

Supplementary Information

Load-release of small and macro molecules from elastomers with reversible gyroid mesoporosity

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Content: FTIR of cross-linked and etched samples; SEC of PDMS before and after DCP treatment; Calculation of contrast factor; Distribution of PEG in the sample; Scattering peak resolution of SANS and SAXS; Calculation of the mesh size and the pore size; Load-release of *d*-SDS.

FTIR of cross-linked and etched samples

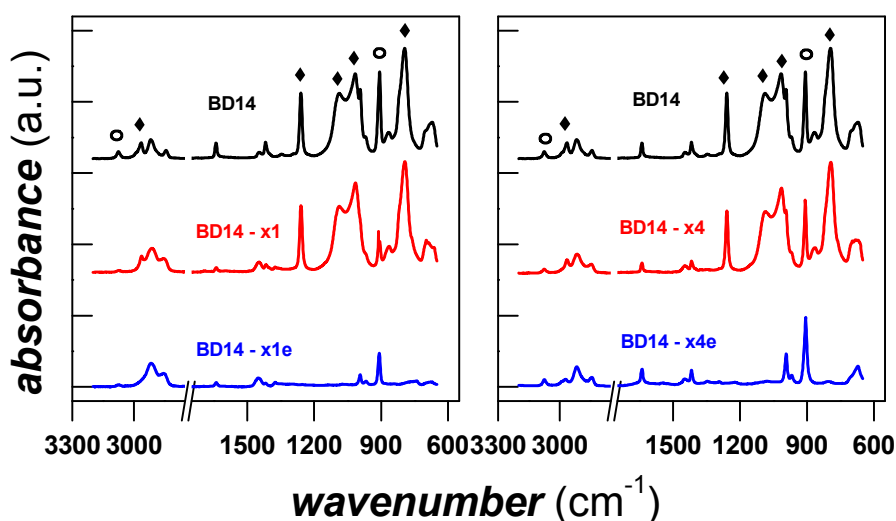


Fig. S1 FT-IR spectra of BD14 precursor, cross-linked samples BD14-x1 and BD14-x4, and etched samples BD14-x1e and BD14-x4e. Diamonds mark the PDMS absorption bands at 2965 cm^{-1} (C-H bending), 1261 cm^{-1} (CH₃ bending), $1093\text{-}1120\text{ cm}^{-1}$ (Si-O-Si stretching), and 800 cm^{-1} (C-Si-C stretching), and open circles mark the 1,2-PB absorption bands at 3075 cm^{-1} (vinyl C-H stretching) and 908 cm^{-1} (out-of-plane vinyl C-H bending). Two peaks at 908 and 1261 cm^{-1} are selected to quantify the concentration of double bonds in the samples after cross-linking relative to the precursor polymer, BD14. Separate measurements (shown in Fig. S2) indicate that the cross-linking does not affect the PDMS block which allows us to take the PDMS peak as an internal standard. After subtraction from FT-IR spectrum of BD14, the peak at 908 cm^{-1} is well separate and the peak at 1261 cm^{-1} completely disappears for the cross-linked sample. Therefore, the ratio between the intensities

at 908 and 1261 cm^{-1} is directly proportional to the number of double bonds present in the sample. (More details of the discussion can be found in the ref. 21 in the paper).

SEC traces of PDMS before and after DCP treatment

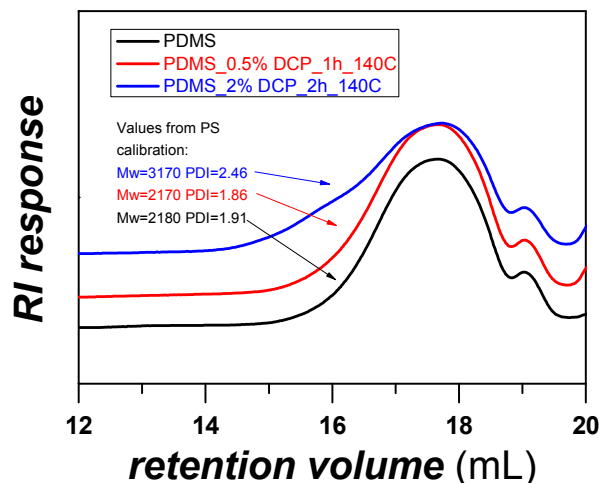


Fig. S2 SEC traces of PDMS, PDMS heated with 0.5 mole % DCP at 140 °C for 1 h and PDMS heated with 2 mole % DCP at 140 °C for 2 h. From the molecular weight values before and after cross-linking PDMS does not change at 0.5% DCP content and 1 h of heating at 140C. For the sample containing 2% DCP and heated for 2 h the weight average Mw has increased by 46%, while the number average Mn by 11% relative to the original PDMS. The modest increase in Mn is consistent with in average one coupling reaction per each 9 chains. Given that each chain contains in average 40 monomers (absolute Mn of original PDMS is about 3000 g/mol) and 80 methyl groups, the fraction of reacted methyl groups is well below 0.5%, therefore not detectable by NMR or FT-IR. This estimate fully justifies the use of silicone methyl bending absorption at 1261 cm^{-1} as internal standard.

