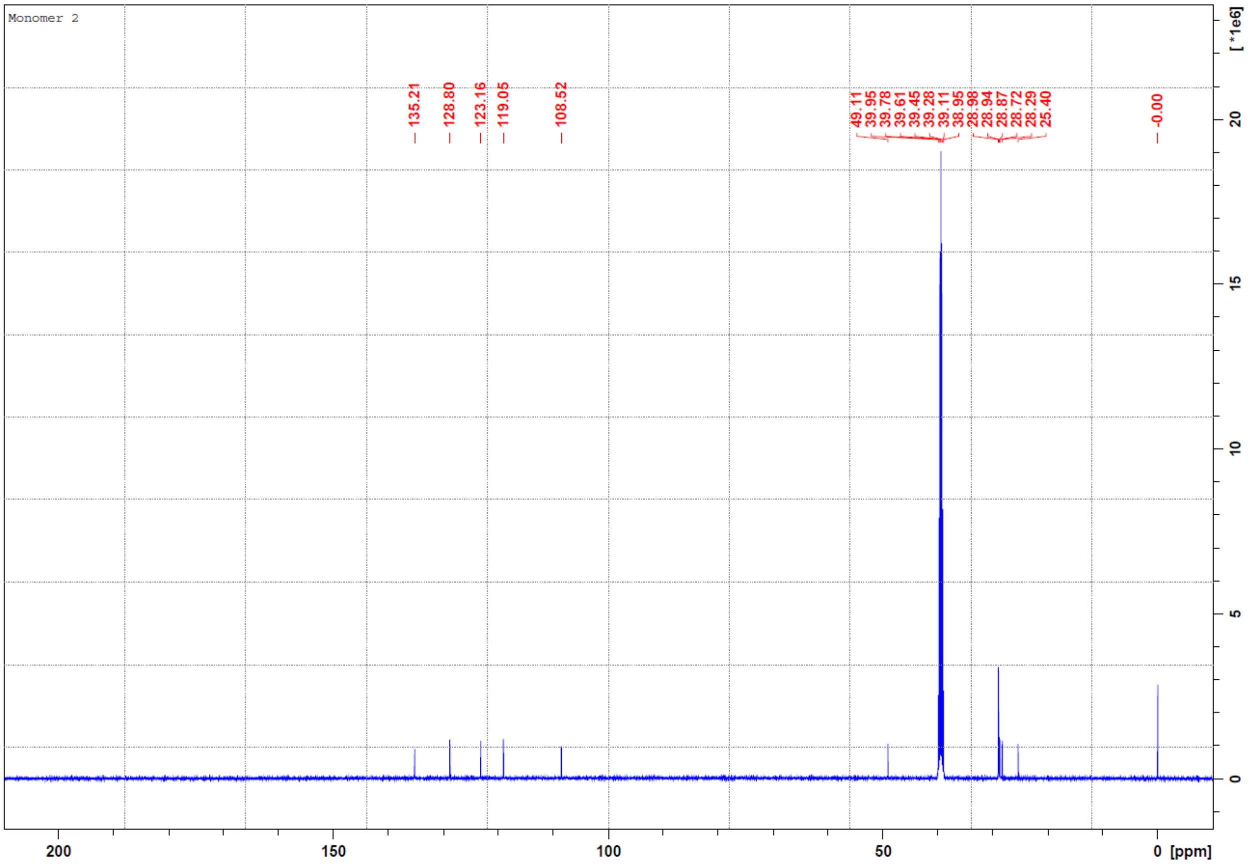
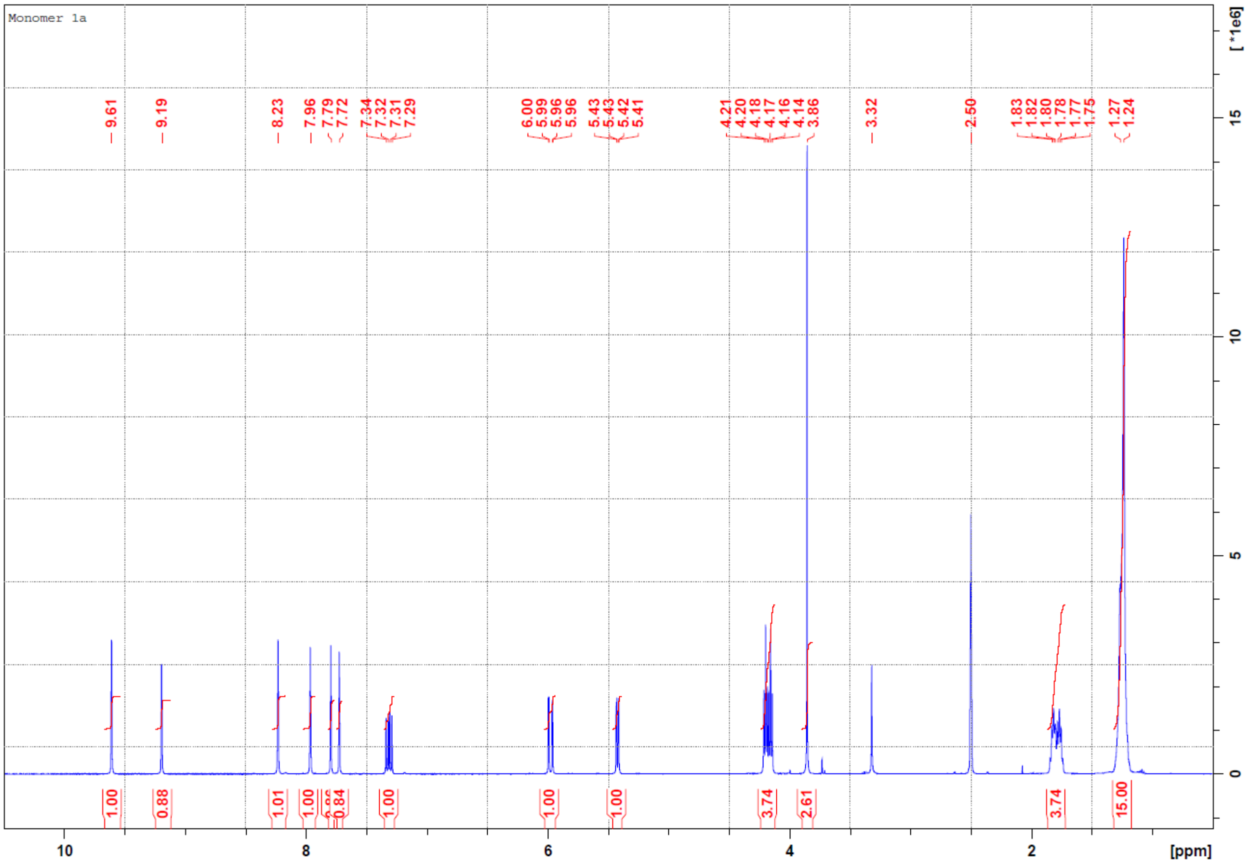


