Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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# SI - Novel finely structured polymer aerogels using organogelators as a structure-directing component

## S1 Crosslinked, finely structured aerogel

Another option to generate a fine structure (and avoid spherulite formation during crystallization) is to significantly crosslink the sample. The aerogel sample shown in Figure S1 was crosslinked using dicumyl peroxide (DCP), swollen with tetramethylbutane (TMB) and then freeze-dried. For the preparation, 60 w% UHMWPE was mixed with 40% iPP (finely powdered), the peroxide (3 w%) dissolved in acetone was added and the acetone was evaporated off. The dry powder was crosslinked in a hot press at 170°C under 500 bar pressure. The pressed pellet was swollen with TMB and then freeze-dried at 0°C under vacuum. The structure shown is the result of crosslinking under mechanical shearing of the melt. Besides the relatively high density (above 250 g/l), the cracking of larger specimens is problematic. The latter can be attributed to stresses in the material caused by the manufacturing process. The density can be adjusted via the degree of crosslinking, but the structure deteriorates with low-density specimens. No satisfying optimum was found by this method.

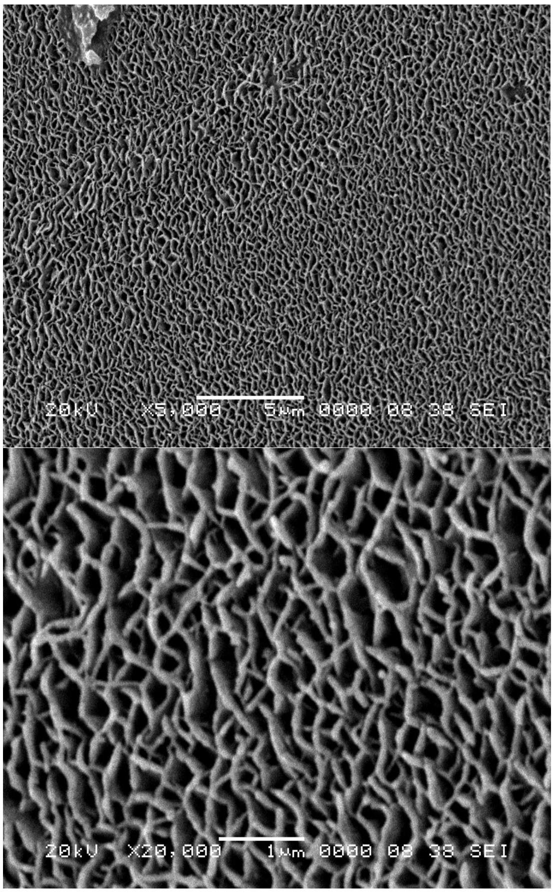


Figure S1: SEM-images of crosslinked UHMWPE-PP-Aerogels (60/40)

## S2 Synthesis HDPE (2)

The polymerization is carried out in an water-free 1 L reactor with stirrer under argon atmosphere. 400 mL of dry toluene is added and 13.5 mL of methylaluminoxane (MAO) is mixed in. Then the catalyst (bis(cyclopentadienyl)zirconium dichloride) is added. 0.0318 g of the catalyst is prepared and diluted in 5 mL of toluene. 1 mL of this solution is transferred to the reactor and the polymerization temperature (30 °C) is adjusted. After 30 minutes, ethene is introduced at a rate of 206 cm³/min. The reaction lasts is carried out for 30 - 45 min. The product is washed with methanol/HCl (1%) and slurried several times. The precipitate is then neutralized with NaOH (0.1 molar) and the remaining polymer is placed in a crystallizing dish and placed in the drying oven at 80°C.