Scattering peak resolution of SANS and SAXS

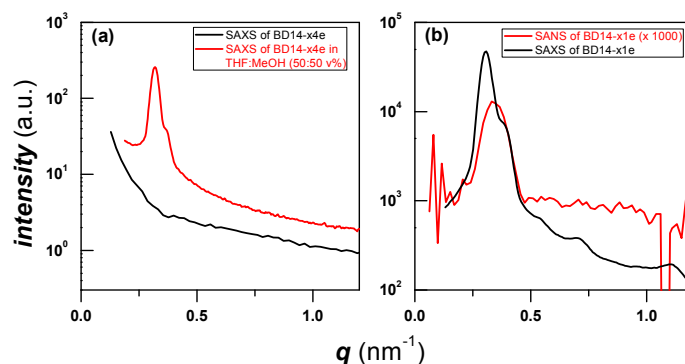


Fig. S3 (a) SAXS traces of the lowly cross-linked BD14-x4e and BD14-x4e in a 1:1 (v:v) mixture of THF and methanol, the traces reveal the gyroid morphology was restored from the collapsed sample. (b) SANS x 1000 and SAXS traces of the highly cross-linked nanoporous BD14-x1e, the comparison reveals a lower resolution in the SANS profile that does not allow to identify the gyroid structure.

Calculation of contrast factor between the swollen sample in *d*-PEG + CHCl₃ and CHCl₃ systems

Distribution of *d*-PEG in the gel can be qualified as follows. From the swelling ratio S_m of 3.2 (page 4 in the paper), the SLD of the swollen matrix without PEG is:

$$\rho_{1,m} = \rho_{CHCl_3} \times \left(1 - \frac{1}{S_m}\right) + \rho_{xPB} \times \left(1 - \frac{1}{S_m}\right) = (2.38 \times 0.68 + 0.417 \times 0.32) \times 10^{10} \text{ cm}^{-2} = 1.75 \times 10^{10} \text{ cm}^{-2}$$

If all *d*-PEG were within the pore volume, then $\rho_{1,m} = \rho_{2,m}$ and the SLD of the pores filled with *d*-PEG + CHCl₃ would have been:

$$\rho_{2,p} = \rho_{d-PEG} \times v_{d-PEG} + \rho_{CHCl_3} \times (1 - v_{d-PEG}) = (6.29 \times 0.023 + 2.38 \times 0.977) \times 10^{10} \text{ cm}^{-2} = 2.47 \times 10^{10} \text{ cm}^{-2}$$

The volume fraction v_{d-PEG} of *d*-PEG is calculated from the total amount of *d*-PEG loaded in the nanoporous polymer, 6% by mass, as measured by gravimetry after sample drying. The expected intensity ratio would then have been:

$$\frac{\Delta\rho_2^2}{\Delta\rho_1^2} = \frac{(2.47-1.75)^2}{(2.38-1.75)^2} = 1.31$$

Different possible reasons may be mentioned for the discrepancy between this estimated value and the experimental value of 1.24. Overall the two-phase model might be too simple for the collapsing system, e.g. the boundary between pore and matrix ‘phases’ is not at all sharp (see Fig. 10 in the main text for a visual rendering of the boundary). In addition, the gel volume of the swollen sample in *d*-PEG + CHCl₃ is slightly smaller than the volume in pure CHCl₃ (as judged from the position of the main scattering peak in the two cases), which was neglected in the estimation.

