

## Supplementary Information

### Tailoring of the porous structure of soft emulsion-templated polymer materials

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#### SI-I. Scheme of the synthesis of porous beads

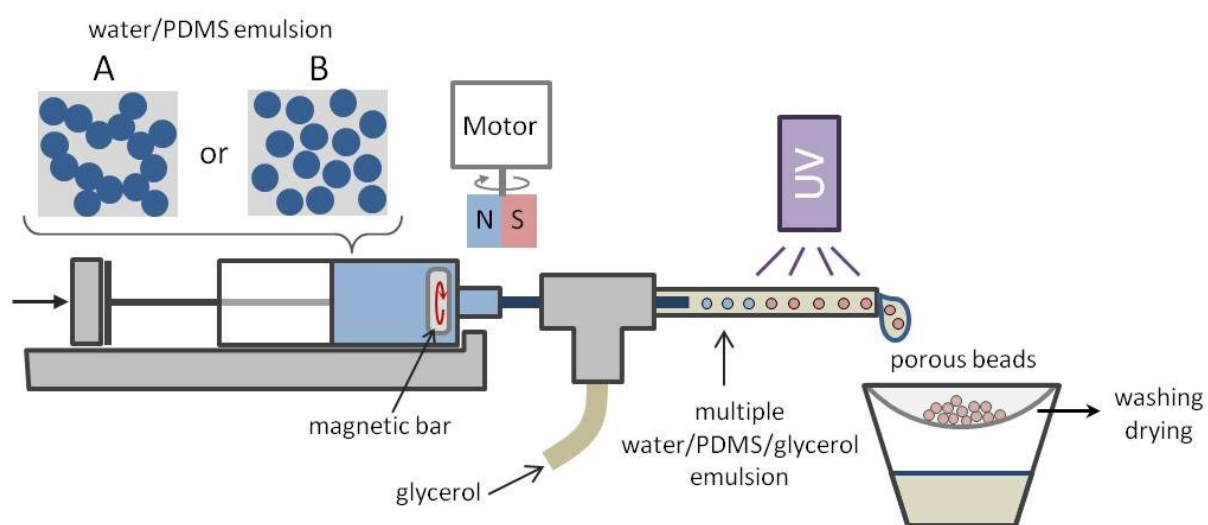


Figure SI 1 - Scheme of the microfluidic device used for the synthesis of porous beads.

**SI-II. Scheme of the preparation of beads dispersion in Carbopol gel**

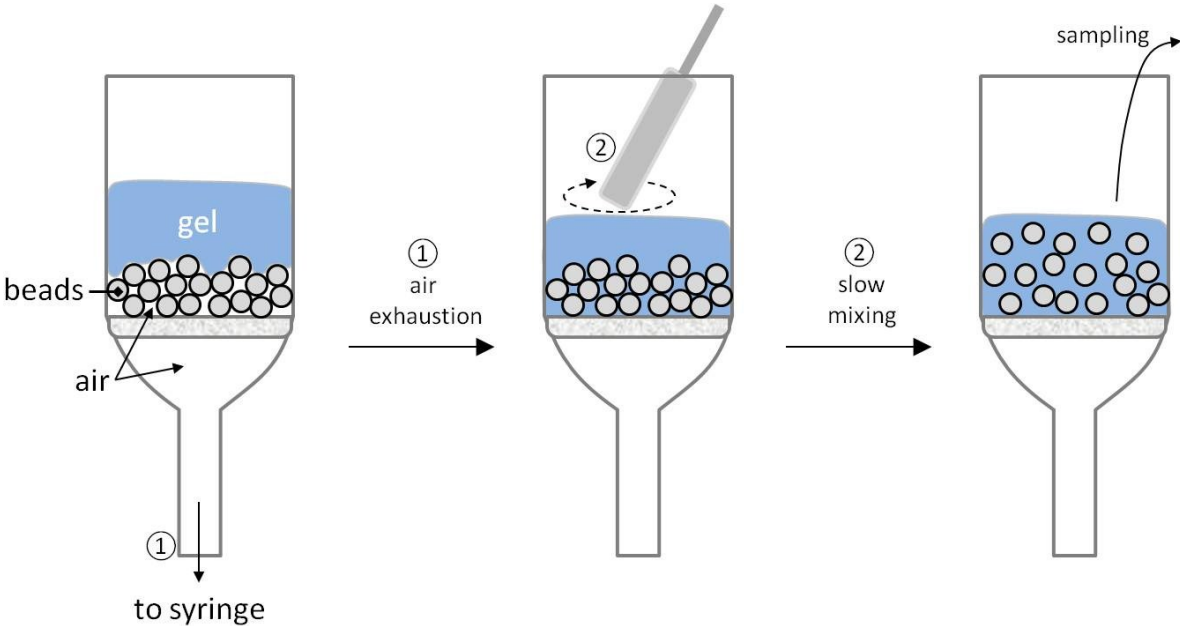


Figure SI 2 – Scheme illustrating the preparation protocol of the beads dispersion in Carbopol gel for acoustic measurements.