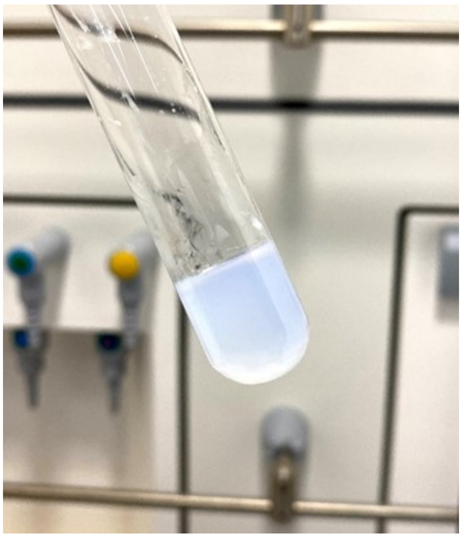


Figure S2: PP-solvogel with relatively high polymer content (35%)

Figure S3: UHMWPE-solvogel with relatively low polymer content (4%)

Figure S4: PP-Aerogel

## S3 Additional information about extraction using tBuOH

Successful extraction of the gelator depends on several parameters and must be adjusted according to sample geometry, composition and density. Soxhlet extraction is a suitable method for relatively small sample volumes. A major advantage of this method is that the tBuOH used can basically be circulated and the extracted gelator and TCB can be collected in the bottom flask and subsequently be recovered. This significantly increases the efficiency of gelator recovery. The challenge is to only remove the proper amount of TBPMN. Complete extraction results in significant shrinkage (> 50%) and the sample may collapse with simultaneous loss of fine structure. With low extraction time and/or insufficient temperature, TCB may remain in the sample resulting in a shrunken xerogel upon drying. Furthermore, in this case the amount of gelator extracted is small (<10 %). Since tBuOH does not flow through the solvogel, the process inside the sample is diffusion-based. In order to obtain the most uniform extraction possible without a relevant concentration gradient of the gelator in the sample, geometries with a low thickness and high surface area are ideal. Furthermore, the density of the sample plays a non-negligible role, as it determines the speed of the diffusion-based exchange. Due to the many influencing variables, the extraction time has to be determined empirically.

## S4 DSC

The recrystallization of PP shifts from 116 °C to 132 °C in the presence of TBPMN. The figure shows an exemplary comparison between pure polymer, a mixture of PP and TBPMN and the final aerogel.

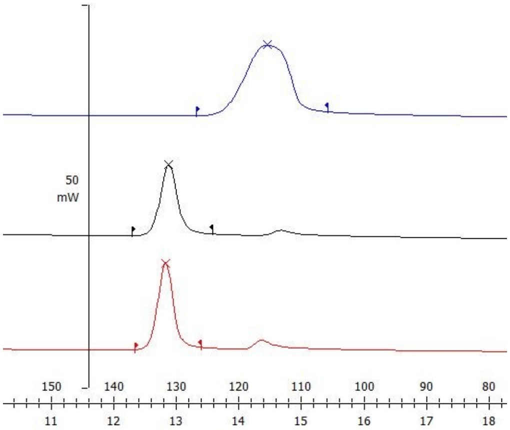


Figure S5: Shift of the crystallization temperature (PP - blue, PP/TBPMN bulk - black, PP/TBPMN aerogel – red)

### S5 Comparison with other polymers

In the case of PVC, the deterioration of the structure due to solvent replacement with benzene (especially for the NX-PVC 1:0.5 sample) is less obvious (Figure S7). The aerogel obtained, however, shows thicker fibrils over the whole area, which partly show signs of bundles of smaller structural segments. This indicates a loss of fine structure. Furthermore, the pore size increases. This effect increases with increasing PVC content. In the NX-PVC 1:4 sample, the aggregation of the fibrils into wall-like structures is clearly visible. Since the aim was to achieve the finest possible structure, the choice of solvent from which to freeze-dry must be adapted to the polymer in order to avoid post-crystallisation or collapse.

