

**Supporting Information for:**

**Depolymerization of PET by Common Alkanolamines Yields Tunable Monomers to Expand the Design Space of 3D-Printable, Self-Healing Polyamide-Ionenes**

Mousumi R. Bepari, Pravin S. Shinde & Jason E. Bara\*

Department of Chemical & Biological Engineering, University of Alabama, Tuscaloosa, Alabama, USA 35487-0203

Corresponding author's email address: [jbara@eng.ua.edu](mailto:jbara@eng.ua.edu)

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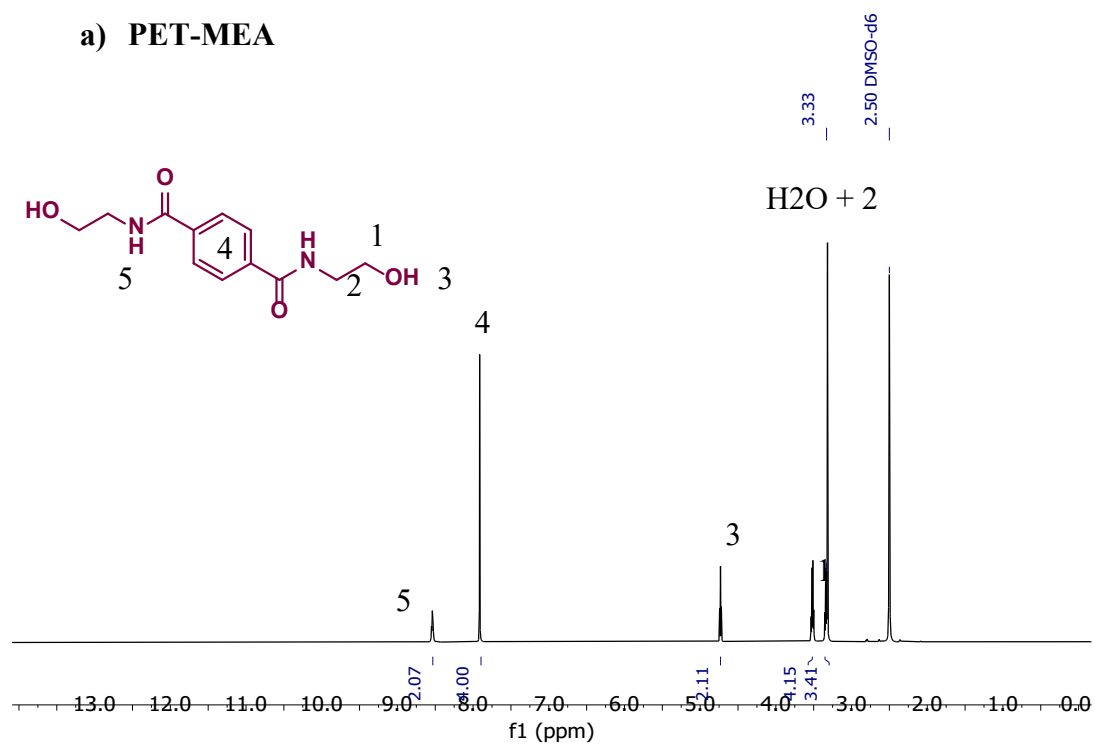
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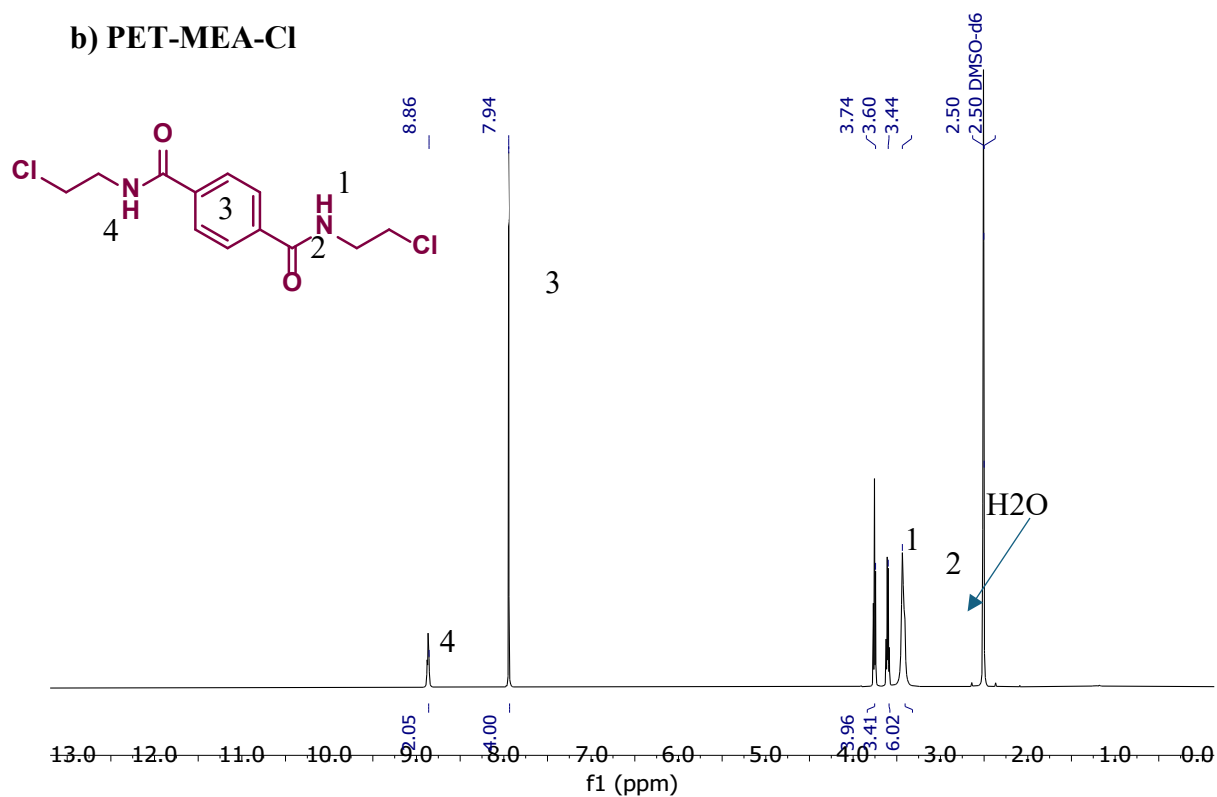
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**S1.  $^1\text{H}$  NMR of depolymerization compounds and chlorinated monomers.**

