

## Supporting information

### Effect of polymer concentration and cross-linking density on the microstructure and properties of polyimide aerogels

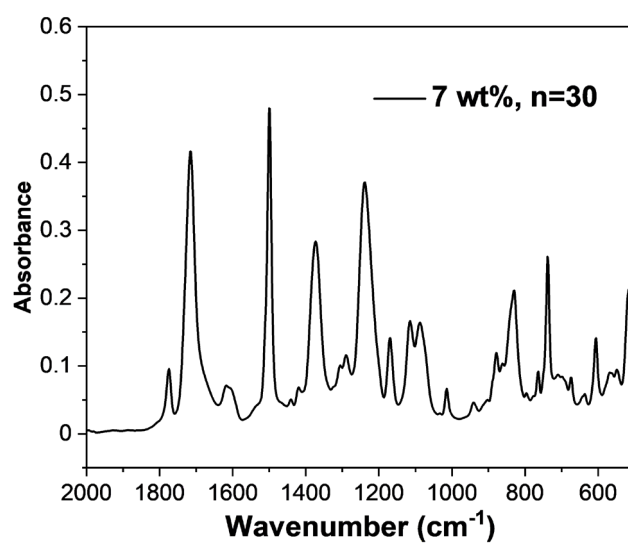
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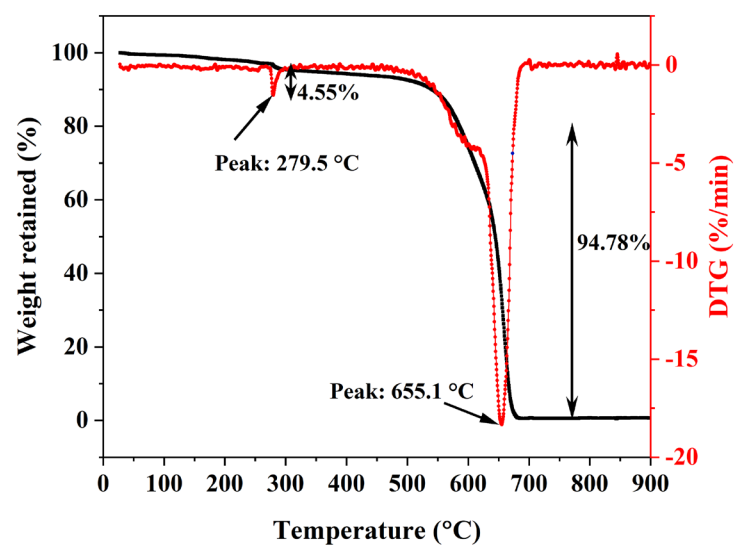
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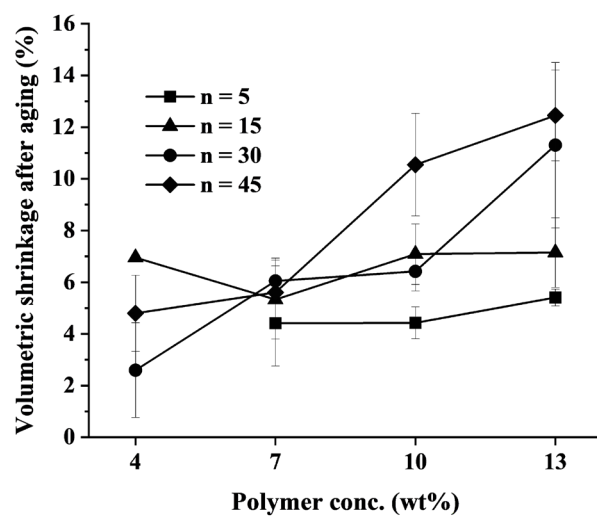
**Email:** [wim.malfait@empa.ch](mailto:wim.malfait@empa.ch), [wu\\_tingting@isce2.a-star.edu.sg](mailto:wu_tingting@isce2.a-star.edu.sg)