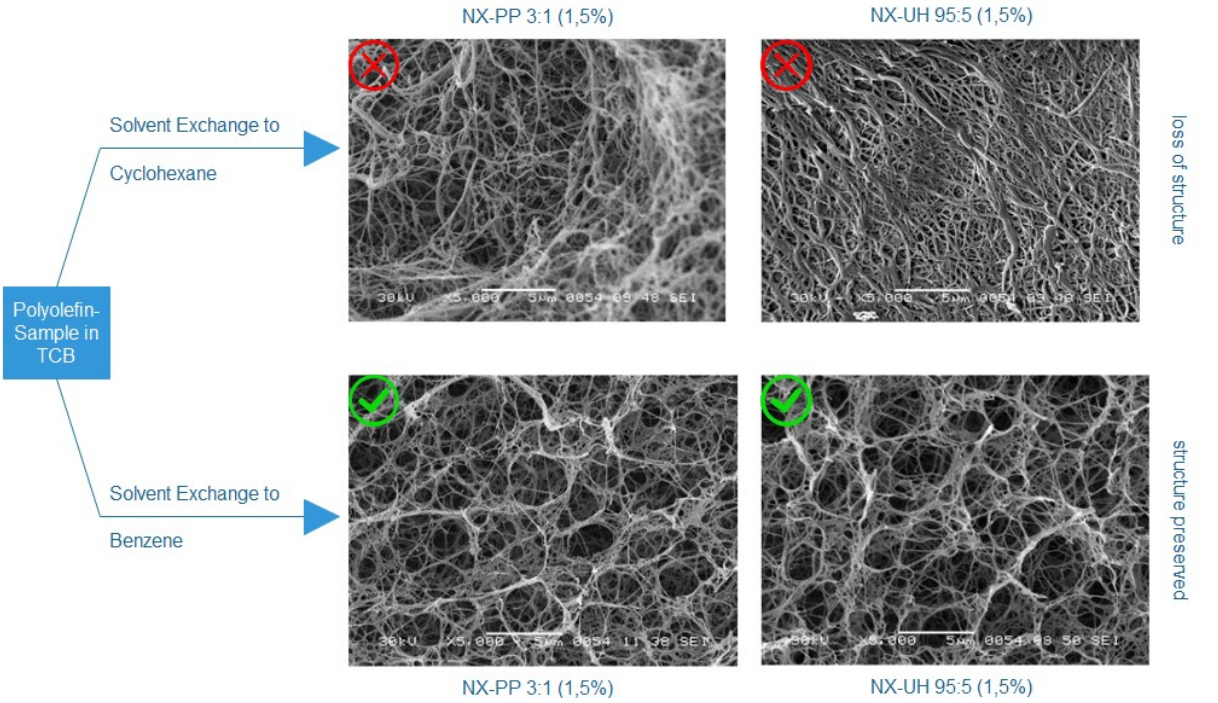


Figure S6: Effect of Solvent for freeze-drying for PP&PE based gels

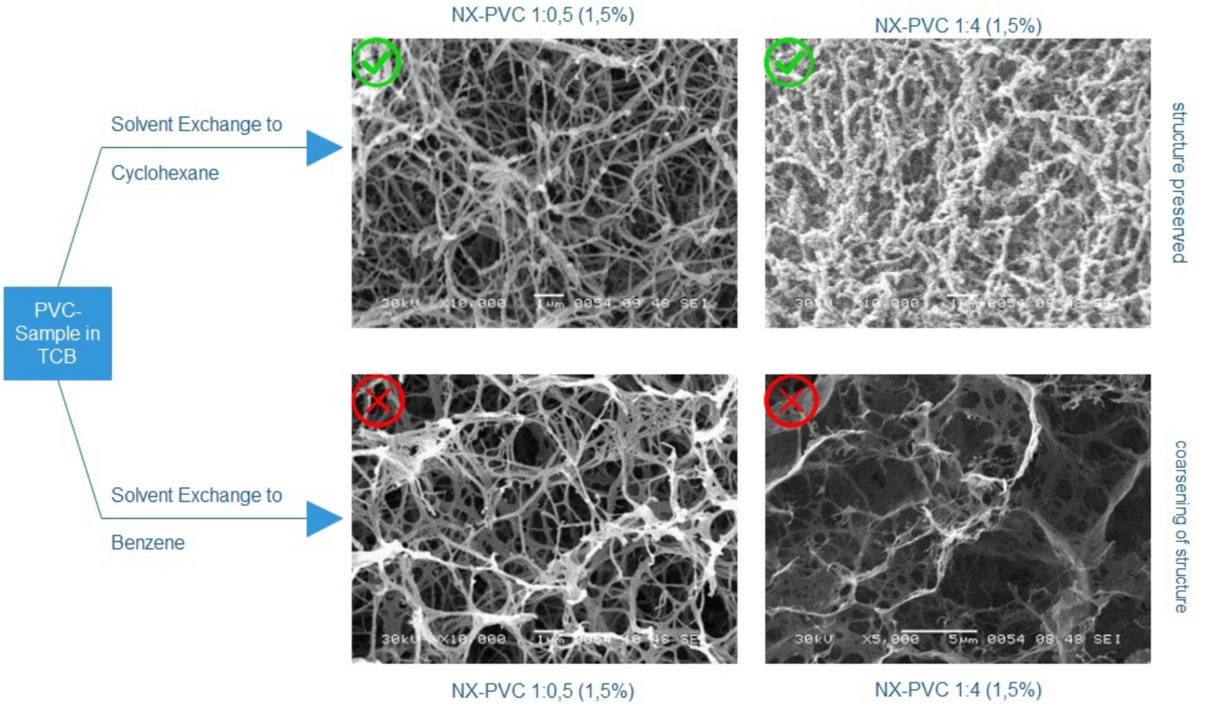