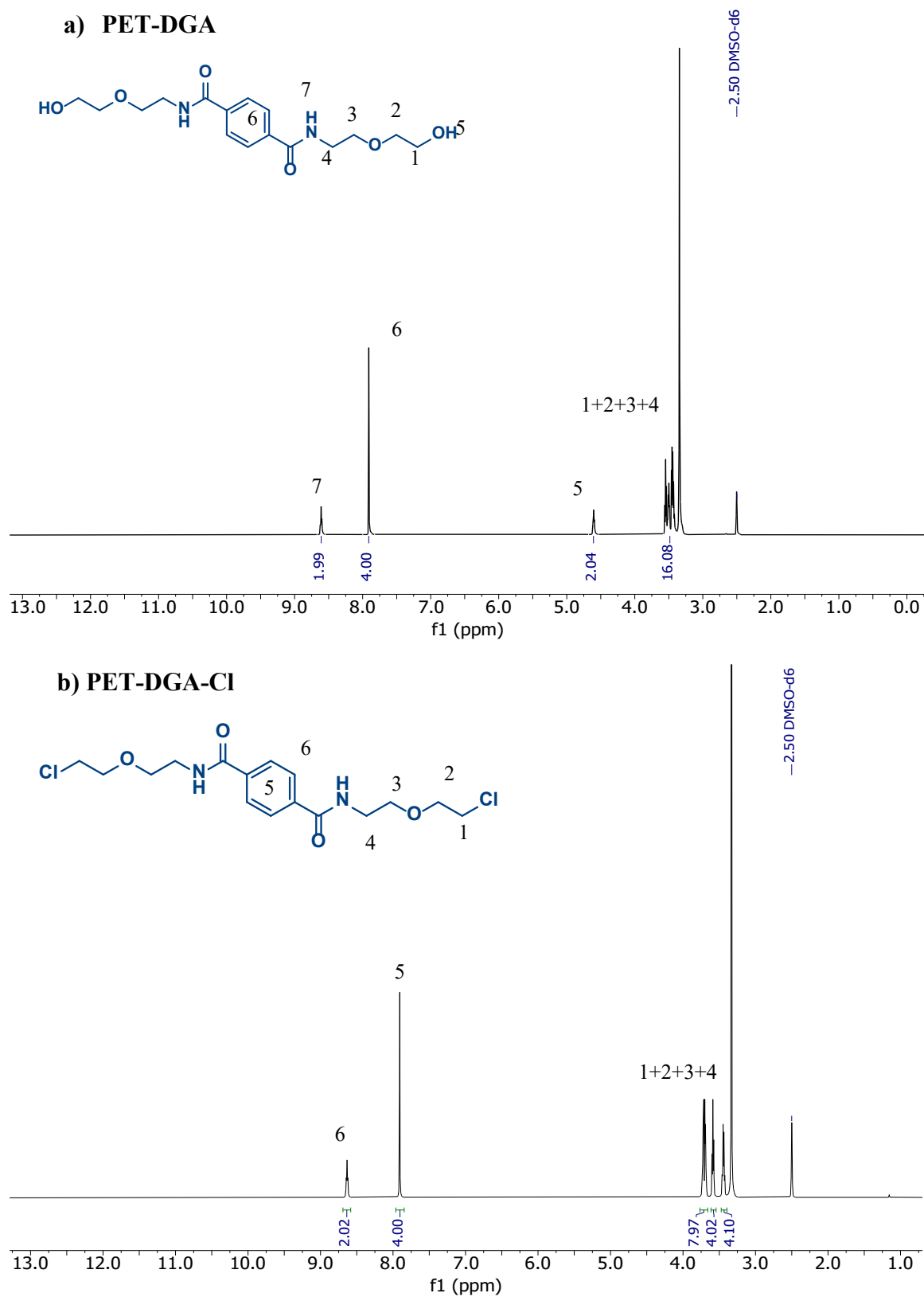
**a) PET-MEA**



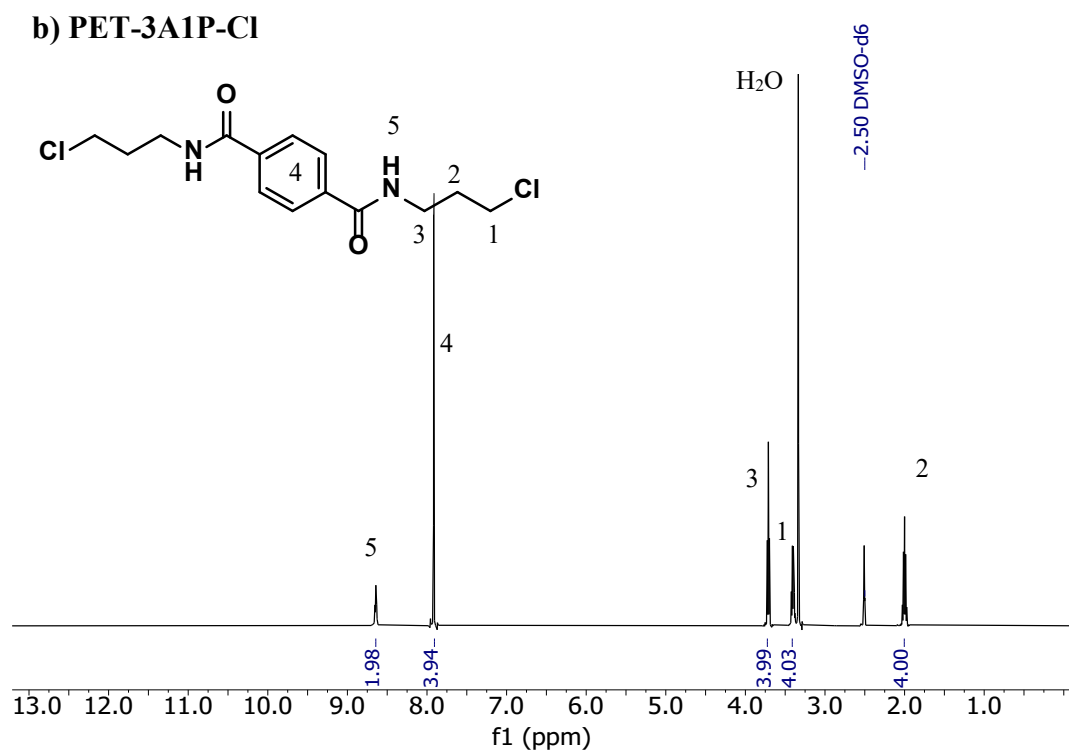
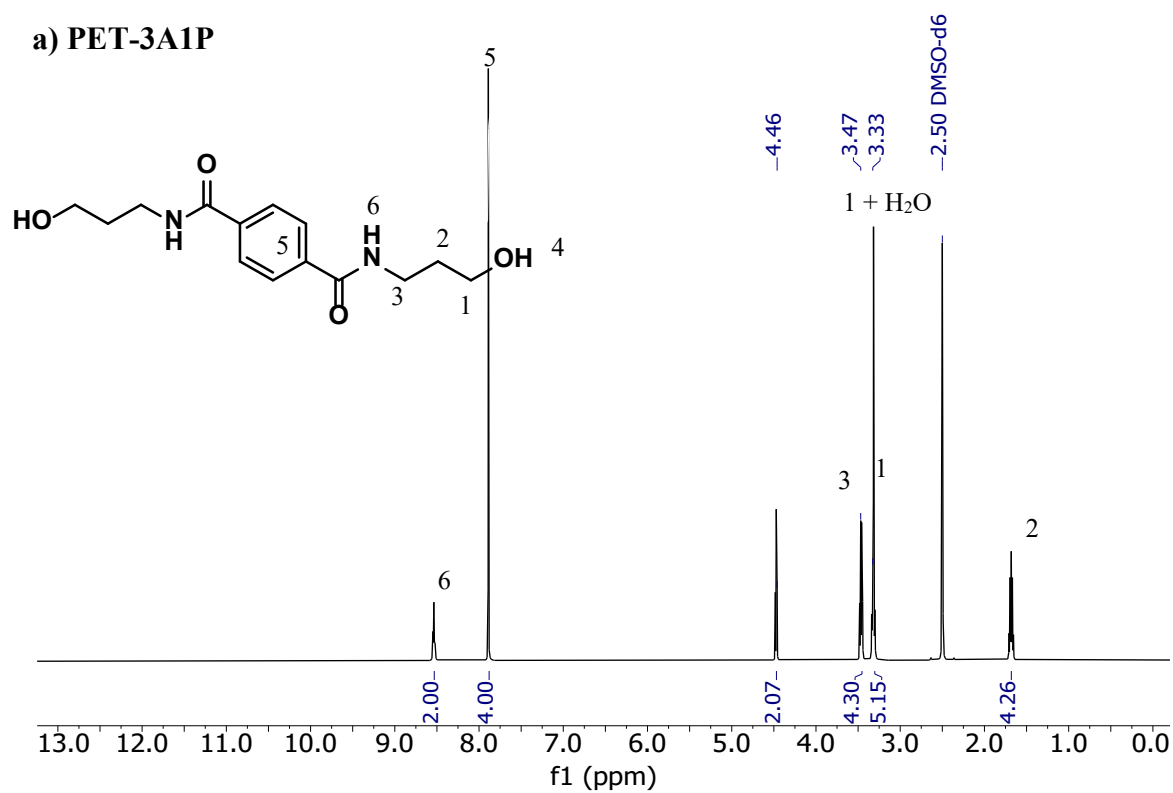
**b) PET-MEA-Cl**



**Fig. S 1**  $^1\text{H}$  NMR (500MHz,  $\text{d}_6\text{-DMSO}$ ) of a) PET-MEA b) PET-MEA-Cl.



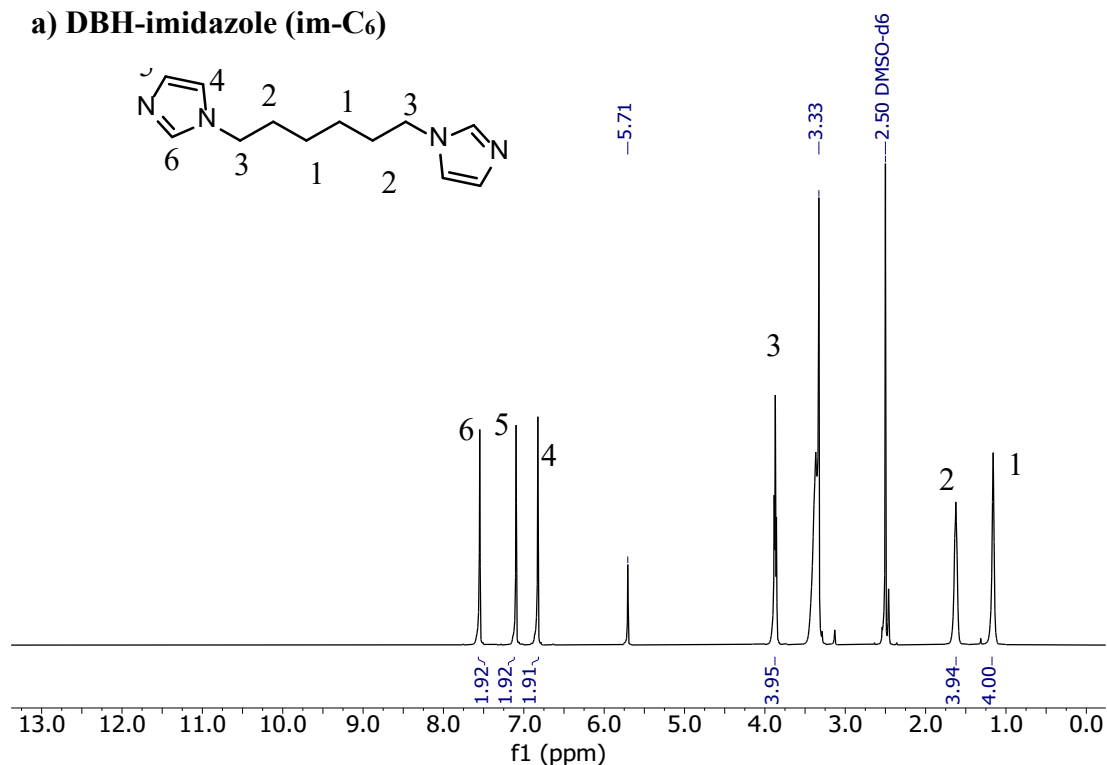
**Fig. S 2**  $^1\text{H}$  NMR (500MHz,  $\text{d}_6\text{-DMSO}$ ) of a) PET-DGA b) PET-DGA-Cl.



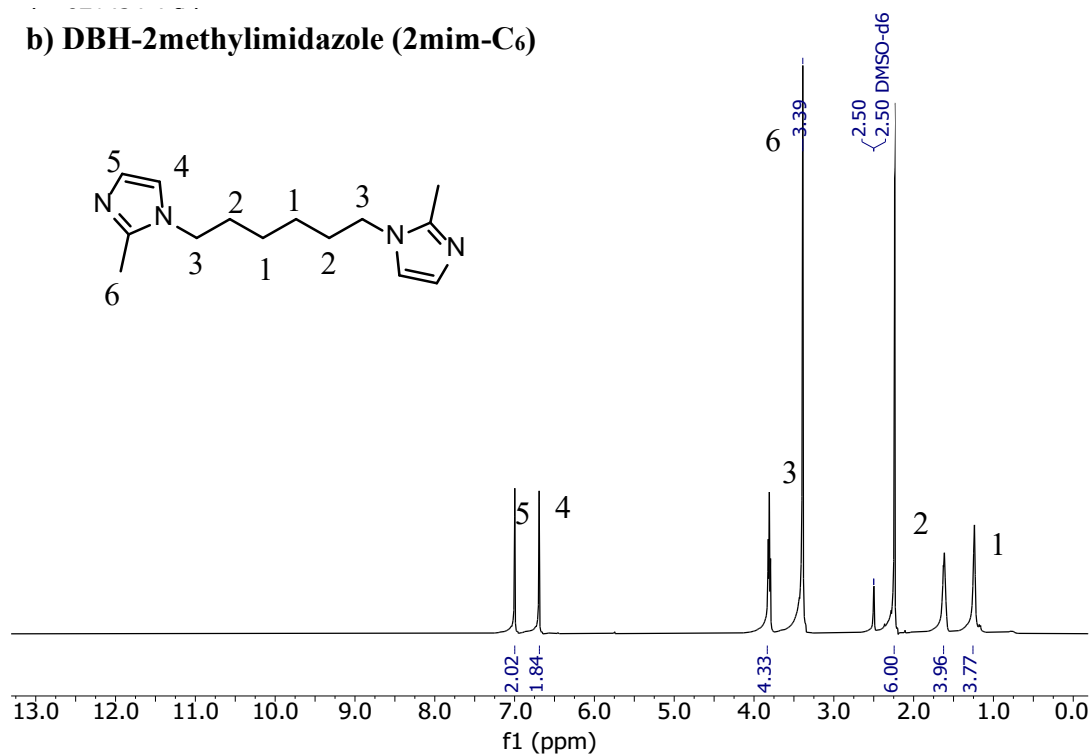
**Fig. S 3** <sup>1</sup>H NMR (500MHz, d<sub>6</sub>-DMSO) of a) PET-3A1P b) PET-3A1P-Cl.