Fig. S7. ^{1}H (500 MHz, DMSO-d_6) of monomer **1a**



Due to the non-selective chemistry, the first reaction step produces monomer **1** that cannot be separated from monomer **1a**. Since monomer **1a** contains a unique CH proton at 9.19 ppm, but both monomer **1** and **1a** contain a CH proton at 9.61 ppm, the ratio of monomer **1a** and **1** is given by:

$$\frac{\text{monomer } \mathbf{1a}}{\text{monomer } \mathbf{1}} = \frac{I_{CH\ at\ 9.19\ ppm}}{(I_{CH\ at\ 9.61\ ppm} - I_{CH\ at\ 9.19\ ppm})/2}$$

The mol % of monomer **1a** can be calculated as follows:

$$\text{monomer } \mathbf{1a}\ (\text{mol }\%) = \frac{I_{CH\ at\ 9.19\ ppm}}{I_{CH\ at\ 9.19\ ppm} + (I_{CH\ at\ 9.61\ ppm} - I_{CH\ at\ 9.19\ ppm})/2}$$

$$= \frac{2\ I_{CH\ at\ 9.19\ ppm}}{I_{CH\ at\ 9.19\ ppm} + I_{CH\ at\ 9.61\ ppm}}$$

Fig. S8. ^{13}C (500 MHz, DMSO-*d*$_6$) of monomer **1a**

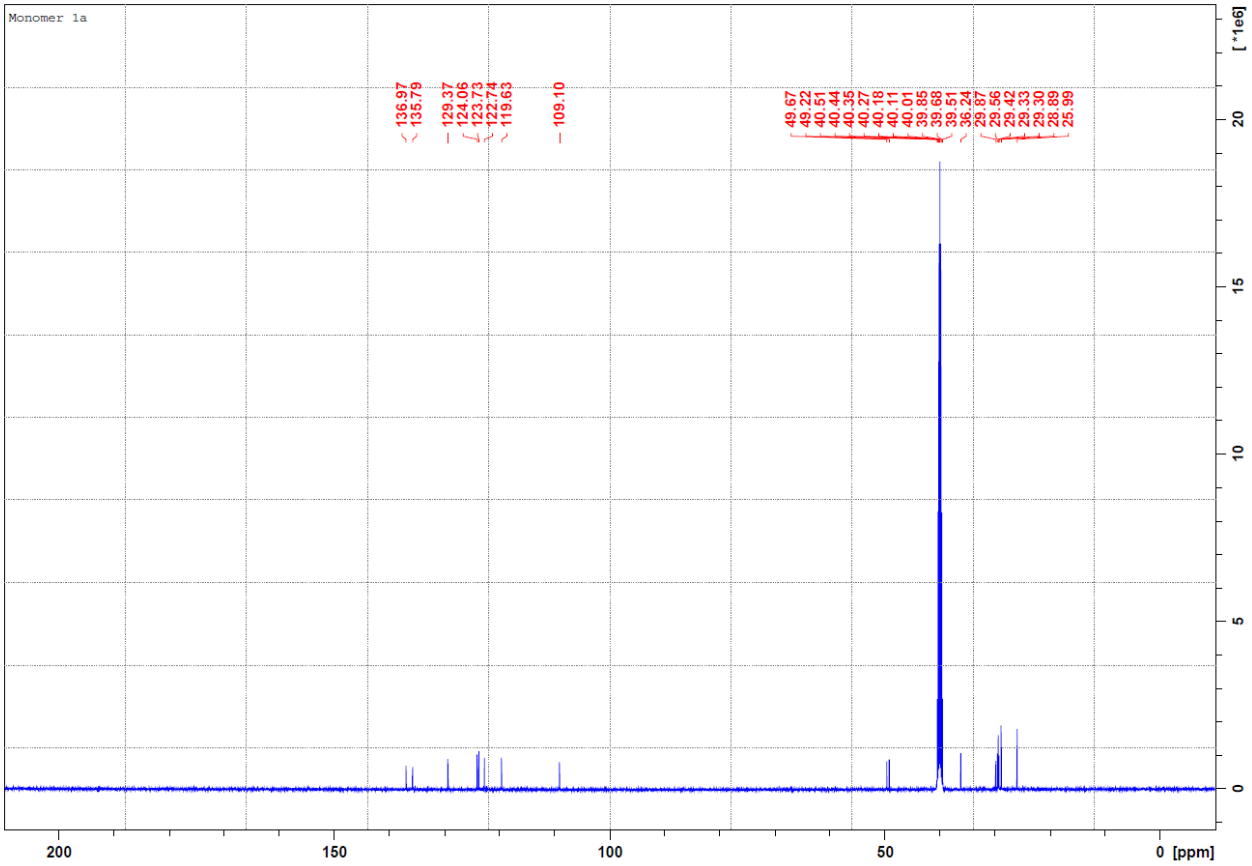
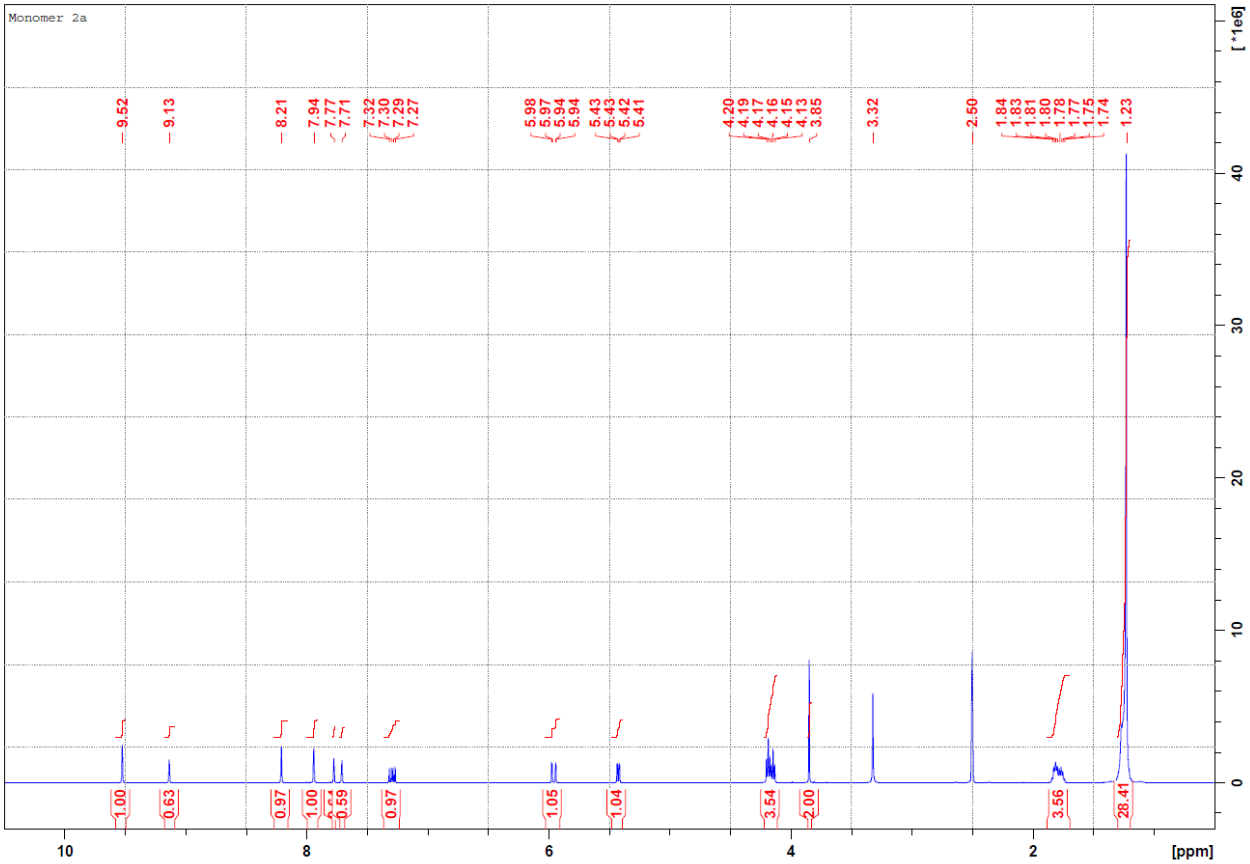