Figure S7: Effect of Solvent for freeze-drying for PVC based gels

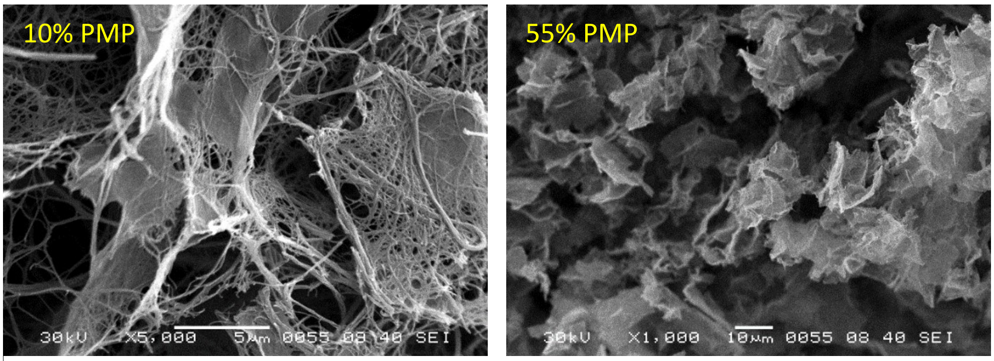
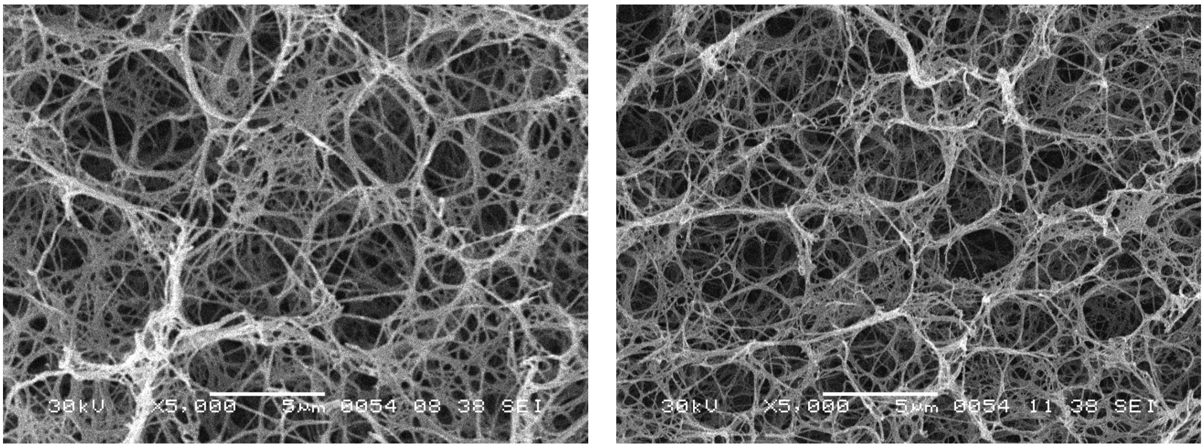