## S2. Confirmation of bisimidazolium monomers by $^1\text{H}$ NMR.

### a) DBH-imidazole (im- $\text{C}_6$ )



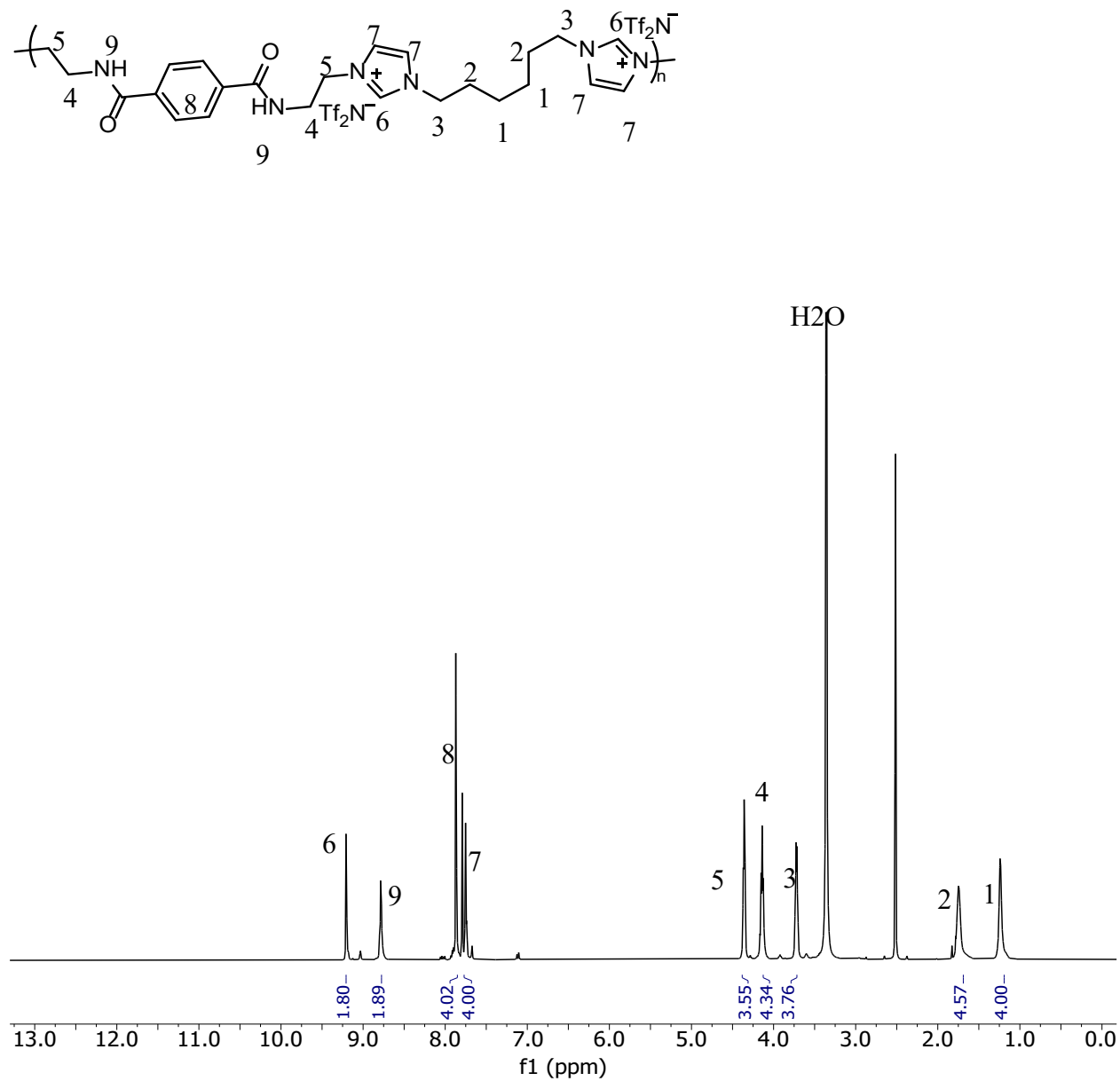
### b) DBH-2methylimidazole (2mim- $\text{C}_6$ )



**Fig. S4**  $^1\text{H}$  NMR (500 MHz,  $\text{d}_6$ -DMSO) of a) 1,1'-(1,6-hexanediyl)bisimidazole (DBH\_im/im- $\text{C}_6$ ) b) 1,1'-(1,6-hexanediyl)-2-methylbisimidazole (DBH\_2mim/2mim- $\text{C}_6$ ).

### S3. Confirmation of PA-ionenes by $^1\text{H}$ NMR.

#### PET-MEA-im- $\text{C}_6$ - $\text{Tf}_2\text{N}$ ionene (MEA-im)



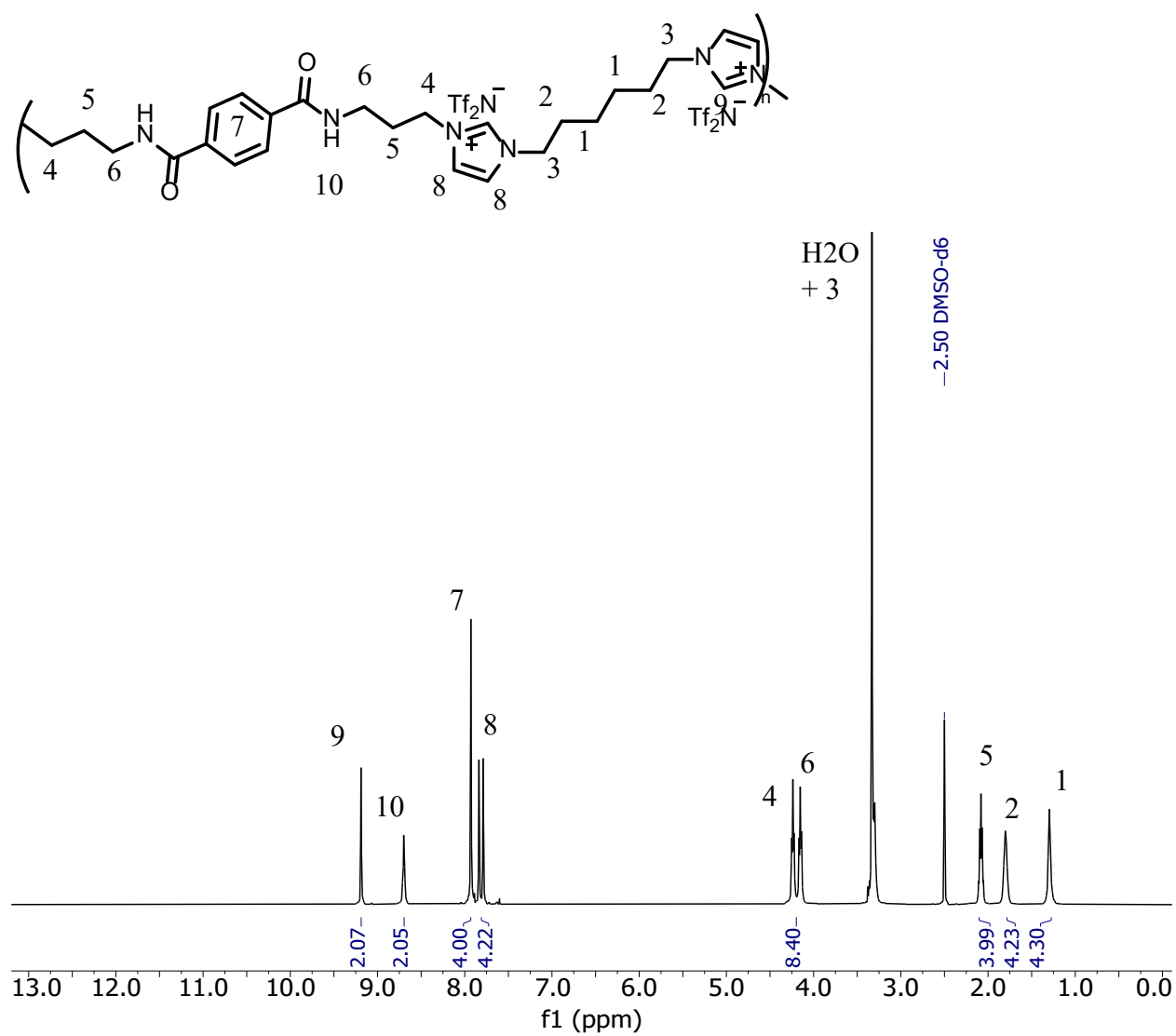
**Fig. S 5**  $^1\text{H}$  NMR (500MHz,  $\text{d}_6$ -DMSO) of PET-MEA-im- $\text{C}_6$ - $\text{Tf}_2\text{N}$  ionene.



[illegible]