Distribution of PEG in the sample

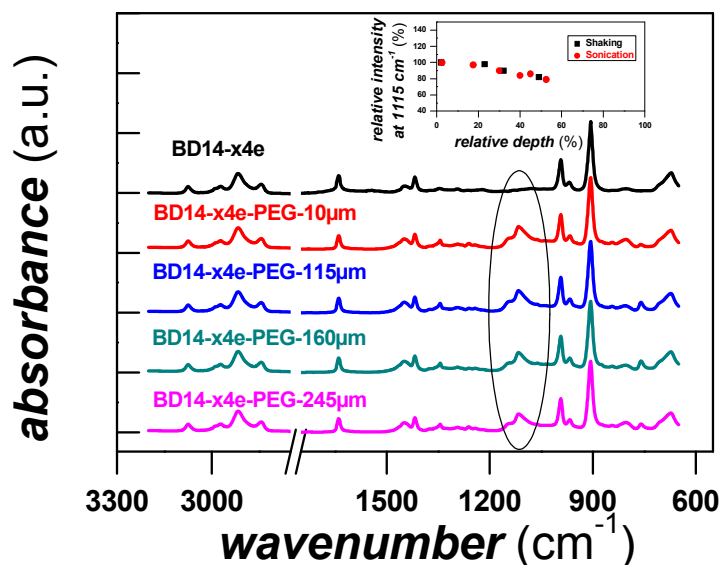


Fig. S4 FT-IR spectra of BD14-x4e and *n*-PEG loaded BD14-x4e with different depth. The band at 1115 cm⁻¹ is the C-O-C stretching vibration of *n*-PEG. Inset presents relative ratio between the absorption intensities at 1115 cm⁻¹ with different depth in the sample by using absorption intensity at 908 cm⁻¹ (vinyl C-H bending of 1,2-PB) as an internal reference for two different loading procedures: shaking and 2h of sonication.

Calculation of mesh size and pore size for the cross-linked 1,2-PB

1st method. The mesh size is defined here as the average diameter of gyration of the network strands in the swollen state. We calculate the average diameter of gyration $2\langle s^2 \rangle_0^{1/2}$ of each 1,2-PB network strand with $M=3000\text{g/mol}$ in the melt (unperturbed chain). Then we use the swelling ratio of 3.2 to estimate the diameter of gyration in the swollen state.

$3000\text{ g/mol} \Rightarrow 55.6\text{ monomers} \Rightarrow n = 111\text{ C-C bonds}$ in the main chain, each of $l = 0.153\text{ nm}$. We do not have the data on $\langle s^2 \rangle_0/nl^2$ for 1,2-PB. For the estimate we use the value 1.01 calculated for polyethylene with 111 C-C bonds (P. J. Flory, Statistical Mechanics of Chain Molecules, p. 149, Interscience Publishing 1969). The value is similar for chain substituted polymers like Polyisobutylene (idem p. 200) or atactic polypropylene (Polymer Data Handbook, p. 773, ed. J.E.Mark, Oxford University Press 1999).

$$2\langle s^2 \rangle_0^{1/2} = 2 \times (1.01 \times 111)^{1/2} \times 0.153 = 3.2\text{ nm}$$

With a uniform swelling ratio of 3.2 the above diameter of gyration increases to:

$$3.2^{1/3} \times 3.2 = 4.7 \text{ nm}$$

2nd method. The mesh size here is defined as the side length a of imaginary identical cubes covering the volume of the swollen 1,2-PB matrix and with a total number of sides equal to the number of 1,2-PB strands. For a tetra functional network a represents the number-average distance between cross-linking points. Now, for cubes in the bulk each side is shared among 4 adjacent cubes, while for cube faces on the surface each side of the face is shared between 2 cubes. For ‘bulk’ cubes there are 3 strands per cube, while for a monolayer of cubes (with 2 faces in the surface and 4 faces in the ‘bulk’) there are 5 strands per cube. We take these values as lower and upper bounds for the actual number of sides per cube.

Starting with 1 g of 1,2-PB with density 0.9 g/cm^3 , the number of strands with $M_{\text{strand}} = 3000 \text{ g/mol}$, or equivalently the number of cube sides is:

$n_s = N_{\text{Av}}/3000 = 2 \times 10^{20}$ and the number of cubes in the two boundary cases is: $n_1 = 0.67 \times 10^{20}$ (‘bulk’) and $n_2 = 0.40 \times 10^{20}$ (‘monolayer’). The single cube volumes (in nm^3) in the two cases are:

$v_i = (10^{21}/0.9)/n_i$ ($i = 1,2$) and the corresponding side lengths $a_i = v_i^{1/3}$, or $a_1 = 2.6 \text{ nm}$ and $a_2 = 3.0 \text{ nm}$.

These are the boundary values for the unswollen 1,2-PB network. The values are close but smaller than $2\langle s^2 \rangle_0^{1/2}$ calculated by the 1st method. In the swollen state, with a swelling ratio of 3.2:

$a_{si} = a_i \times 3.2^{1/3}$, or $a_{s1} = 3.8 \text{ nm}$ and $a_{s2} = 4.4 \text{ nm}$. The actual value of $3.8 \text{ nm} < a < 4.4 \text{ nm}$ is again somewhat smaller than the mesh size estimated by the 1st method.