**SI-III. Mercury intrusion porosimetry of beads**

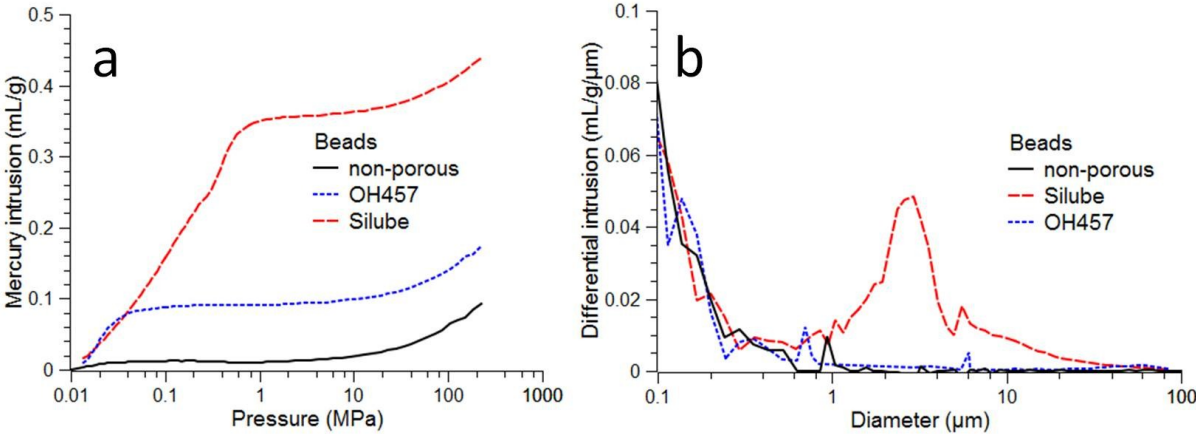


Figure SI 3 - Mercury intrusion curves (a) and pore interconnection size distributions (b) of beads. The non-zero intrusion at high pressures (corresponding to low diameter values) is due to bulk compression of the PDMS matrix.

#### SI-IV. Density distribution of beads from flotation experiments

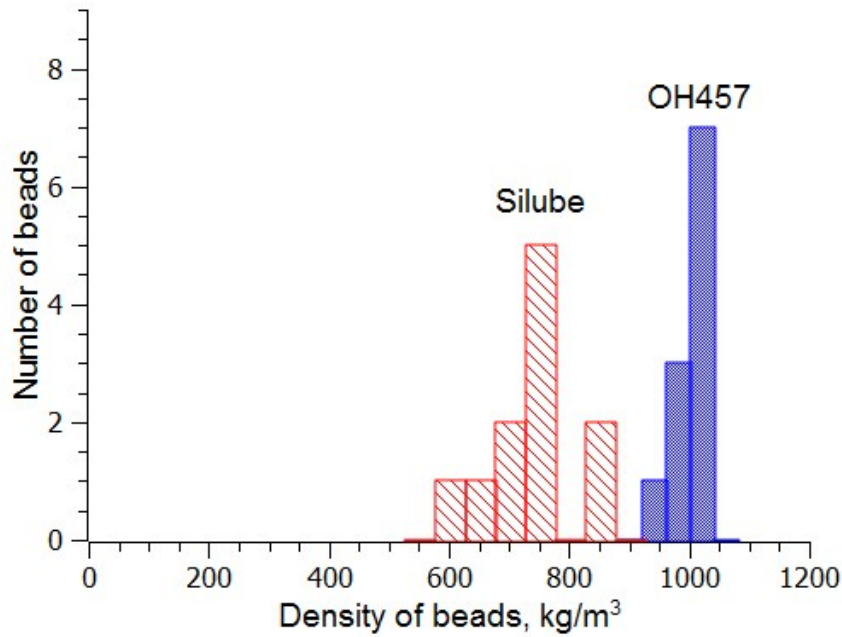


Figure SI 4 - Density distributions of dried beads deduced from flotation speed experiments with the emulsions stabilized by Silube (dashed bars) and OH457 (dark grey bars).

#### SI-V. Characterization of the cross-linking degree by $T_g$ measurements

In order to characterize the cross-linking of the PDMS, we performed thermal analysis by differential scanning calorimetry (DSC). Samples were encapsulated in TZero cells and measured in Q2000 calorimeter (TA Instruments) equipped with liquid  $N_2$  cell. The samples were rapidly cooled to  $-150^\circ\text{C}$  and then heated to  $-50^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$ . The midpoint of the endothermal change associated with the glass transition was used to determine  $T_g$ . The reproducibility of the  $T_g$  measurements was within  $0.5^\circ\text{C}$ .

The cross-linking degree of beads and bulk samples was estimated from the shift of the glass transition temperature ( $T_g$ ) of the samples. This approach was chosen with respect to other methods, based on swelling and mechanical studies, because the glass transition is independent of the macro-structure and the shape of samples. The increase of  $T_g$  with cross-linking density was studied before for non-porous PDMS<sup>1</sup>. According to the Stutz, Illers and Mertes model,<sup>2</sup> the  $T_g$  can be expressed as the following:

$$T_g = T_g^0 \left( 1 + \frac{K_2 X_c}{1 - X_c} \right) \quad (8)$$

where  $T_g^0$  is the  $T_g$  of uncross-linked polymer,  $X_c$  is the cross-link density expressed as the mole fraction of all cross-links present in the system weighed by functionality, and  $K_2$  is the constant, characterizing the influence of the cross-links.