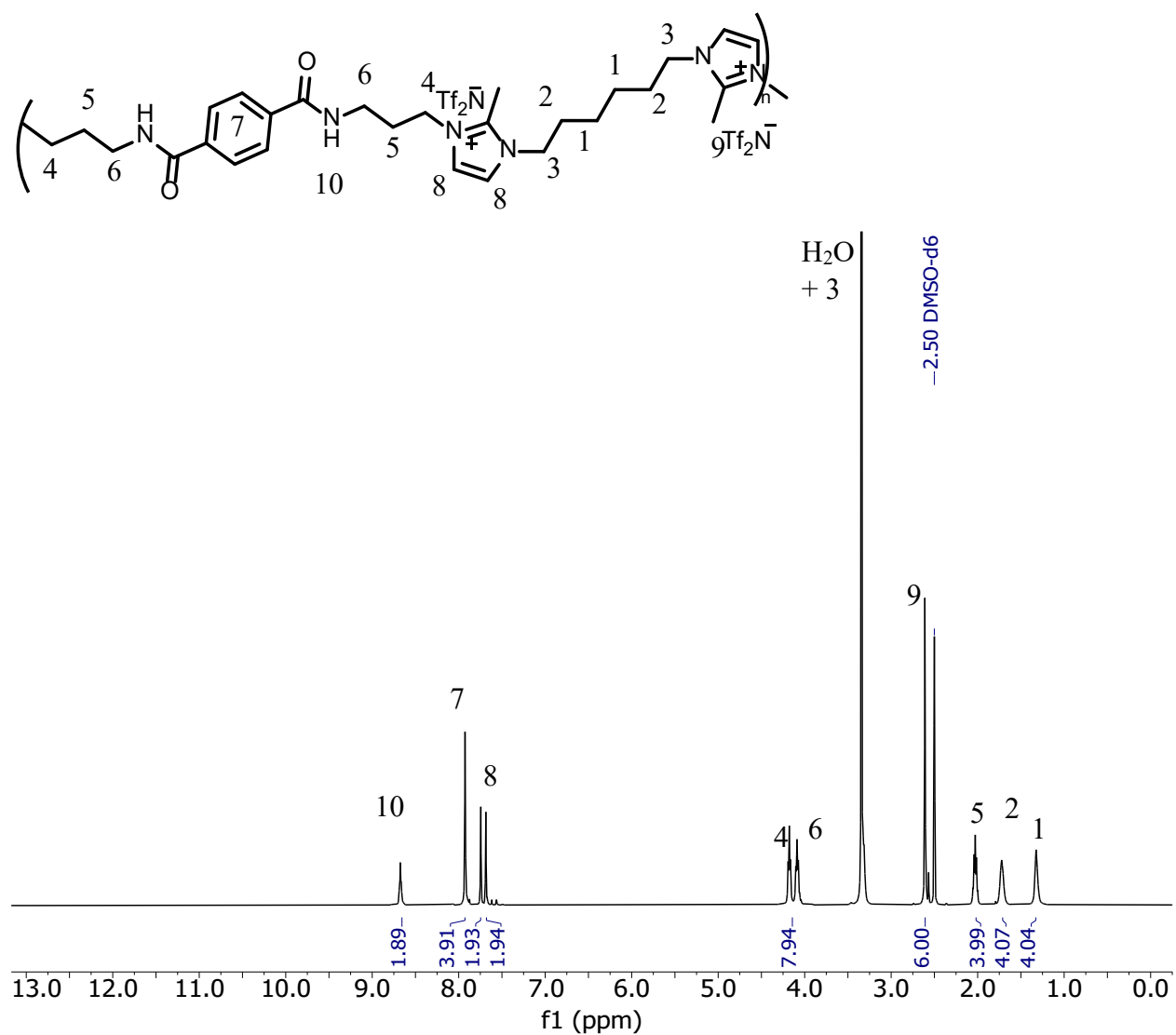
S-9

**PET-3A1P- im-C<sub>6</sub>-Tf<sub>2</sub>N ionene (3A1P-im)**



**Fig. S 7** <sup>1</sup>H NMR (500MHz, d<sub>6</sub>-DMSO) of PET-3A1P-im-C<sub>6</sub>-Tf<sub>2</sub>N ionene.

**PET-3A1P-2mim-C<sub>6</sub>-Tf<sub>2</sub>N ionene (3A1P-2mim)**



**Fig. S 8** <sup>1</sup>H NMR (500MHz, d<sub>6</sub>-DMSO) of PET-3A1P-2mim-C<sub>6</sub>-Tf<sub>2</sub>N ionene.

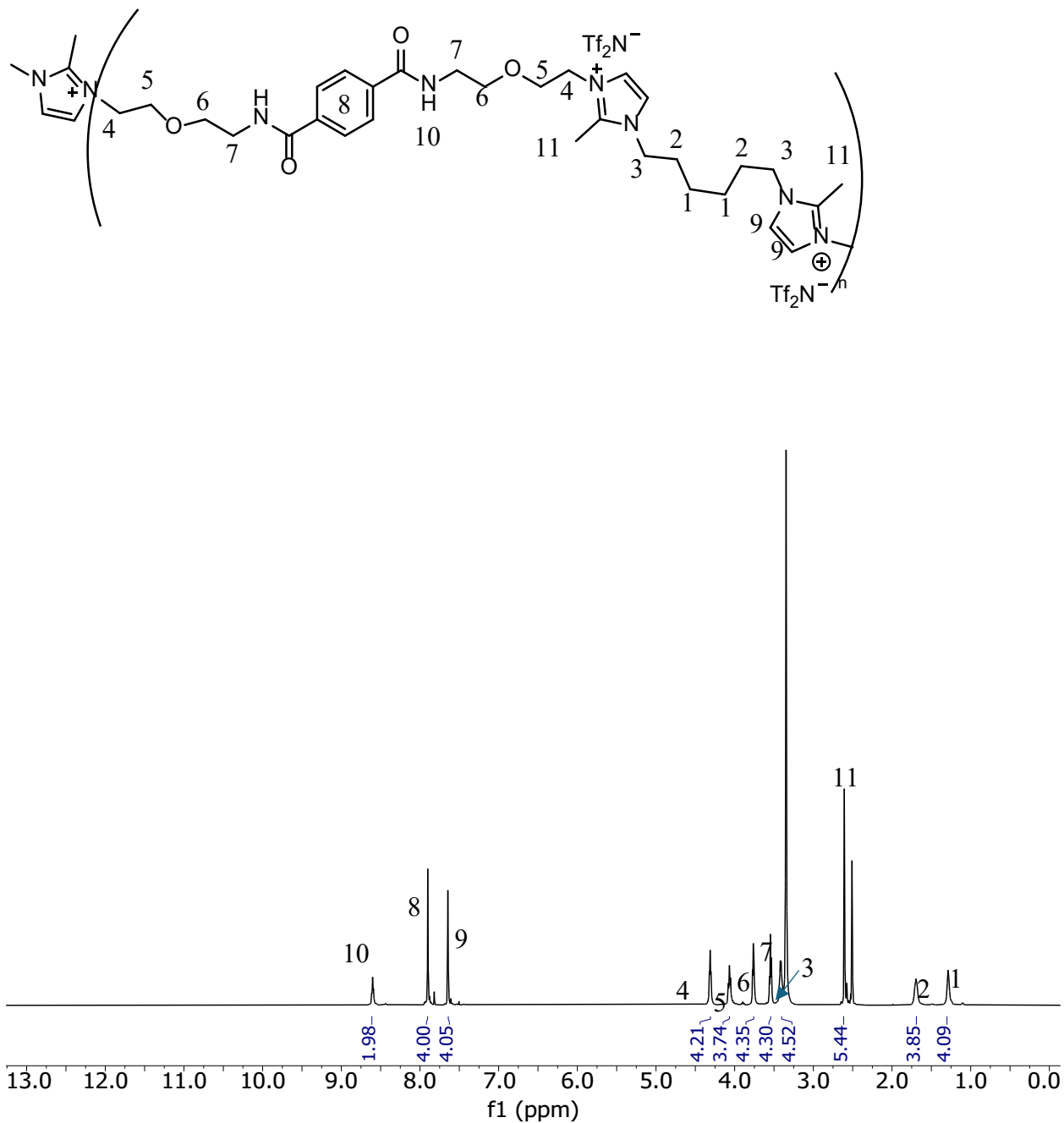
Chemical structure of the dendritic polymer is shown above the  $^1\text{H}$  NMR spectrum. The structure features a central benzamide core, two imidazolium rings, and a polyether chain. Protons are numbered 1 through 11. The  $^1\text{H}$  NMR spectrum (DMSO- $d_6$ ) shows peaks corresponding to these protons, with integration values provided below the peaks.

| Proton Number | Chemical Shift (ppm) | Integration |
|---------------|----------------------|-------------|
| 1             | ~1.0                 | 3.86        |
| 2             | ~1.8                 | 4.10        |
| 3             | ~3.4                 | 4.02        |
| 4             | ~4.3                 | 3.96        |
| 5             | ~4.1                 | 4.01        |
| 6             | ~4.0                 | 3.92        |
| 7             | ~4.2                 | 4.08        |
| 8             | ~7.8                 | 4.00        |
| 9             | ~7.6                 | 3.89        |
| 10            | ~8.8                 | 1.88        |
| 11            | ~9.0                 | 1.88        |

The solvent peak for DMSO- $d_6$  is indicated at 2.50 ppm.