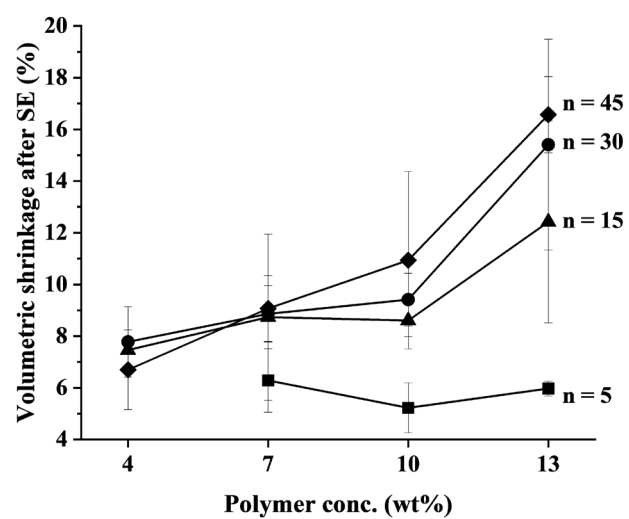
**Figure S1.** Fourier transform infrared (FTIR) spectrum of selected polyimide aerogel sample (7 wt%, 30n).



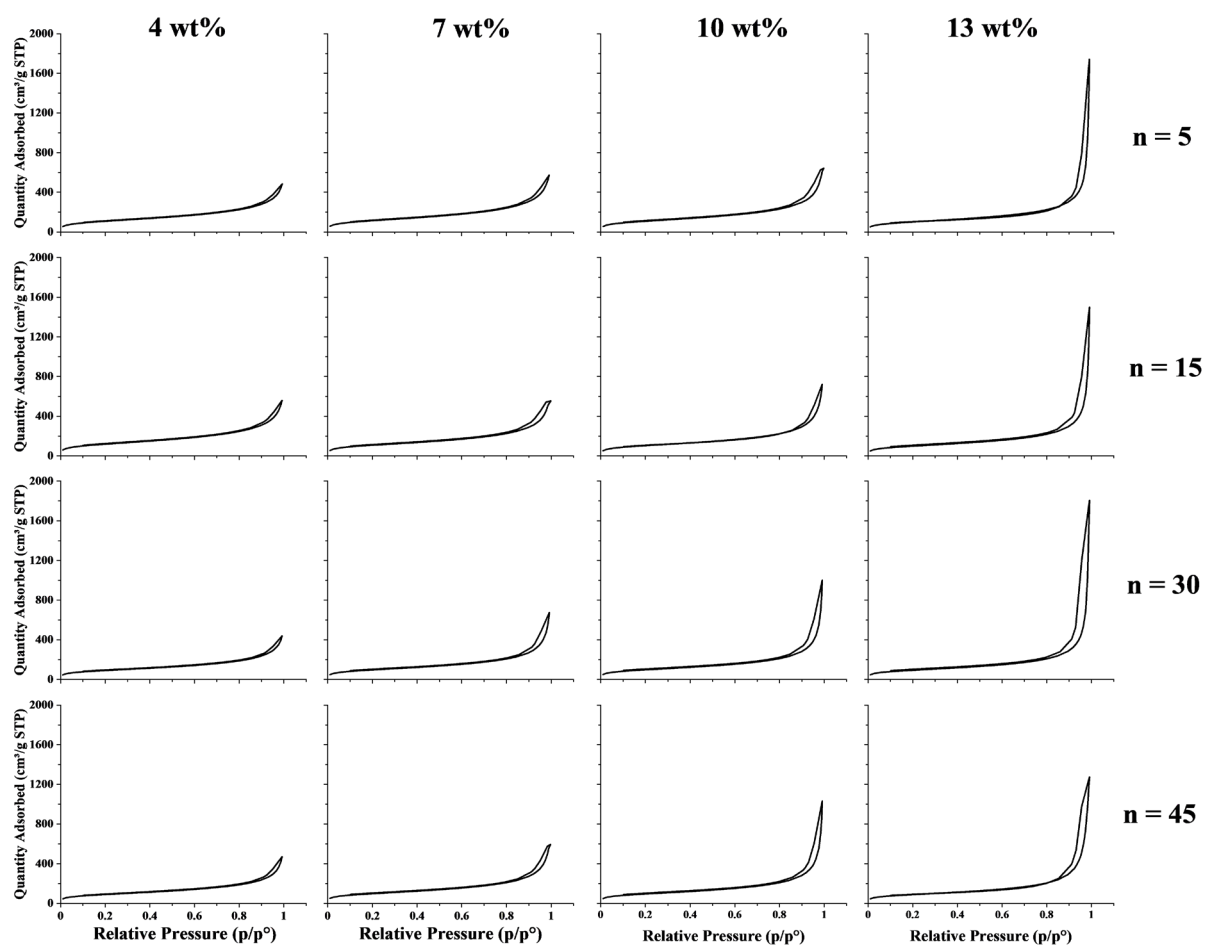
**Figure S2.** Thermogravimetry analysis (TGA) curve of selected polyimide aerogel sample (4 wt%, 45n).