Figure S8: SEM-images of aerogels - PMP and TBPMN at 1,5% solid content prepared in TCB and freeze-dried from benzene

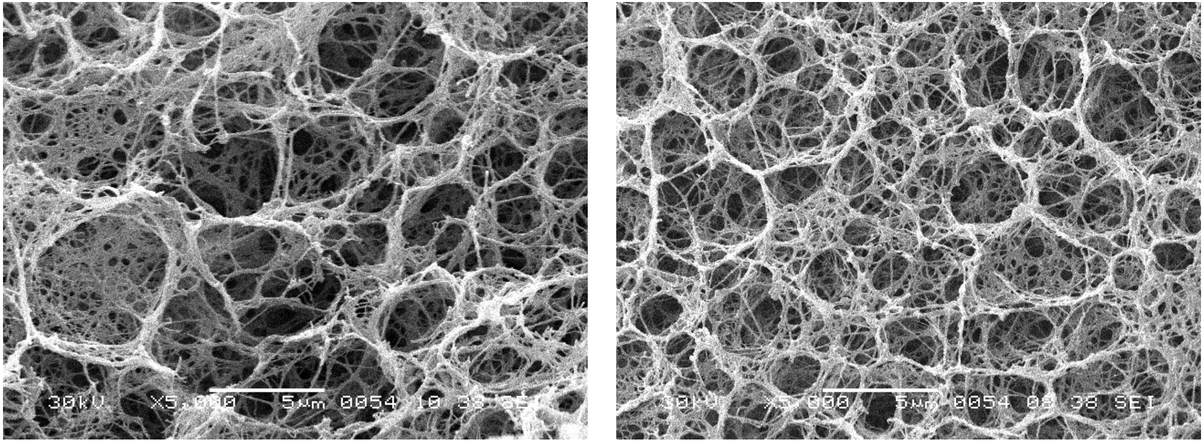
The tendency of low-crystalline and slow-crystallising polymers to build up more walls or more compact structures can have several reasons. On the one hand, the precipitation of amorphous fractions during solvent exchange can lead to locally dense structures. On the other hand, a kinetic effect cannot be excluded. Since the interaction between the polymer chains will be at least energetically slightly more favourable than that with the gelator, slow crystallisation is more likely to lead to the formation of separated polyolefin domains. Low chain lengths intensify this effect.

## S6 Influence of polymer content



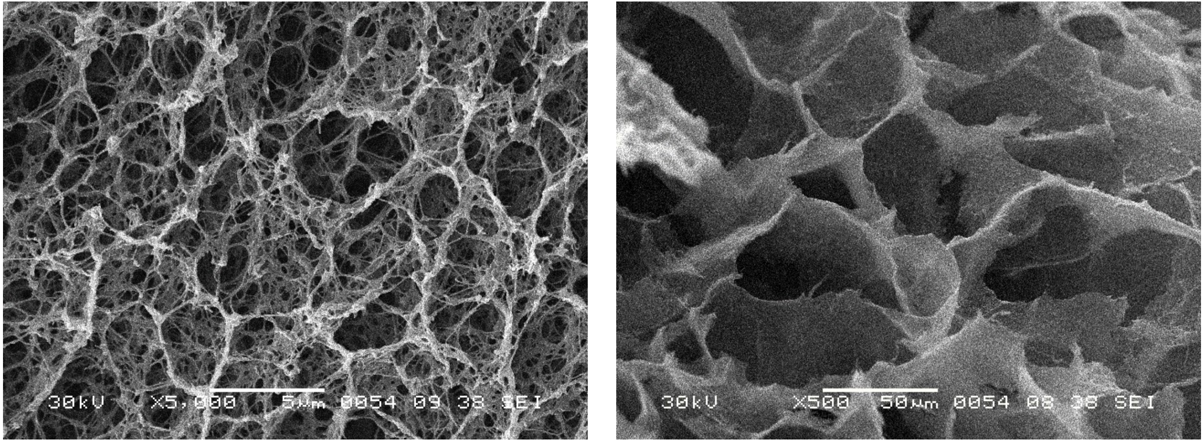
10% PP - low mechanical stability, good structure

25% PP - good polymer based aerogel



35% PP - good polymer based aerogel

50% PP - increasingly solid, one walls



65% PP - Structure becomes increasingly compact and slightly inhomogeneous

80% PP - no fine structure present

Figure S9: SEM of aerogels of PP and gelator at 1,5% solid content prepared in TCB and freeze-dried from benzene

### S7 Density dependence of thermal conductivity and hardness

Besides the observation that UHMWPE forms more stable samples with increasing density relative to PP, both polymers behave similarly. The polyethylene has a better mechanical performance, but is also used in lower proportions (1:5 relative to PP), which is why the samples are in a similar range.