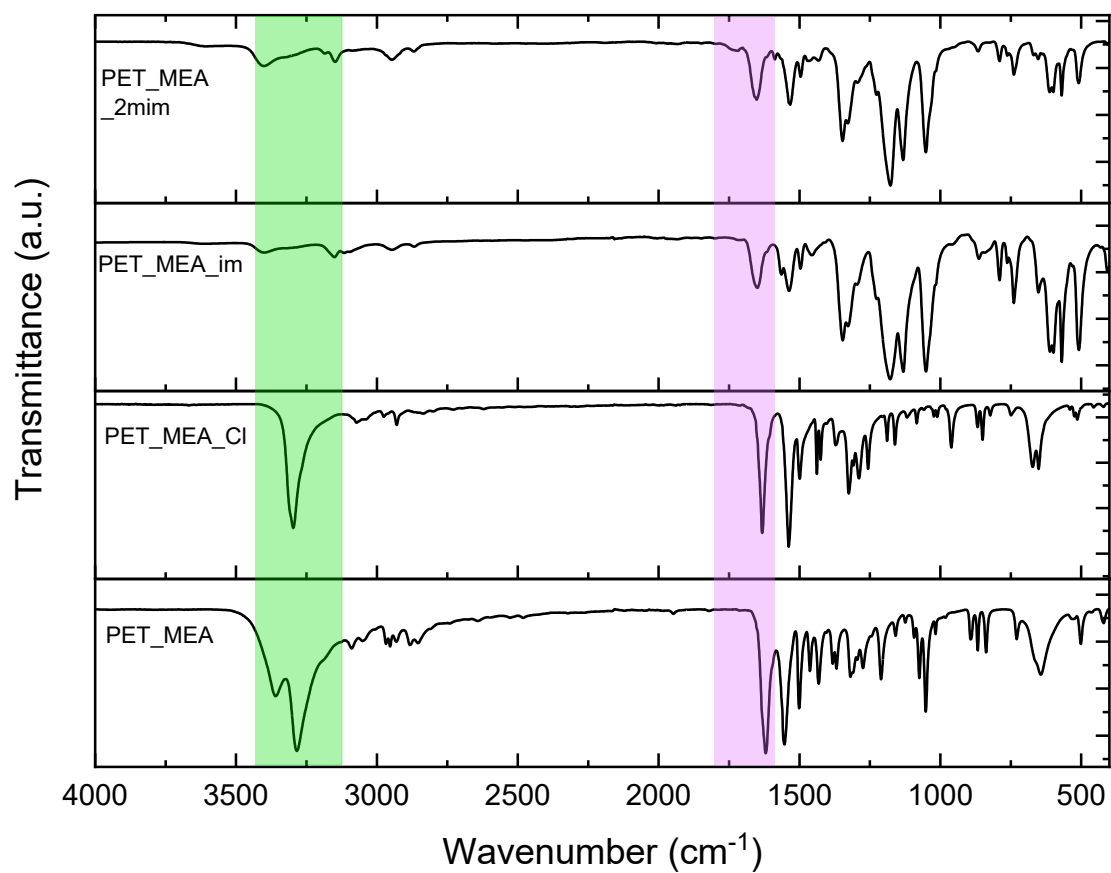
S-12

**PET-DGA-2mim-C<sub>6</sub>-Tf<sub>2</sub>N ionene (DGA-2mim)**

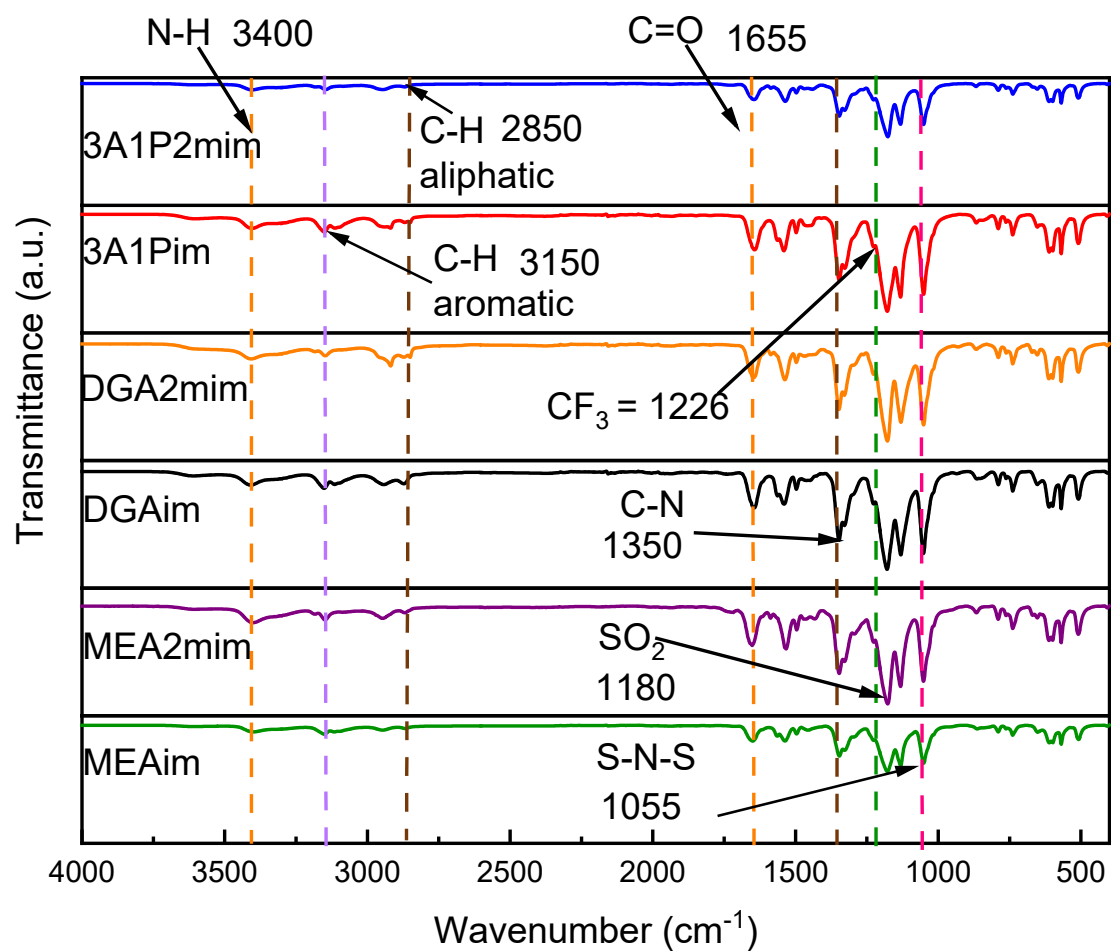


**Fig. S 10** <sup>1</sup>H NMR (500MHz, d<sub>6</sub>-DMSO) of PET-DGA-2mim-C<sub>6</sub>-Tf<sub>2</sub>N ionene.

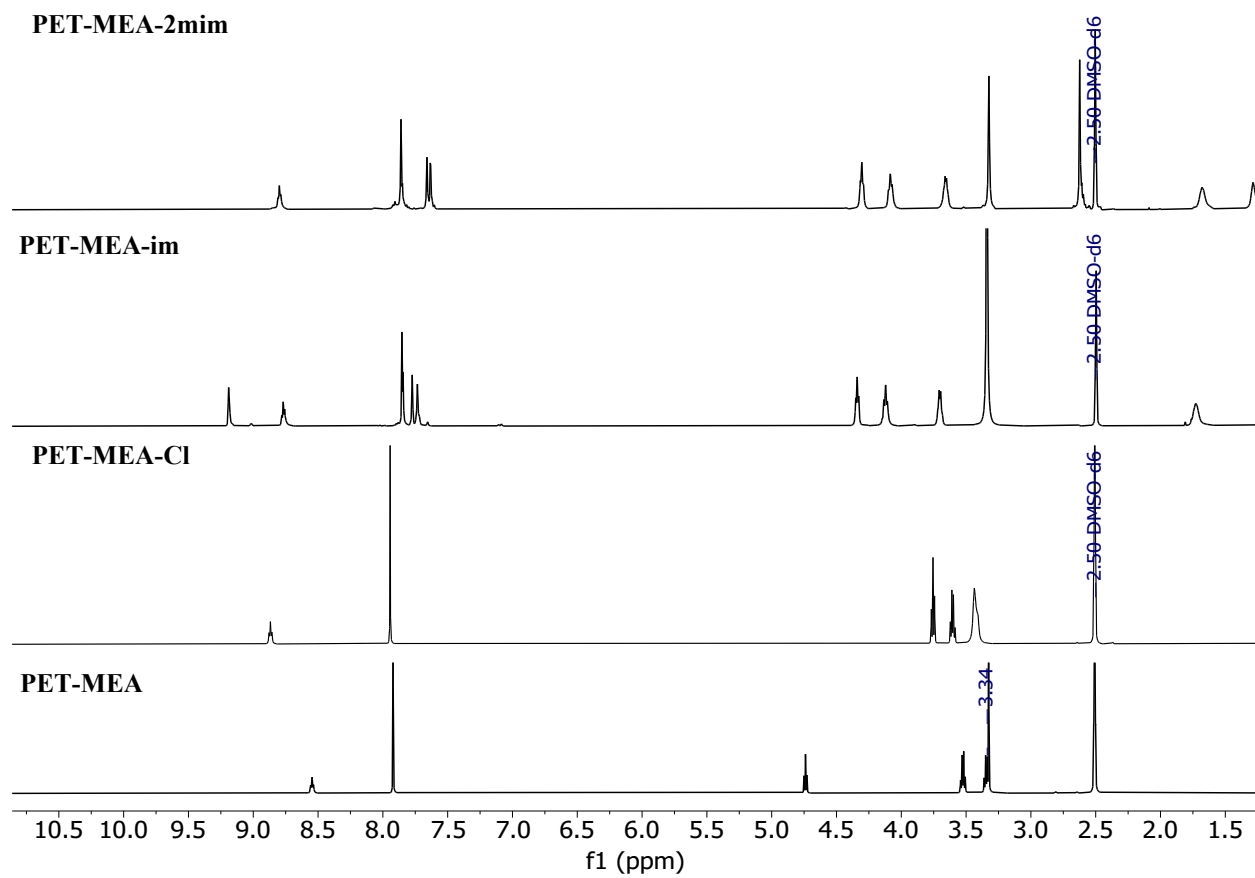
**S4. Structural verification of monomers (PET-MEA, PET-MEA -Cl) and corresponding polymers by FTIR.**



**Fig. S 11** Transformation of PET-MEA compound to valuable ionene showed by ATR-FTIR.



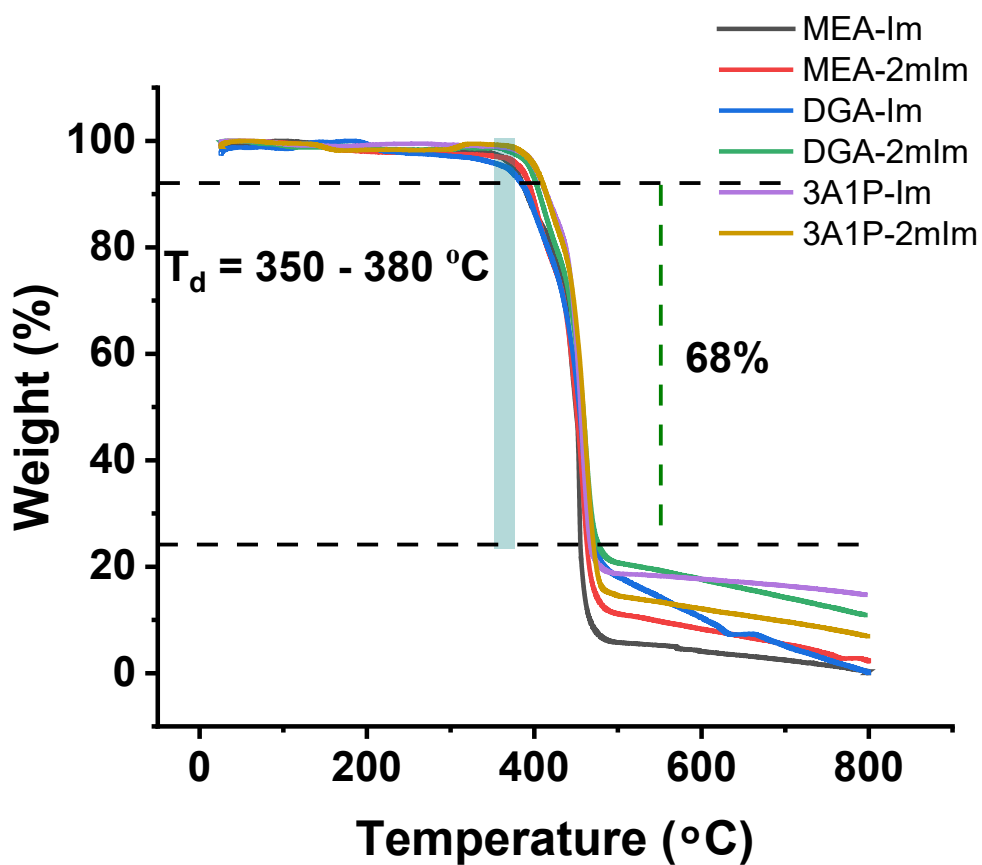
**Fig. S 12** Incorporation of ionic moieties and functional groups observed in ATR-FTIR of PA-ionenes.



**Fig. S 13** Comparison of  $^1\text{H}$  NMR spectra for building blocks and final PA-ionene products “PET-MEA-im” and “PET-MEA-2mim”.



**S5. Thermal property (TGA,  $T_m$ ), monomers composition toward ionene synthesis and printing parameters.**



**Fig. S 14** TGA plots of PA-ionenes derived from waste PET.

**Table S 1.** Reactant amounts and polymer yields for all six PA-ionenes

| PA-Ionene | Amide dihalide | Amount             | Bis-imidazole | Amount             | KI                  | LiTf <sub>2</sub> N | Ionene yield | Yield (%) |
|-----------|----------------|--------------------|---------------|--------------------|---------------------|---------------------|--------------|-----------|
| DGA_Im    | PET-DGA-Cl     | 10 g   26.6 mmol   | C6-Im         | 5.8 g   26.6 mmol  | 0.044 g   0.27 mmol | 14.27               | 21           | 72.7      |
| DGA_2mlm  | PET-DGA-Cl     | 10 g   26.5 mmol   | C6-2mlm       | 6.5 g   26.5 mmol  | 0.044 g   0.26 mmol | 16.14               | 23           | 78        |
| 3A1P_im   | PET-3A1P-Cl    | 8 g   25.2 mmol    | C6-Im         | 5.5 g   25.2 mmol  | 0.04 g   0.25 mmol  | 18.8                | 18.3         | 70.7      |
| 3A1P_2mim | PET-3A1P-Cl    | 11 g   34.7 mmol   | C6-2mlm       | 8.54 g   34.7 mmol | 0.06 g   0.35 mmol  | 20.5                | 22           | 82.84     |
| MEA_im    | PET-MEA-Cl     | 8 g   27.7 mmol    | C6-Im         | 6.04 g   27.7 mmol | 0.045 g   0.27 mmol | 17.8                | 21.5         | 78        |
| MEA_2mim  | PET-MEA-Cl     | 10.5 g   36.3 mmol | C6-2mlm       | 8.94 g   36.3 mmol | 0.06 g   0.36 mmol  | 20.6                | 20.7         | 55.6      |

**Table S 2.** Printing parameters obtained from a 3D bioplotter.

| PA-Ionene      | Temperature (°C) | Speed (mm/s) | Pressure (bar) | Pre-flow (s) | Post-flow (s) |
|----------------|------------------|--------------|----------------|--------------|---------------|
| DGA-Im         | 72               | 2.5          | 4.7            | 0.2          | 0.05          |
| DGA-2mlm       | 80               | 4            | 5.5            | 0.2          | 0.05          |
| 3A1P-im        | 170              | 4            | 5.5            | 0.2          | 0.05          |
| 3A1P-2mim      | 150              | 4            | 3.5            | 0.2          | 0.05          |
| MEA-im         | 75               | 2.5          | 5.5            | 0.2          | 0.05          |
| MEA-2mim*      | 180              | N/A          | 7              | 0.2          | 0.05          |
| (MEA-2mim) +IL | 75               | 2.5          | 5.5            | 0.2          | 0.05          |