Fig. S9. ^{1}H (500 MHz, DMSO-d_6) of monomer **2a**



Due to the non-selective chemistry, the first reaction step produces monomer **2** that cannot be separated from monomer **2a**. Since monomer **2a** contains a unique CH proton at 9.13 ppm, but both monomer **2** and **2a** contain a CH proton at 9.52 ppm, the ratio of monomer **2a** and **2** is given by:

$$\frac{\text{monomer } \mathbf{2a}}{\text{monomer } \mathbf{2}} = \frac{I_{CH\ at\ 9.13\ ppm}}{(I_{CH\ at\ 9.52\ ppm} - I_{CH\ at\ 9.13\ ppm})/2}$$

The mol % of monomer **2a** can be calculated as follows:

$$\text{monomer } \mathbf{2a}\ (\text{mol }\%) = \frac{I_{CH\ at\ 9.13\ ppm}}{I_{CH\ at\ 9.13\ ppm} + (I_{CH\ at\ 9.52\ ppm} - I_{CH\ at\ 9.13\ ppm})/2}$$

$$= \frac{2\ I_{CH\ at\ 9.13\ ppm}}{I_{CH\ at\ 9.13\ ppm} + I_{CH\ at\ 9.52\ ppm}}$$

Fig. S10. ^{13}C (500 MHz, DMSO-d_6) of monomer **2a**

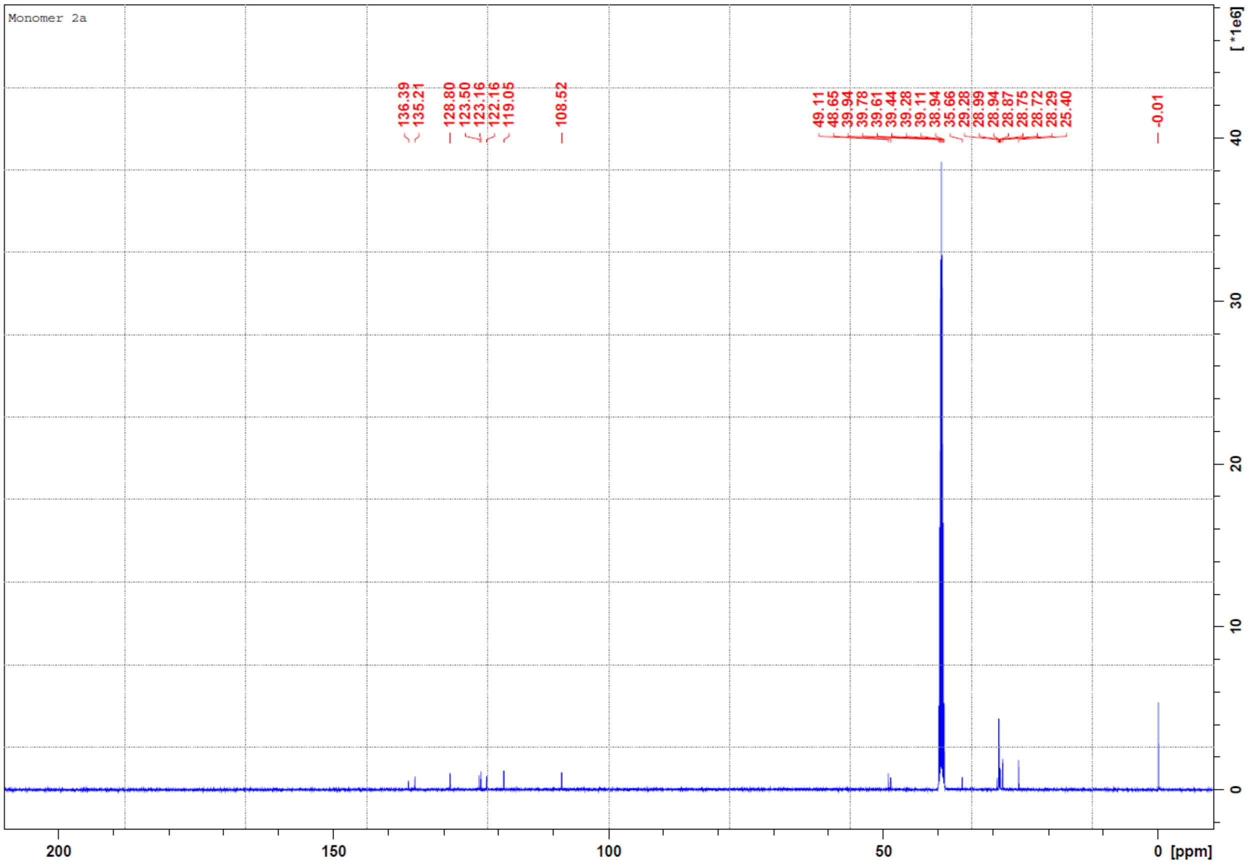


Fig. S11. Temperatures used to prepare membranes at different prepolymerization solvent contents. Curing was performed by photopolymerization.

Prepolymerization solvent content (wt. %)	Solvent	Monomer	Polymerization temperature (°C)
12.50	Water	**1** or **1a**	80
25.00	Water	**1** or **1a**	20
37.50	Water	**1** or **1a**	20
50.00	Water	**1** or **1a**	20
31.25	Methanol	**1** or **1a**	45
37.50	Methanol	**1** or **1a**	35
43.75	Methanol	**1** or **1a**	35
50.00	Methanol	**1** or **1a**	25
25.00	Methanol	**2** or **2a**	40
31.25	Methanol	**2** or **2a**	35
37.50	Methanol	**2** or **2a**	35
50.00	Methanol	**2** or **2a**	25

Fig. S12. Representative ATR FTIR spectra of monomer **1** before and after polymerization. Polymer was dried in a vacuum oven to remove solvent prior to measurement.