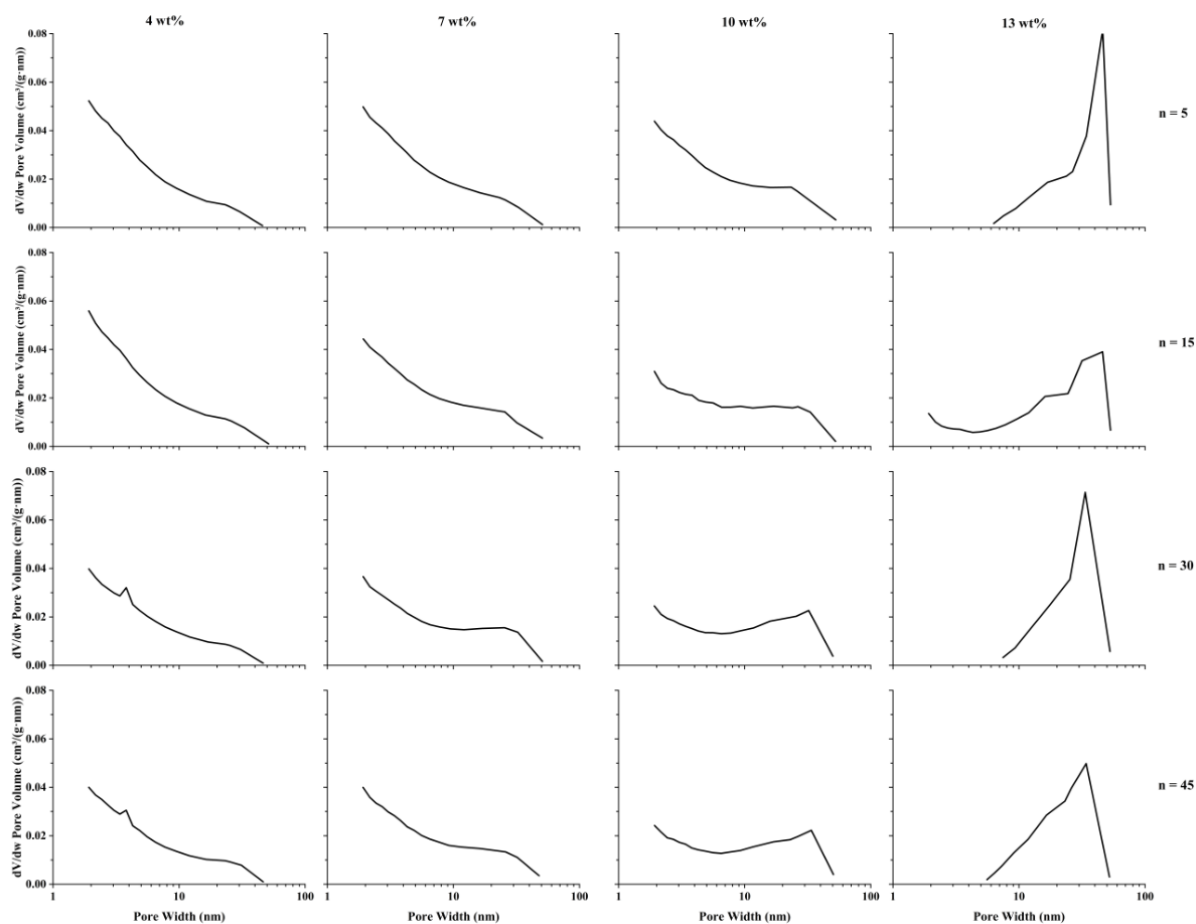
**Figure S3.** Volumetric shrinkage after aging vs. polymer concentration and number of repeat units  $n$ .