\* The ionene was not printable at this condition\*

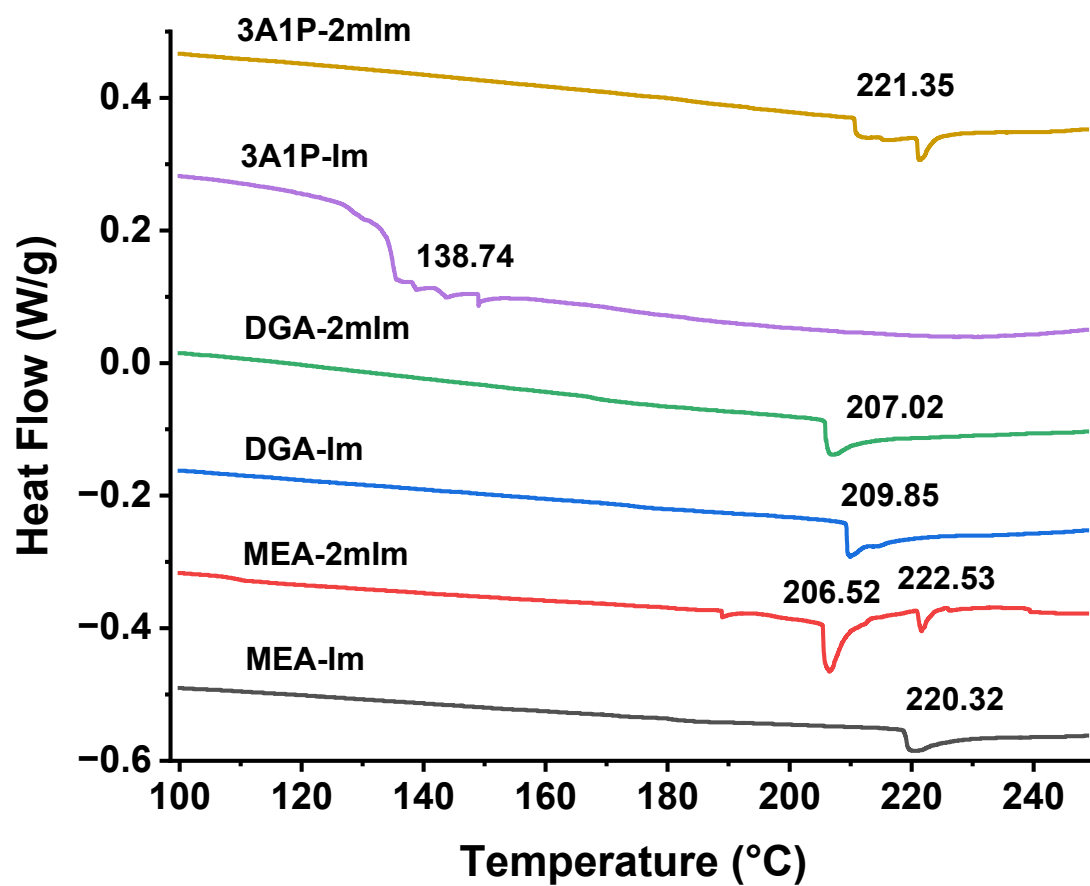
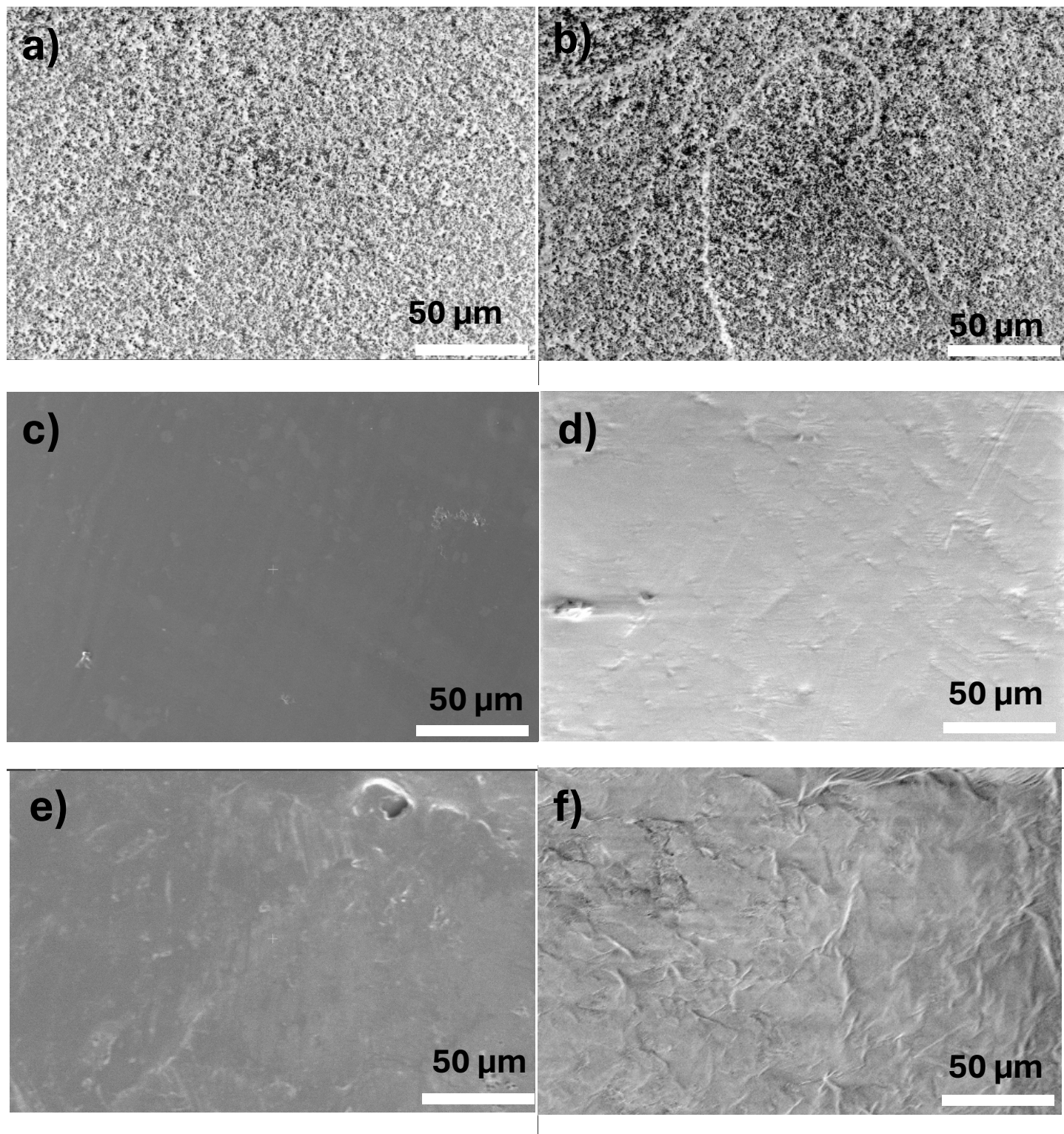


Fig. S 15 Endothermic melting peaks ( $T_m$ ) of ionene-PAs.



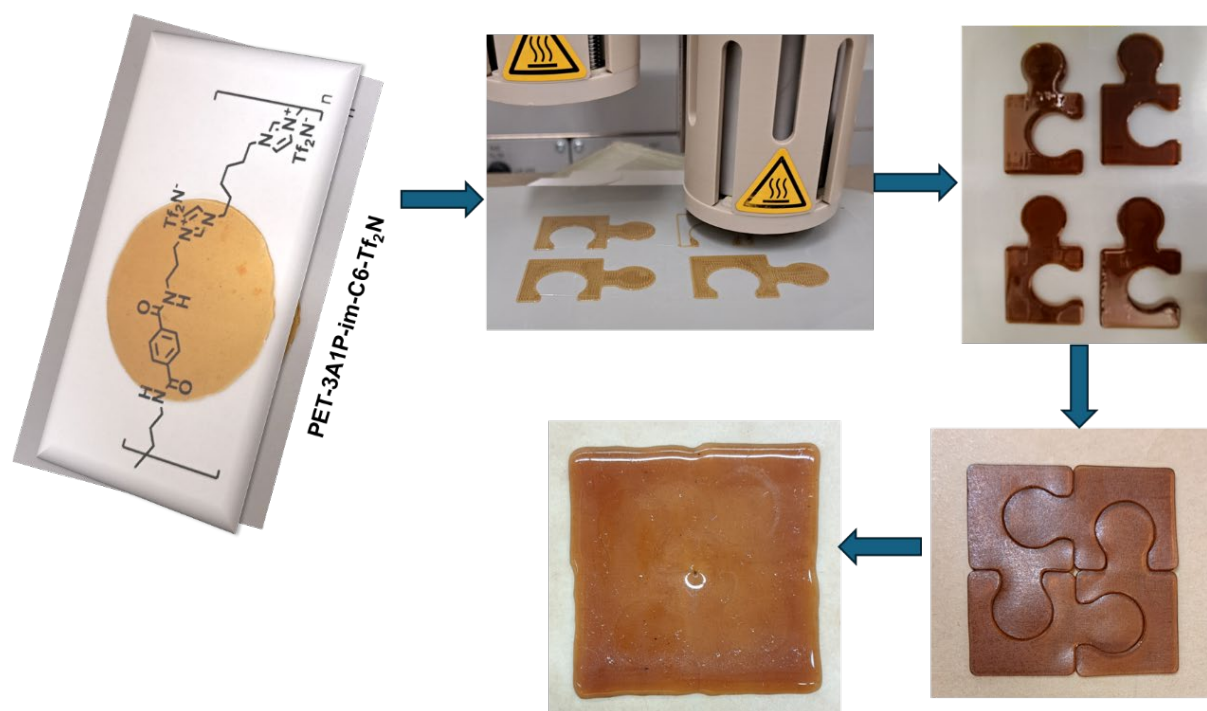
**Fig. S 16** SEM images of neat ionic liquids a) MEA-im b) MEA-2mim c) 3A1P-im d) 3A1P-2mim e) DGA-im f) DGA-2mim

**S6. Printability of ionenes and self-healing observed by SEM.**



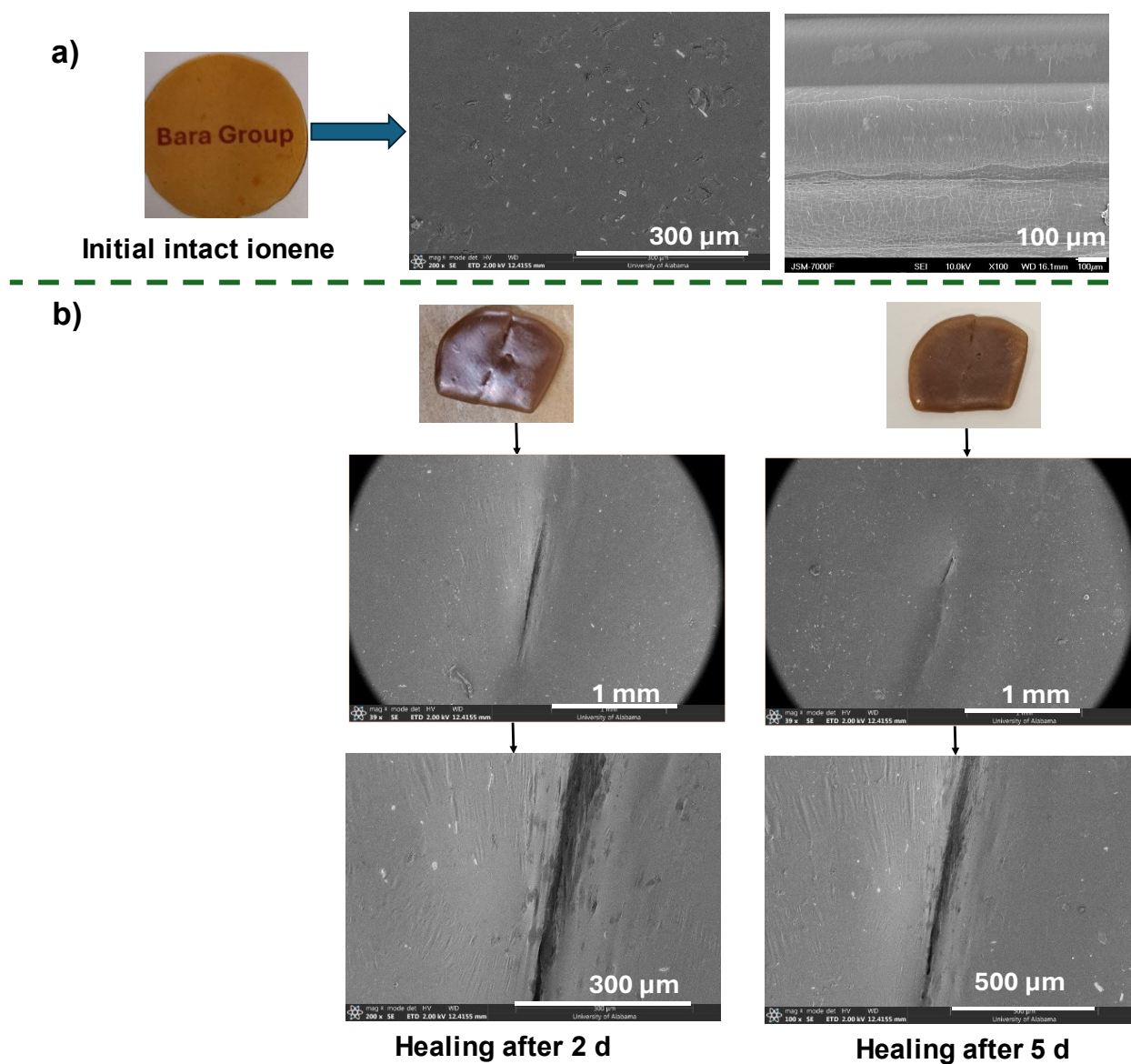
**Extrusion of PET-DGA-im-C<sub>6</sub>-Tf<sub>2</sub>N ionene fibers**