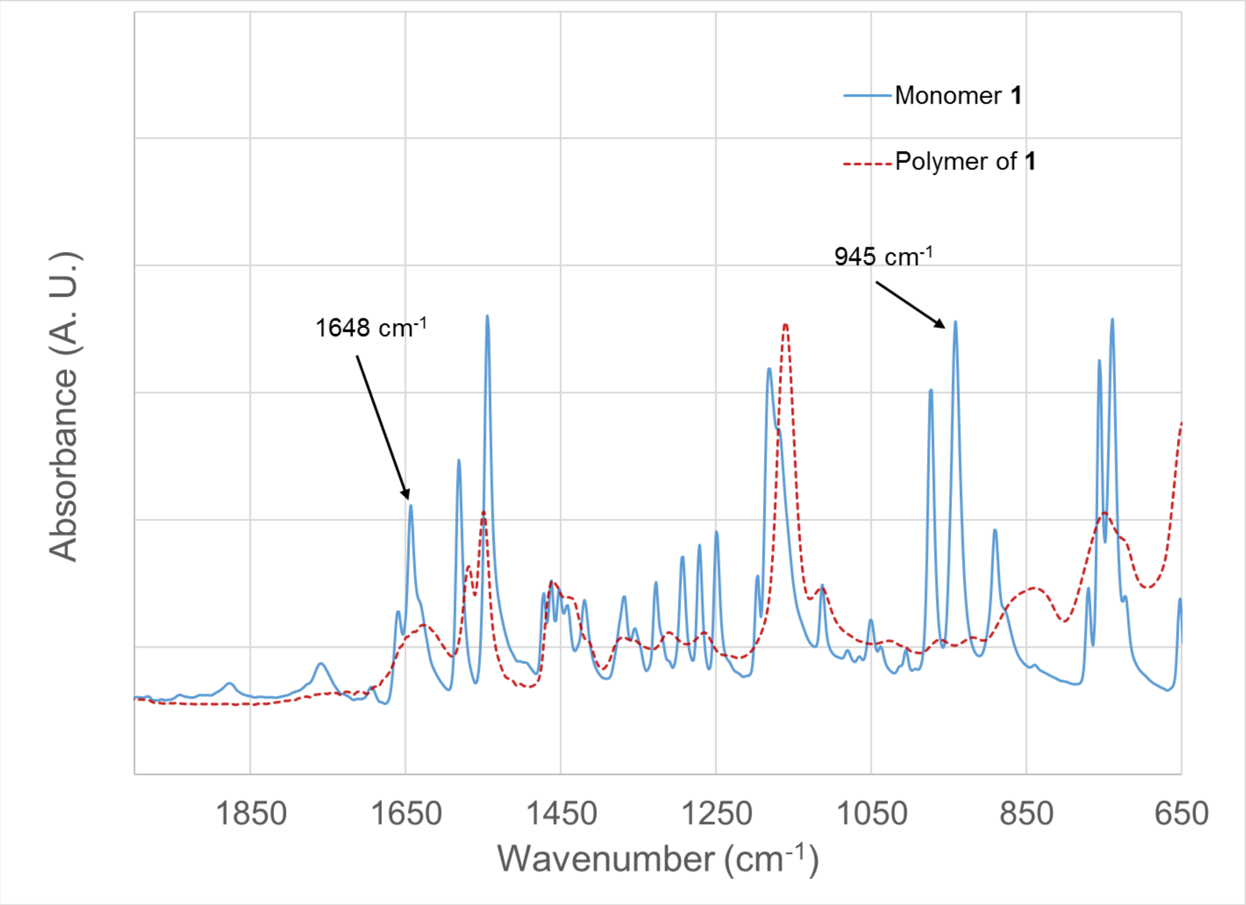


Fig. S13. Representative ATR FTIR spectra of monomer **2** before and after polymerization. Polymer was dried in a vacuum oven to remove solvent prior to measurement.

