Supporting Information

Mechanically strong hydrogels with reversible behaviour under cyclic compression with MPa loading

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Comparison of swelling behavior between SN and DN hydrogels

A high **PAAm** content in DN gels is supported by the values for volume increase of DN in comparison to the SN hydrogels after second polymerization, evaluated by (Equation S1):

$$\frac{V_2}{V_1} = \frac{\pi \cdot r_2^2 \cdot h_2}{\pi \cdot r_1^2 \cdot h_1} \cdot 100 \qquad \text{(S1)}$$

where r_i and h_i indicate the radii and the thicknesses of the specimens of SN and DN after respective polymerization reactions and extraction with water (Table S1). In case of photo polymerization, higher **AAm** monomer concentration results in significant volume increase of DN hydrogels what indicates attractive interactions between **AAm** and the polyether-backbone of **sPEOPO**.

Table S1. Volume increases of DN hydrogels after polymerization of **AAm** in the SN with respect to volume of the SN gels.

sPEOPO SN [w/w-%]	Volume increase of **sPEOPO$_x$/AAm$_y$** DN [%] c (**AAm**) [mol/L]			
	Photo polymerization		Thermo polymerization	
	2	3	2	3
10	563 ± 11	651 ± 13	397 ± 7	401 ± 10
15	507 ± 9	581 ± 7	389 ± 8	390 ± 11
20	537 ± 10	601 ± 5	406 ± 12	393 ± 9

When the concentration of **sPEOPO$_x$** SN is raised from 10 to 15 w/w-%, a significant decline in the volume increase at each constant **AAm** monomer concentration is observed. Higher NCO concentration leads to the greater cross-linking density, and hence denser network, what hinders hydrogels to absorb more water. Surprisingly further increase up to 20 w/w-% does not result in significant changes. This indicates that the 10 w/w-% SN gels

possess more free void space than the 15 and 20 w/w-% SN gels for **PAAm** polymerization. A comparison of the scale bars in Fig. 1 c (SN) and 1 d (photo-polymerized DN) gives an optical impression of the volume increase.

In comparison to photo polymerization, thermo-polymerized DN hydrogels generally show lower volume increases after DN formation. This behavior was independent of NCO amount in SN as well as on **AAm** concentrations. The above observation might be attributed due to the non-selective thermo-initiated mechanism where secondary reactions produce less consistent reactants. Also, the elevated temperatures may influence the **sPEOPO - PAAm** interaction and limit the concentration of **AAm** during polymerization.

Equilibrium water content (EWC)

Hydrogel samples of SN and DN with defined dimensions were weighed after drying at ambient temperature under vacuum for 24 hours. Then, they were immersed into distilled water (200 mL) for 7 days in order to reach the equilibrium swelling state. After 7 days swelling, the weight of the samples did not change further. The EWC was determined by applying the following relationship (Equation S2):

$$\mathrm{EWC}\,[\%] = \left(\frac{w_{sw} - w_d}{w_{sw}} \right) \cdot 100 \qquad \text{(S2)}$$

where w_{sw} and w_d are the weight of the sample in the swollen and in the dry state, respectively.

EWC of all kinds of SN and DN hydrogels prepared in this study was determined in a series of three independent measurements per gel. All DN hydrogels show a similar high EWC of more than 92 %. While no significant trend can be extracted from the data for thermo-

polymerized DN (data not shown), the EWC of photo-polymerized DN gels decreases with increasing **sPEOPO** concentration, which may be explained with decreasing share of the more hydrophilic **PAAm** in the gels (Table 1). Interestingly, the 10 w/w-% SN gel is the only SN that possesses a higher EWC than the corresponding DN although the **PAAm** content is highest amongst all DN. We explain this effect by steric constraints within the DN gel that do not allow swelling of the **PAAm** network to equilibrium conditions due to the high content of **PAAm**.