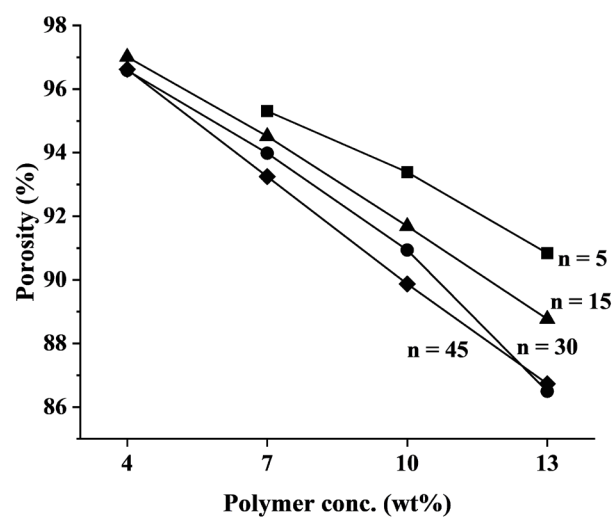
**Figure S4.** Volumetric shrinkage after solvent exchange (SE) vs. polymer concentration and number of repeat units n.



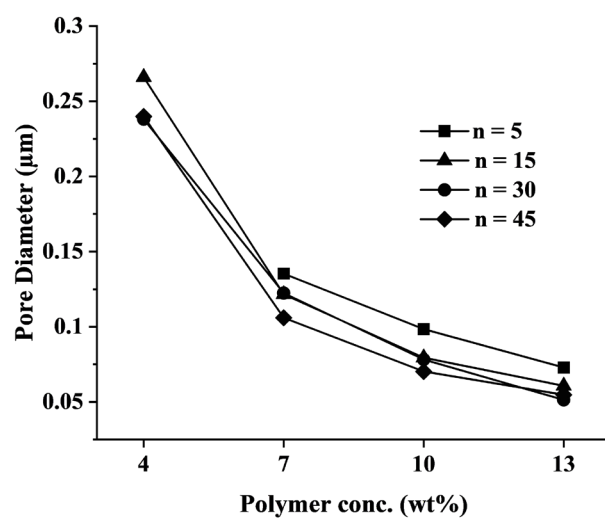
**Figure S5.**  $N_2$  adsorption-desorption isotherms for all polyimide aerogels from this study.



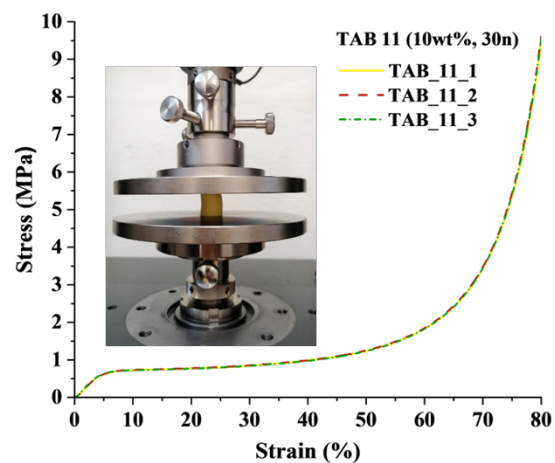
**Figure S6.** BJH pore size distribution for all polyimide aerogels from this study.