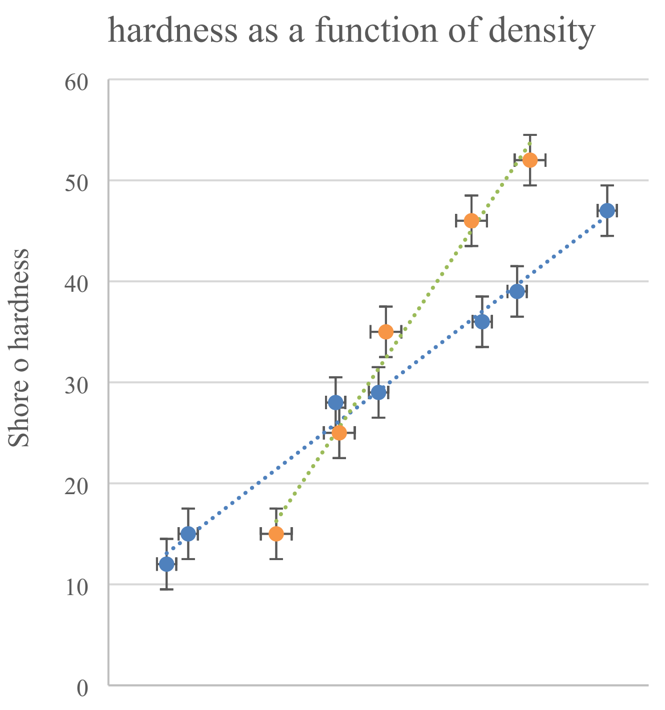


Figure S10: Shore 0 hardness as a function of density - comparison between PP and UHMWPE-stabilised aerogels

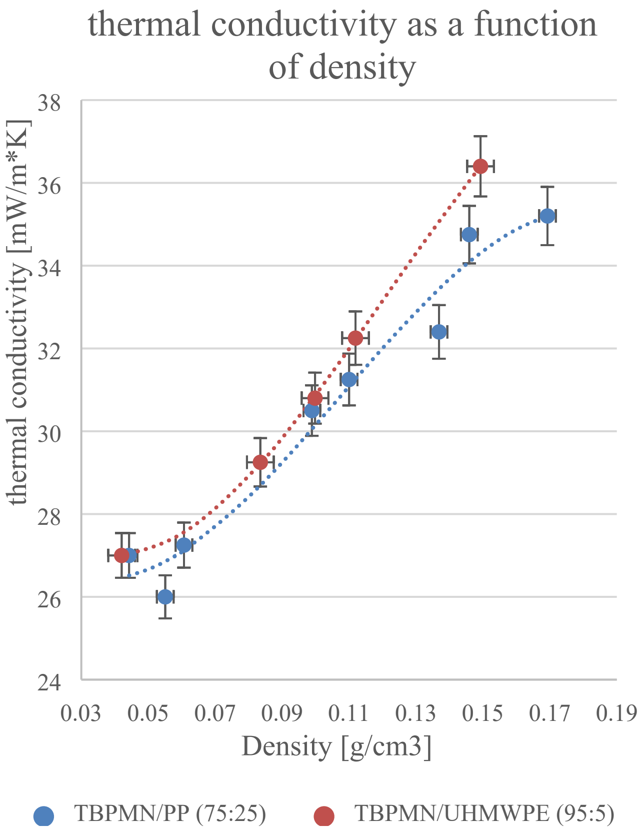


Figure S11: thermal conductivity as a function of density - comparison between PP and UHMWPE-stabilised aerogels