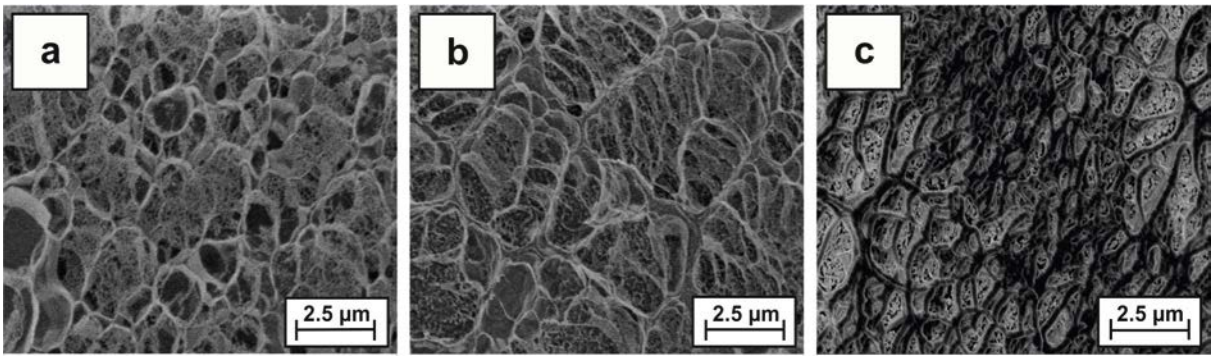

Figure S1: Cryo-FESEM images of a) **sPEOPO$_{10}$**, b) **sPEOPO$_{15}$** and c) **sPEOPO$_{20}$** SN.

Table S2: Determination of the pore size distribution in SN hydrogels

Pore diameter [nm]	Relative amount of pores [%] in SN hydrogels		
	10 w/w-% SN	15 w/w-% SN	20 w/w-% SN
300 - 700	43	50	67
700 - 1100	40	23	26
> 1100	17	27	7

Interestingly, a maximum amount of pores with largest diameter are created by **sPEOPO$_{15}$**. Although this determination of pore diameters from SEM images is not precise, the lack of signs of water crystal formation indicates that the cryo procedure preserved the structure of the swollen hydrogels.

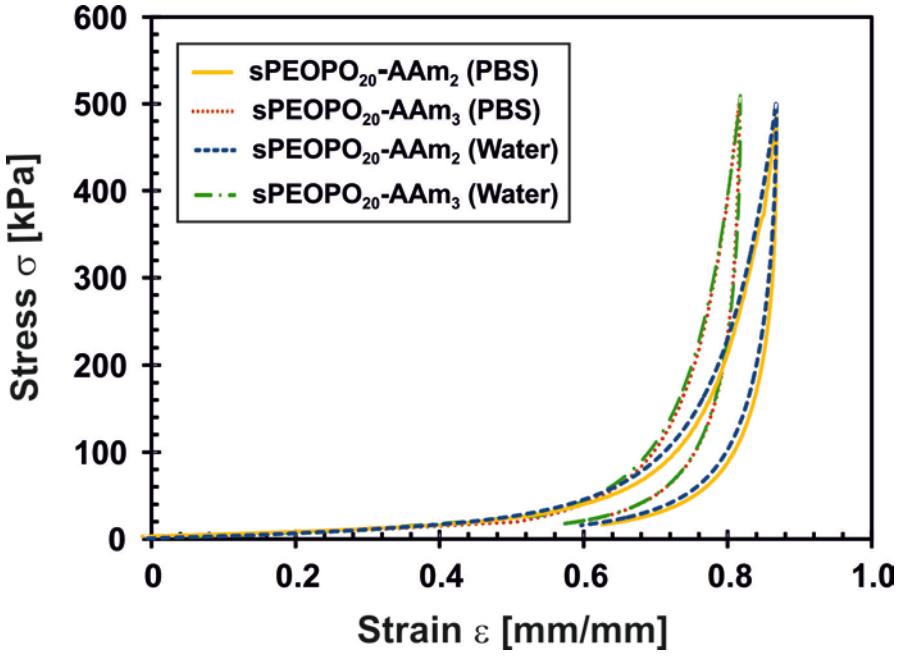

Figure S2: Hysteresis cycles of **sPEOPO$_{20}$/AAm$_Y$** DN hydrogels (Y = 2 and 3 M **AAm**) accomplished under distilled water and PBS surroundings.