**Fig. S 17** Extruded fiber and disc printed from DGA-im ionene.

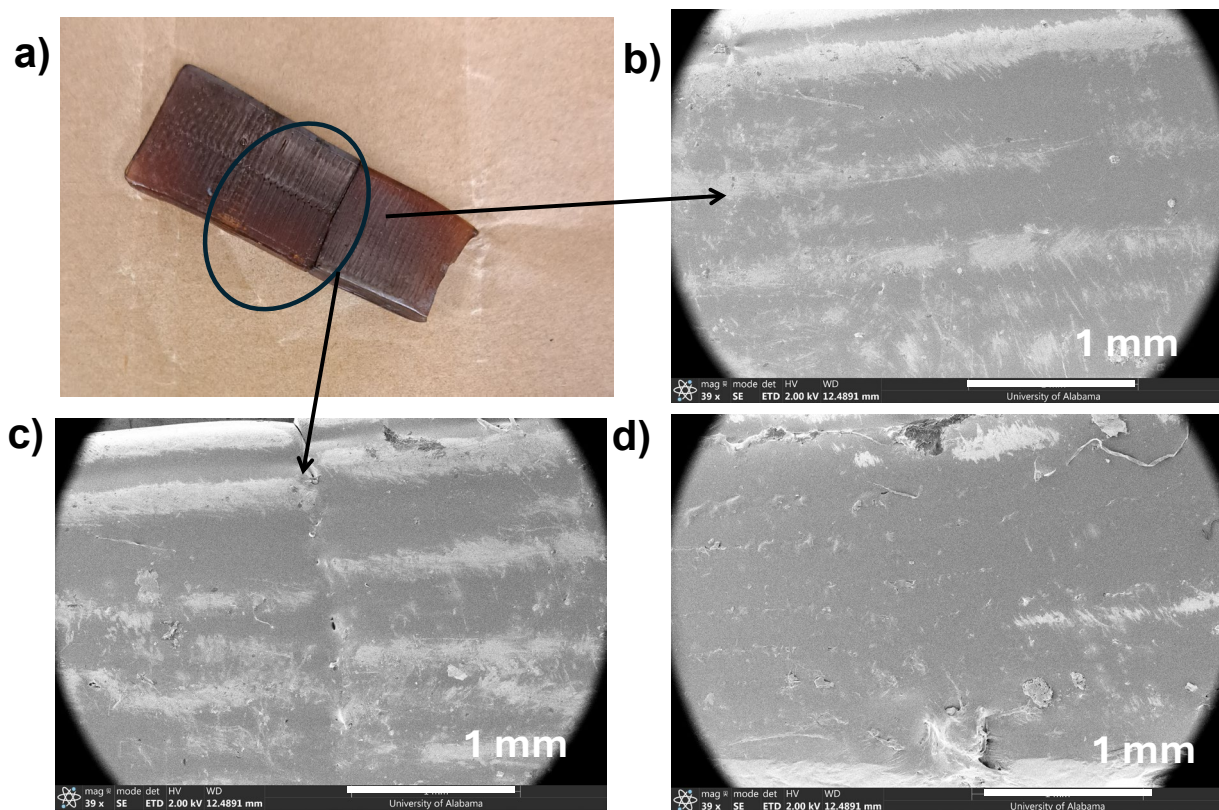


**Fig. S 18** Four puzzle pieces prepared from 3A1P-im PA ionene gradually fusing via self-healing to a single shape.

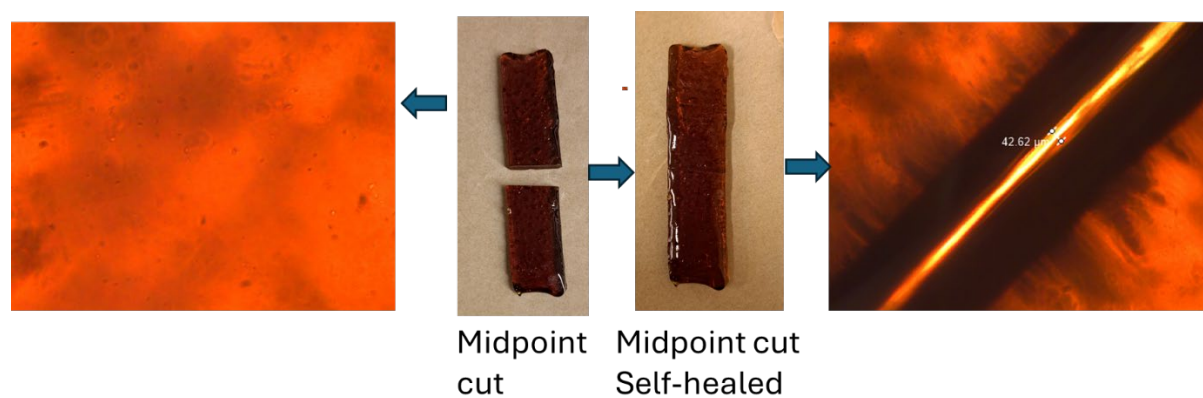




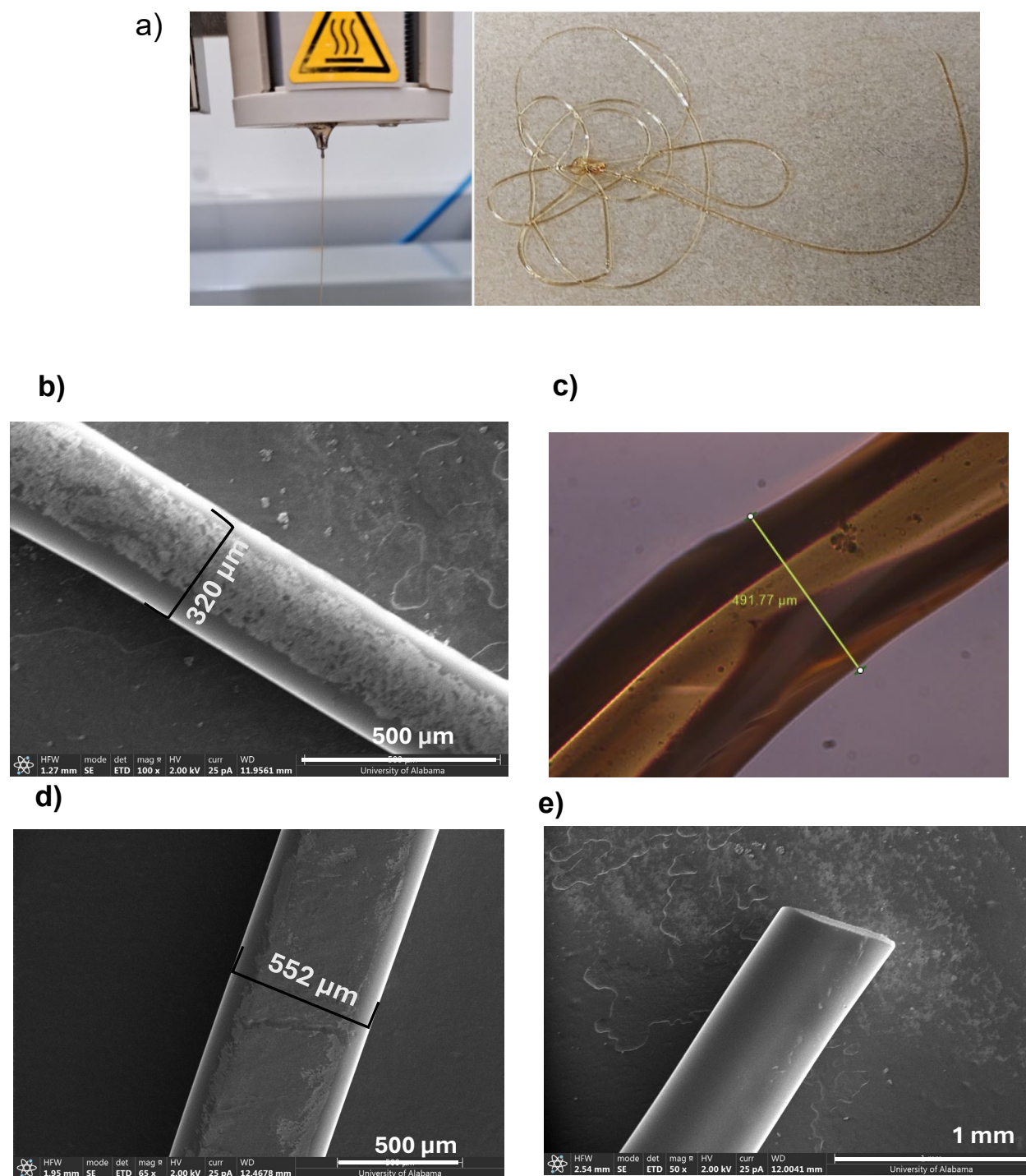
**Fig. S 19 a)** Images for thin film membrane prepared from 3A1P-im PA ionene and top surface image of the membrane by SEM. **b)** the adhered part of the midpoint cut ionene with the cross-sectional view of the self-healed images after 2 d and 5 d by SEM.



**Fig. S 20** **a)** Part of 3D printed slab after tensile testing of 3A1P-2mim ionene. **b)** the infill pattern of the printed bar is unaffected by a cut or seam. **c)** cross-sectional view of the self-healed image of the slab from an intermediate seam restored after 4 days. **d)** edge of the self-healed slab.

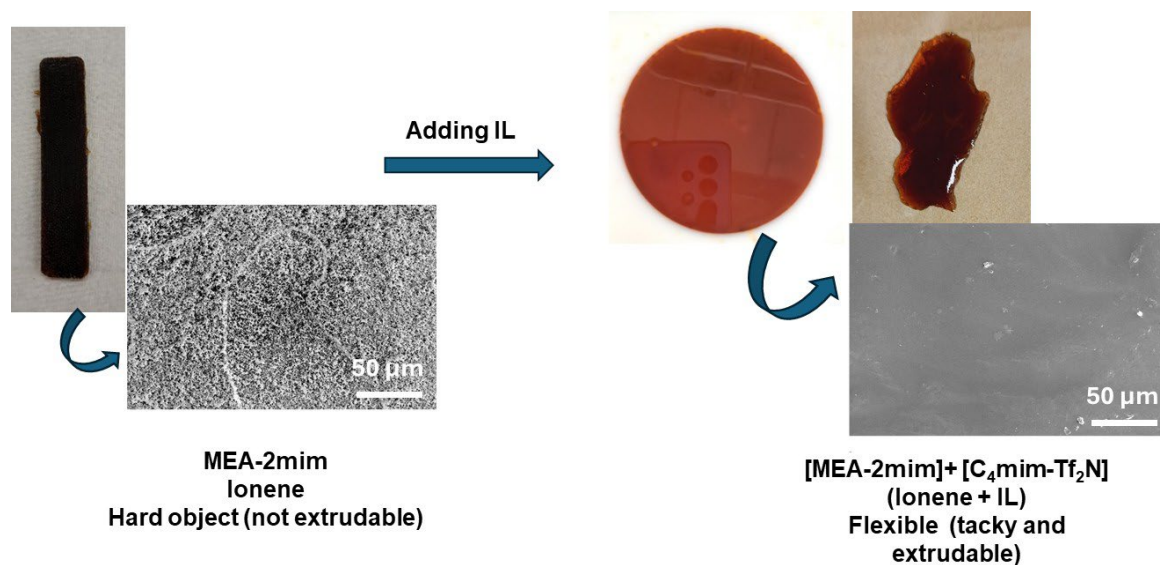


**Fig. S 21** A melt-casted rectangular bar from 3A1P-2mim compound was cut in the center, and an optical image captured the self-healed seam after 4 days.