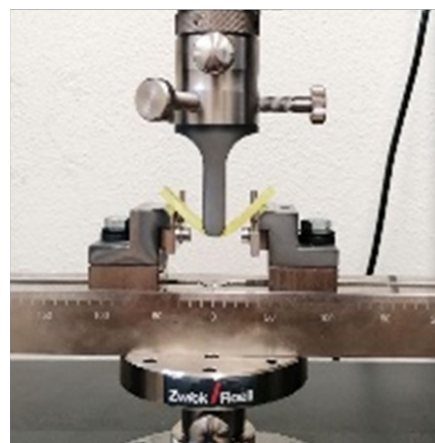
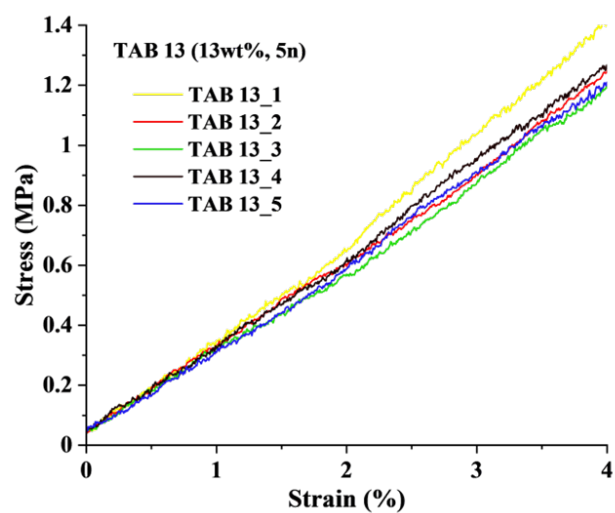
**Figure S7.** Porosity vs. polymer concentration and  $n$ .



**Figure S8.** Pore diameter (calculated from density and surface area) vs. polymer concentration and number of repeat units  $n$ .



**Figure S9.** The three stress-strain curves from the same TAB 11 formulation show the repeatability of aerogel samples with the inserted compression testing photo.



**Figure S10.** The 3-point bending stress-strain curves from the same TAB 13 formulation show the repeatability of aerogel samples. The picture of the 3-point bending setup mounted in a load frame specimen. The initial linear part of typical stress-strain curves from 3-point bending of selected series.