An estimation of the effective pore size in the swollen state can be done by modelling the pores locally as cylinders with radius R and the PEG1.1k molecules as hard spheres with radius $r = R_g = 1.3 \text{ nm}$. The excluded volume is then a cylindrical shell of thickness r around the outer perimeter. The concentration of PEG1.1k inside the pores C_{in} relative to the concentration in the solution outside the pores C_{out} is calculated from the ratio of SEC traces heights in Fig. 9. A 7% reduction of the peak height for the SEC of PEG1.1k in solution is made in order to compensate for the ‘neighbour effect’, i.e. from the tail of the adjacent peak of PEG4.6k. The reduced value of C_{in} relative to C_{out} is ascribed to the excluded volume, which allows to calculate R , as follows:

$$C_{\text{in}}/C_{\text{out}} = 0.72 = [(R-r)/R]^2 = [(R-1.3)/R]^2 \rightarrow R = 8.6 \text{ nm}$$

Load-release of *d*-SDS

The loading of *d*-SDS was carried out prior to SANS measurements by submerging a BD14-x4e in a 30 mg/ml *d*-SDS solution in THF/H₂O. After being dried under vacuum, the sample took 7 mass % of *d*-SDS. The releasing experiment in a 4:1 (v/v) mixture of THF and D₂O was recorded by SANS as shown in Figure S4. The q position of the weak scattering peak of pre-loaded sample is 0.35 nm⁻¹. After being in THF/H₂O for 15 min, both scattering intensity and q position of the peak reach their equilibrium values, 15 cm⁻¹ and 0.30 nm⁻¹, respectively. After 1 h, the sample was taken out and dried under vacuum. The scattering profile of the dried sample is at the back and shows no nanoporous structure, indicating that the previously trapped *d*-SDS has been released from the sample.

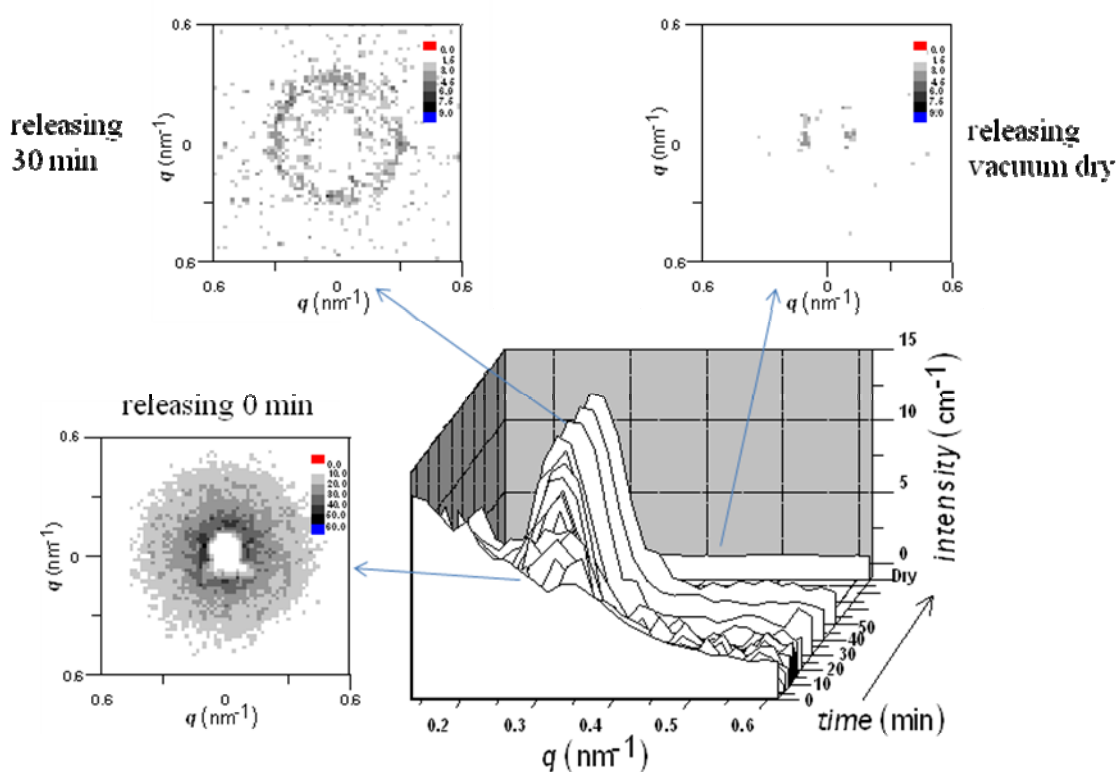


Fig. S5 Time-resolved SANS data of *d*-SDS releasing process for BD14-x4e.