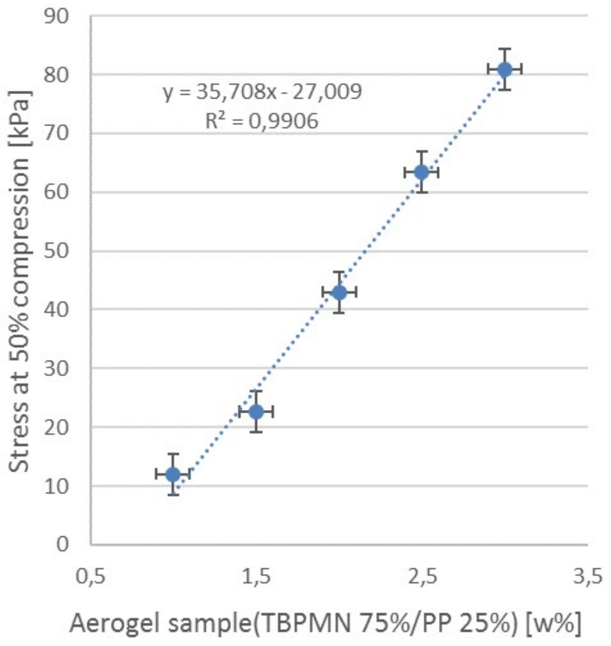


Figure S12: Mechanical stress of TBPMN/PP aerogels at 50% compression

The mechanical testing was carried out in accordance with ISO 7214:2012 and ISO 3386-1:1986 + Amd 1:2010. The measurements were carried out with a Zwick / Z2.5. Due to the geometry of the samples, it was not possible to perform a standard test. For this reason, the double standard deviation was used for the defect indication. However, there is a linear relationship between the mechanical strength and the solids content of the original solvogel that was transferred into the aerogel. Especially at higher concentrations, UHMWPE shows better mechanical properties, but the use of PP is generally considered more reasonable*, which is why the series of measurements was carried out with PP.

*PP can be used in larger proportions, thus saving the more expensive component (TBPMN). Furthermore, the PP aerogels achieve higher surface areas, are more thermally stable due to the higher melting point and show minimally lower thermal conductivities at the same density.

## S8 SEM-Raman coupling image

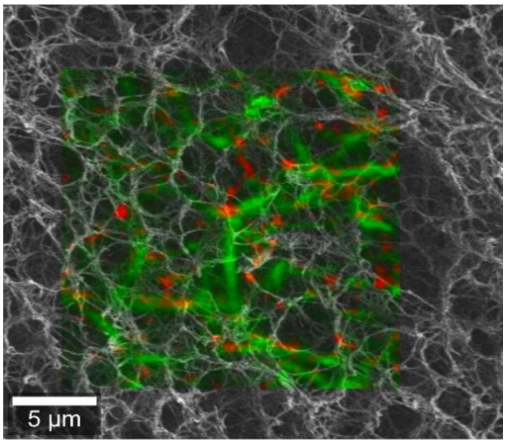


Figure S13: SEM-Raman coupling image of a 25% PP 75% TBPMN sample (polymer red / gelator dominant region green)

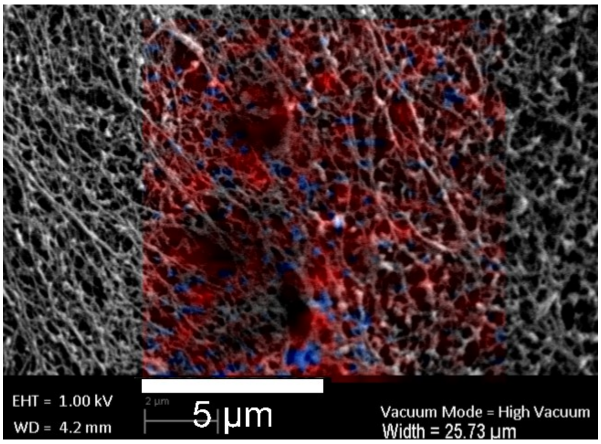


Figure S14: SEM-Raman coupling image of an extracted 25% PP 75% TBPMN sample Polymer/gelator ratio by mass after extraction 1:1) (polymer red / gelator dominant area blue)