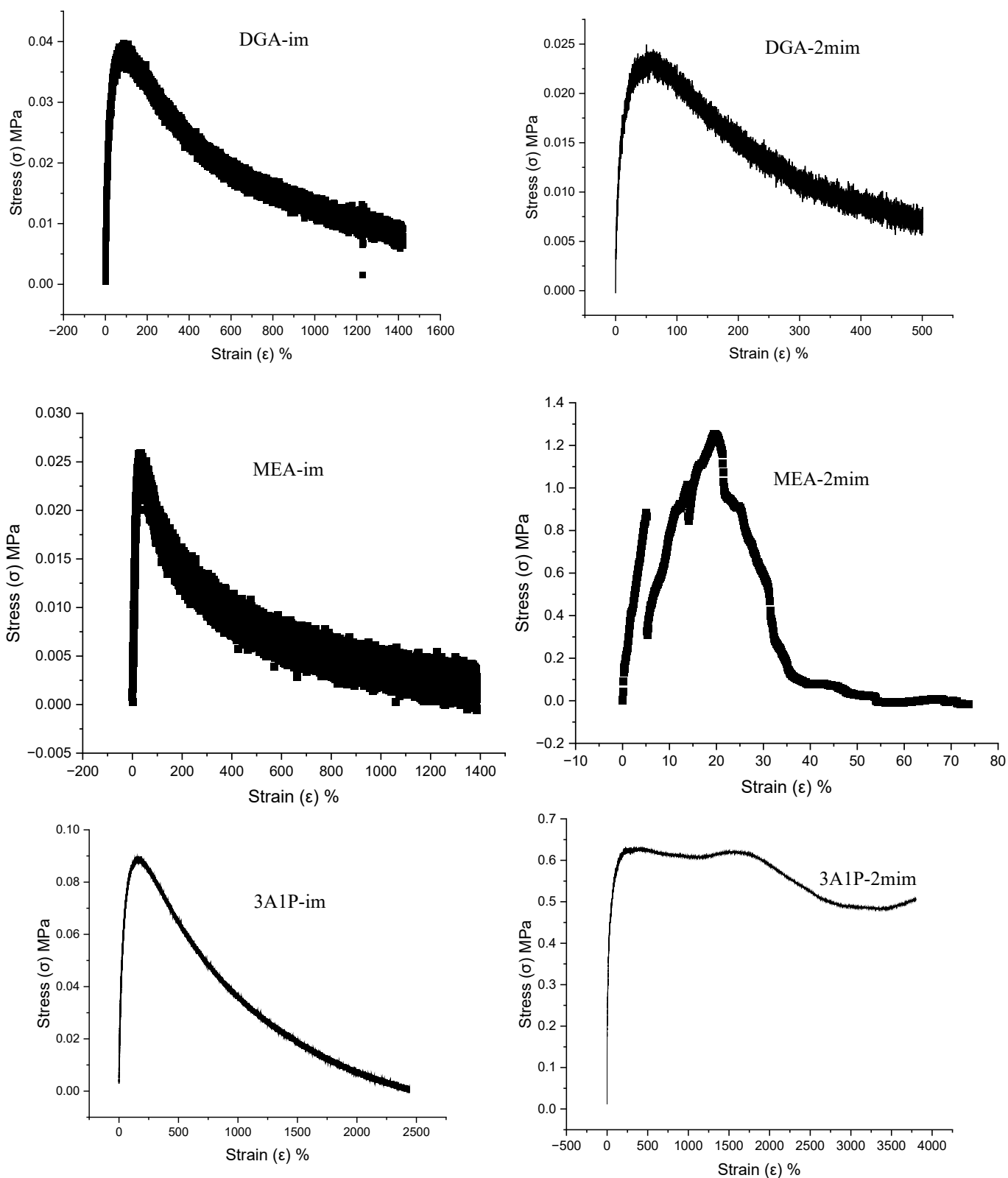
**Fig. S 22** a) 3D printed single layer extruded filament by optical microscopy and SEM of different materials. b) 3A1P-im ionene c) MEA-2mim ionene + [C<sub>4</sub>mim][Tf<sub>2</sub>N] IL. d) 3A1P-2mim e) edge of the fiber of 3A1P-2mim.



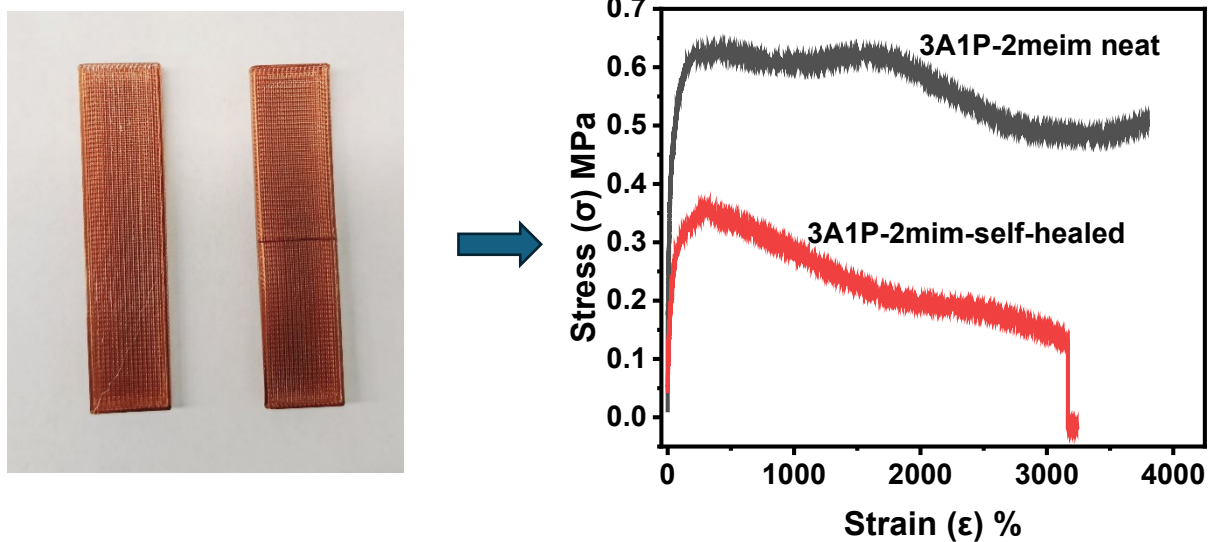


**Fig. S 23** PET-MEA-2mim-C<sub>6</sub>-Tf<sub>2</sub>N (MEA-2mim) exhibiting a change in texture after adding [C<sub>4</sub>mim] [Tf<sub>2</sub>N] ionic liquid (IL).

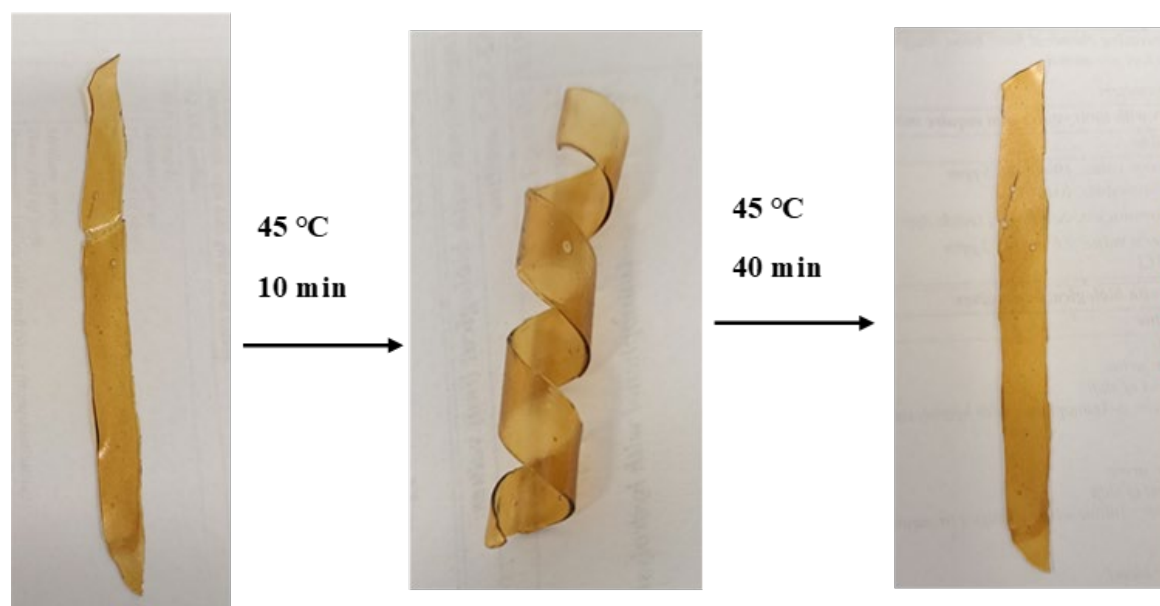
**S7. Mechanical property of PA-ionenes and demonstrating self-healing, shape memory (SM) and shape recovery behavior.**



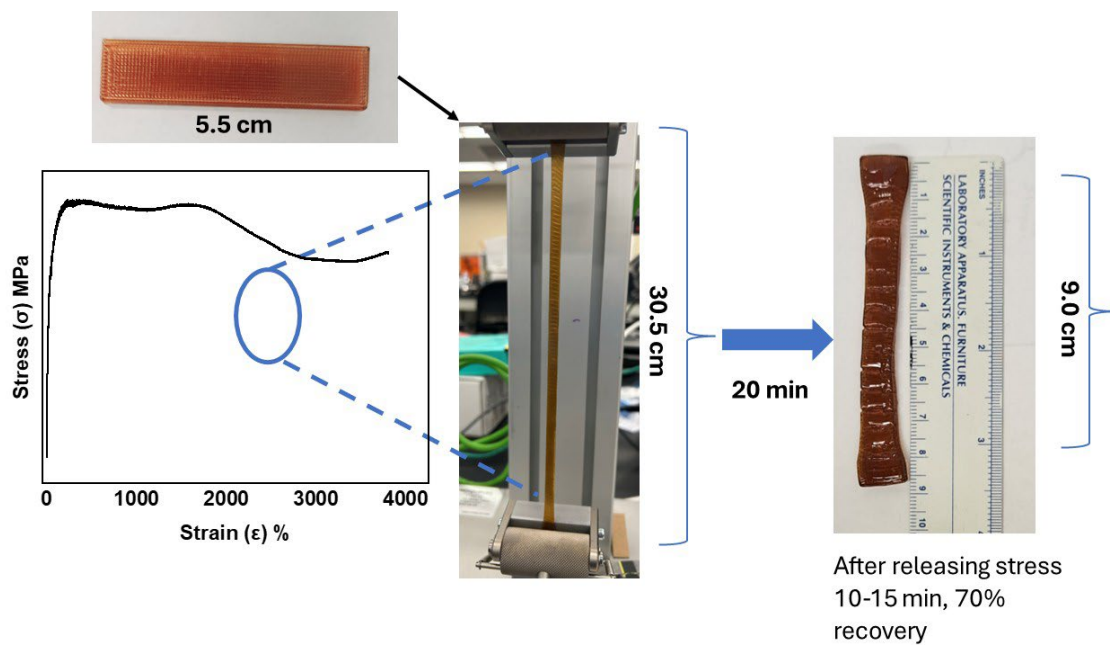
**Fig. S 24** Full stress-strain curve of six different PA-ionenes.



**Fig. S 25** Self-healing after midpoint cut of 3A1P-2mim ionene printed slab.



**Fig. S 26** SM behavior observed by 3A1P-2mim ionene.



**Fig. S 27** 70% Shape recovery of 3A1P-2mim rectangular bar.