**Table S1.** The summary of density, shrinkage, porosity, and gelation time.

| Samples | wt % | n  | Average density (g cm <sup>-3</sup> ) | Average shrinkage (%) |          |           | Porosity (%) | V pore cal. (cm <sup>3</sup> g <sup>-1</sup> ) | D pore cal. (nm) | Skeletal density (g cm <sup>-3</sup> ) | Apparent gelation time (min) |
|---------|------|----|---------------------------------------|-----------------------|----------|-----------|--------------|------------------------------------------------|------------------|----------------------------------------|------------------------------|
|         |      |    |                                       | after aging           | after SE | after SCD |              |                                                |                  |                                        |                              |
| TAB 1   |      | 5  |                                       |                       |          | broken    |              |                                                |                  |                                        | 150                          |
| TAB 2   | 4    | 15 | 0.045                                 | 7.0                   | 7.5      | 18.6      | 97.0         | 21.8                                           | 266              |                                        | 140                          |
| TAB 3   |      | 30 | 0.051                                 | 2.6                   | 7.8      | 26.5      | 96.6         | 19.0                                           | 238              |                                        | 115                          |
| TAB 4   |      | 45 | 0.050                                 | 4.8                   | 6.7      | 23.6      | 96.6         | 19.2                                           | 240              |                                        | 116                          |
| TAB 5   |      | 5  | 0.070                                 | 4.4                   | 6.3      | 16.9      | 95.3         | 13.6                                           | 135              |                                        | 45                           |
| TAB 6   | 7    | 15 | 0.082                                 | 5.3                   | 8.7      | 27.5      | 94.5         | 11.6                                           | 122              |                                        | 44                           |
| TAB 7   |      | 30 | 0.090                                 | 6.1                   | 8.9      | 30.5      | 94.0         | 10.5                                           | 122              |                                        | 40                           |
| TAB 8   |      | 45 | 0.101                                 | 5.6                   | 9.1      | 37.7      | 93.3         | 9.3                                            | 106              |                                        | 38                           |
| TAB 9   |      | 5  | 0.099                                 | 4.4                   | 5.2      | 20.1      | 93.4         | 9.5                                            | 98               | 1.491                                  | 13                           |
| TAB 10  | 10   | 15 | 0.124                                 | 7.1                   | 8.6      | 31.8      | 91.7         | 7.4                                            | 79               |                                        | 10                           |
| TAB 11  |      | 30 | 0.135                                 | 6.4                   | 9.4      | 38.5      | 90.9         | 6.7                                            | 78               |                                        | 9                            |
| TAB 12  |      | 45 | 0.151                                 | 10.6                  | 10.9     | 44.2      | 89.9         | 6.0                                            | 70               |                                        | 10                           |
| TAB 13  | 13   | 5  | 0.137                                 | 5.4                   | 6.0      | 28.1      | 90.8         | 6.7                                            | 73               |                                        | 7                            |
| TAB 14  |      | 15 | 0.167                                 | 7.2                   | 12.4     | 39.9      | 88.8         | 5.3                                            | 61               |                                        | 5                            |
| TAB 15  |      | 30 | 0.201                                 | 11.3                  | 15.4     | 50.4      | 86.5         | 4.3                                            | 51               |                                        | 4                            |
| TAB 16  |      | 45 | 0.198                                 | 12.5                  | 16.6     | 51.3      | 86.7         | 4.4                                            | 55               |                                        | 2                            |

**Table S2.** Specific surface area, mechanical properties, and thermal conductivity.

| Samples | wt% | n  | Surface area<br>(m <sup>2</sup> g <sup>-1</sup> ) | Modulus<br>(MPa) | Flexural<br>modulus<br>(MPa) | $\lambda$ ,<br>(mW m <sup>-1</sup> K <sup>-1</sup> ) |
|---------|-----|----|---------------------------------------------------|------------------|------------------------------|------------------------------------------------------|
| TAB 1   | 4   | 5  | 384                                               | 1.72             | broken                       | 26.3                                                 |
| TAB 2   |     | 15 | 328                                               |                  | broken                       |                                                      |
| TAB 3   |     | 30 | 319                                               |                  | 4.49                         |                                                      |
| TAB 4   |     | 45 | 320                                               |                  | 4.11                         |                                                      |
| TAB 5   | 7   | 5  | 403                                               | 3.92             | broken                       | 23.0                                                 |
| TAB 6   |     | 15 | 381                                               | 4.44             | 10.91                        | 21.6                                                 |
| TAB 7   |     | 30 | 342                                               | 5.74             | 11.64                        | 23.0                                                 |
| TAB 8   |     | 45 | 349                                               | 7.16             | 8.89                         | 21.9                                                 |
| TAB 9   | 10  | 5  | 385                                               | 8.19             | 16.23                        | 21.4                                                 |
| TAB 10  |     | 15 | 373                                               | 11.23            | 19.90                        | 23.7                                                 |
| TAB 11  |     | 30 | 344                                               | 12.40            | 20.55                        | 24.3                                                 |
| TAB 12  |     | 45 | 339                                               | 15.67            | 18.32                        | 23.6                                                 |
| TAB 13  | 13  | 5  | 365                                               | 14.03            | 29.16                        | 23.3                                                 |
| TAB 14  |     | 15 | 349                                               | 23.34            | 38.32                        | 27.2                                                 |
| TAB 15  |     | 30 | 335                                               | 26.80            | 59.98                        | 32.3                                                 |
| TAB 16  |     | 45 | 320                                               | 19.09            | 71.79                        | 30.2                                                 |