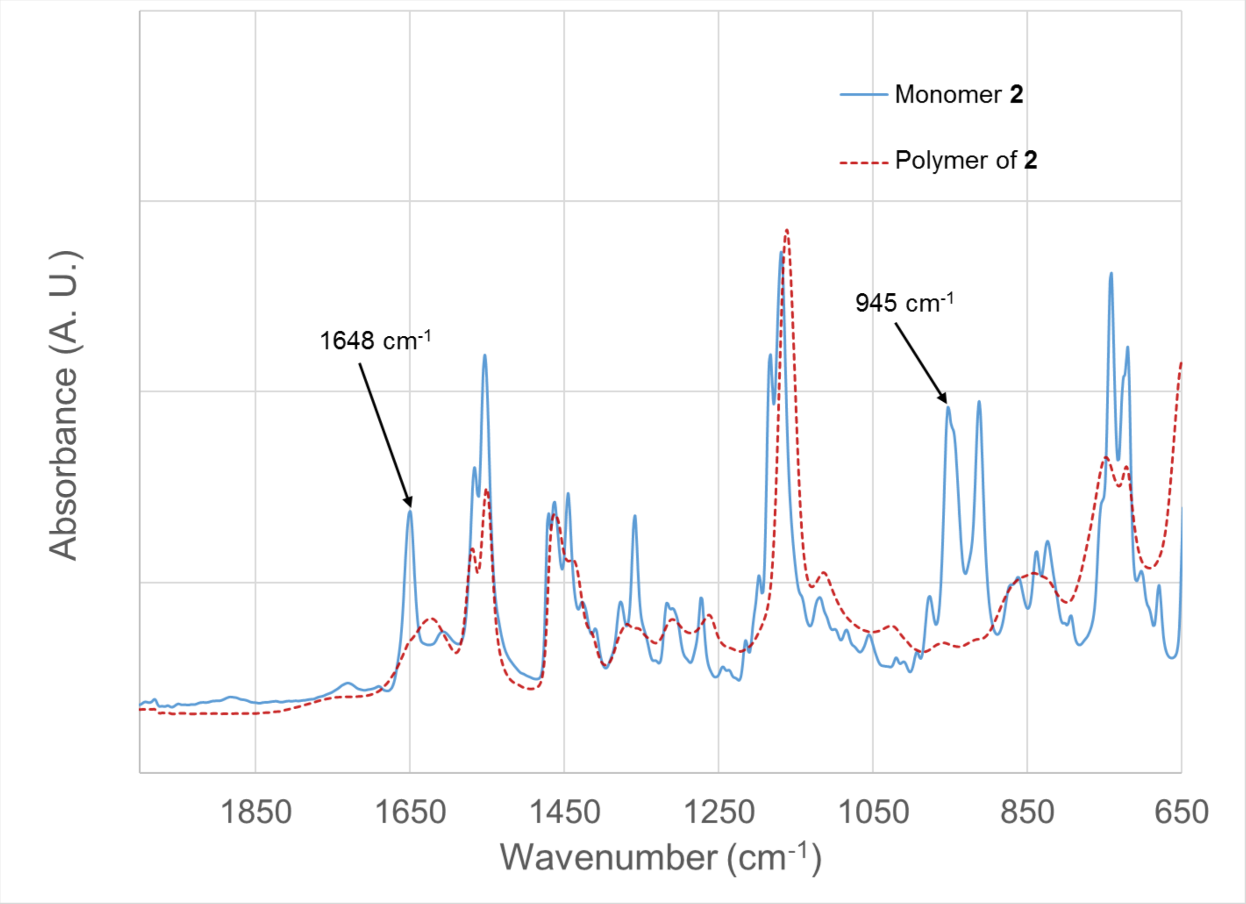


Fig. S14. Representative ATR FTIR spectra of monomer **1** and **1a** before and after polymerization. Polymers were dried in a vacuum oven to remove solvent prior to measurement.

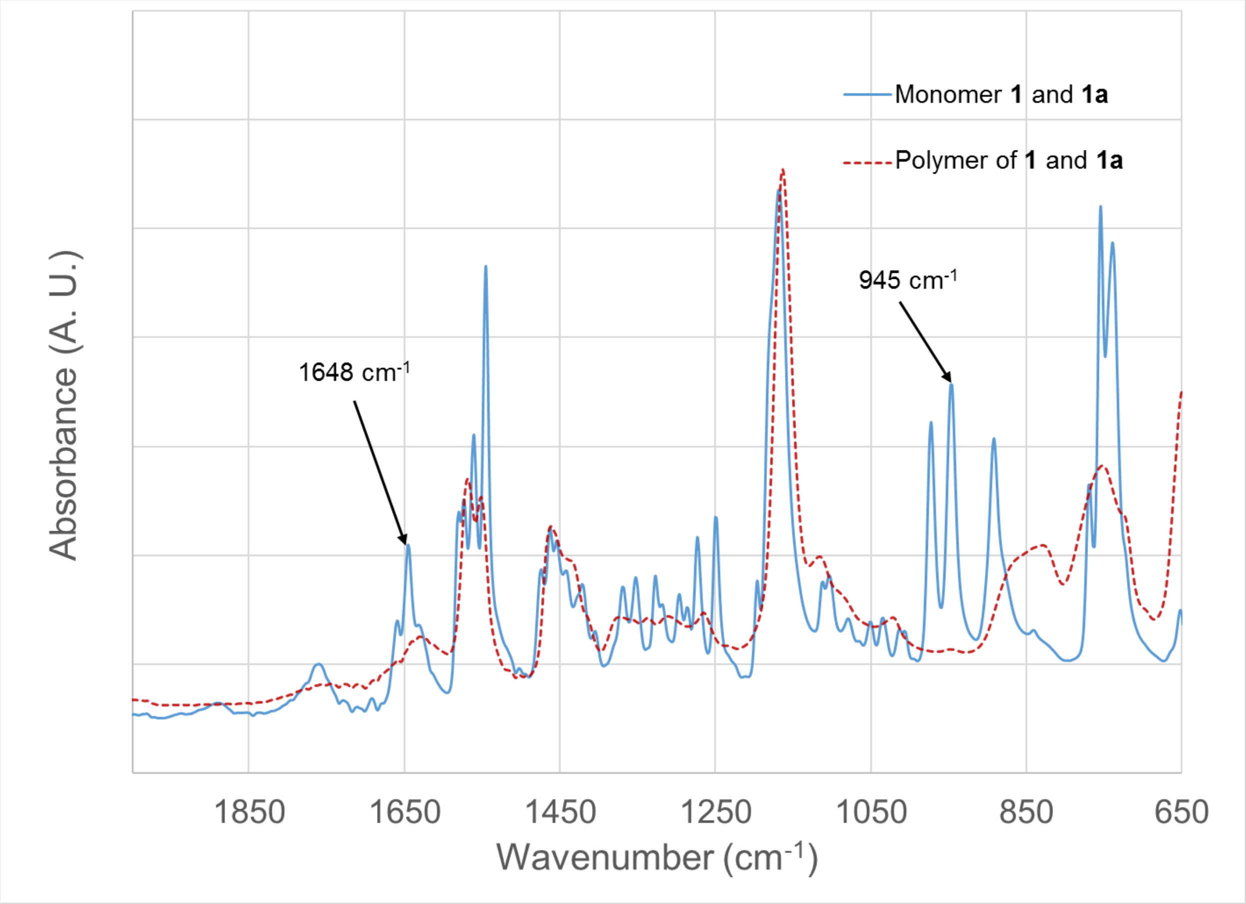
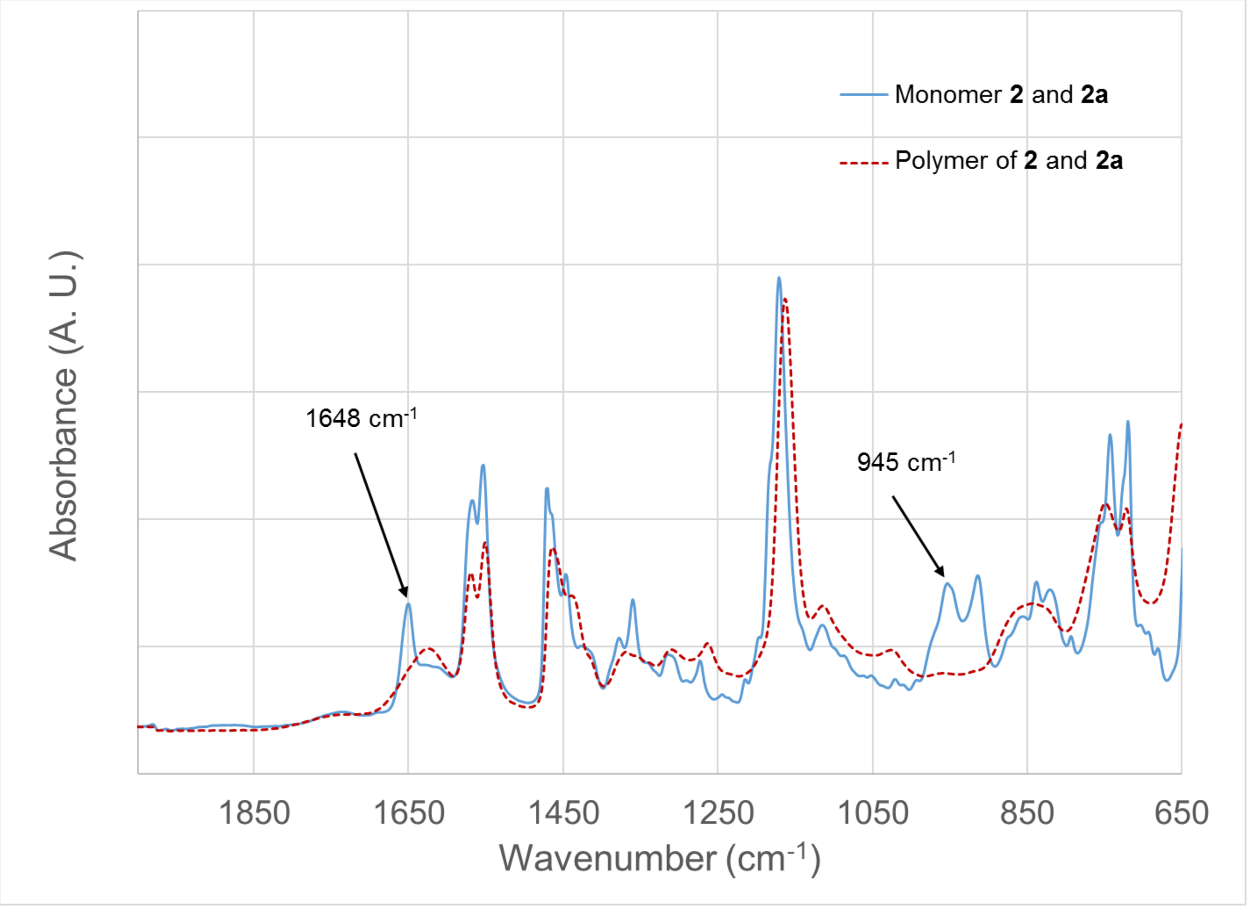


Fig. S15. Representative ATR FTIR spectra of monomer **2** and **2a** before and after polymerization. Polymers were dried in a vacuum oven to remove solvent prior to measurement.



2.10 Thermal characterization

Differential scanning calorimetry (DSC) was performed on dried polymer films using a TA Instruments Q20 (New Castle, DE). All samples were dried under vacuum (< 1 Torr, 40 °C) for a minimum of 24 h before analysis. To erase the thermal history of the samples, they were heated to 200 °C at 10 °C/min or 20 °C/min, held isothermally for 5 min, and then cooled to -80 °C at 5 °C/min or 10 °C/min and held isothermally for 5 min. This cycle was repeated and the second cycle was used for analysis.

Thermogravimetric analysis (TGA) was performed on dry polymer films using a TA Instruments Q50 (New Castle, DE). All samples were dried under vacuum (< 1 Torr, 40 °C) for a minimum of 24 h before analysis. Samples were equilibrated at 25 °C, then heated to 500 °C at 5 °C/min and held isothermally for 5 min.