## S9 Nitrogen sorption / BET analysis

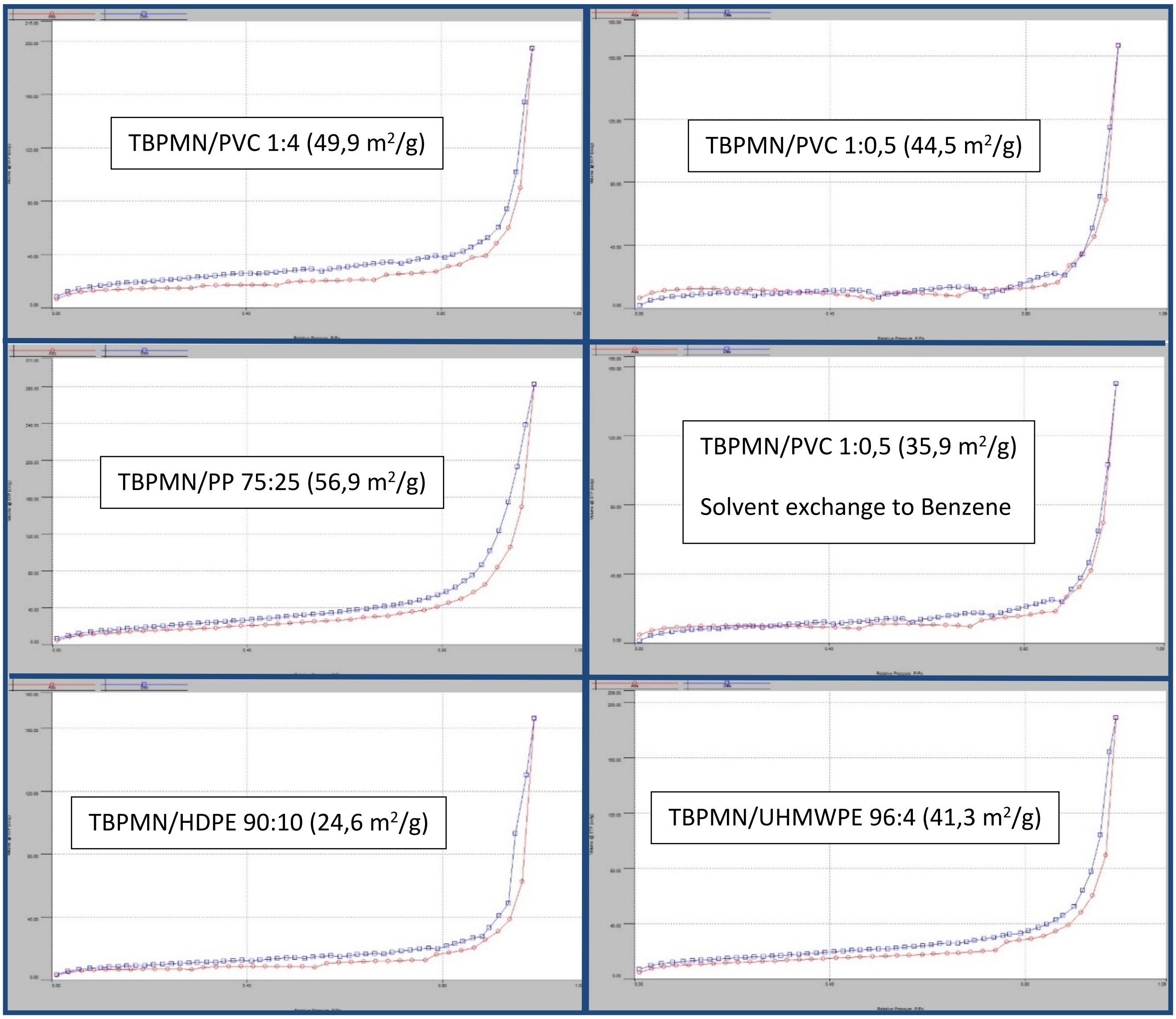


Figure S15: BET measurements of different TBPMN-Polymer-samples