Figure SI 5 shows the differential scanning calorimetry (DSC) curves of the silicone beads and bulk samples, synthesized in this work. A curve of the uncross-linked PDMS is added for comparison. As expected, the glass transition endotherms of cross-linked samples are shifted to higher temperatures with respect to the liquid PDMS. The largest shift is observed for the non-porous samples (1a and 1b), which indicates the largest attainable cross-linking degree of the epoxy groups. The cross-linking density of these samples was presumed to be equal to the molar epoxy content, i.e. 10 %. The curves of the porous samples with Silube (2a and 2b) and OH457 (3a and 3b) show the transition at temperatures which lay between that of the non-porous solid (1) and the liquid (4) sample. Thus, the cross-linking degree of the samples is lower than the expected one. This is most likely due to the influence of water droplets on the cross-linking reaction initiation and propagation.

Using equation (8), we estimated the cross-linking density of the porous samples. The midpoint of the glass transition endotherm was taken as the  $T_g$  value. The obtained values of the cross-linking density are listed in Table SI-1. The cross-linking density of bulk samples with either Silube or OH457 is about 0.04, indicating that there is no influence of the surfactant and of the emulsion structure on the cross-linking. However, only about a half of epoxy groups are cross-linked in these samples. The cross-linking degree of beads is lower than that of beads and equals 0.034 for Silube and 0.023 for OH457. This can be related to the different time of UV exposure: the illumination time of the emulsion droplets inside the co-flow device is less than 1 s, which may be insufficient for the complete cross-linking. The better cross-linking of the Silube-stabilized emulsion droplets is probably due to better penetration of the UV light inside the emulsion, which may be supported by the presence of transparent regions inside the beads on the optical microscopy images (Figure 5a in the manuscript).

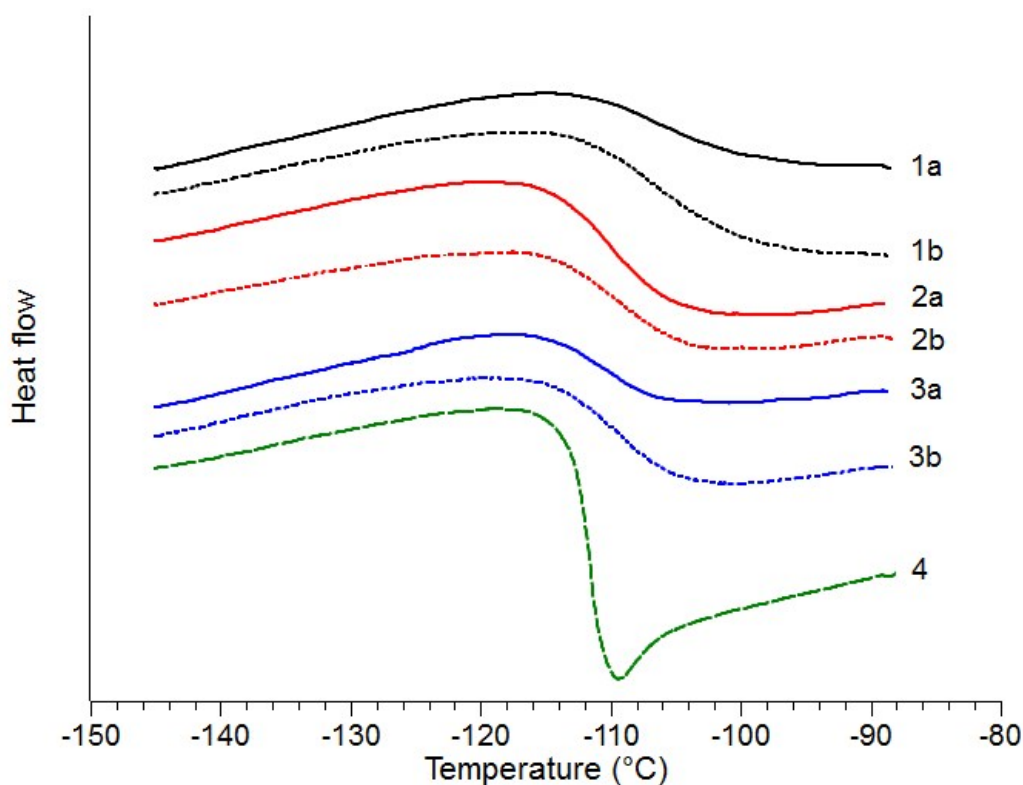


Figure SI 5– Differential scanning calorimetry curves of PDMS samples in the  $T_g$  region used for the cross-linking characterization. The heating rate is  $5^\circ\text{C}/\text{min}$ . Curve numbers indicate the solid non-porous samples (1), the porous samples with Silube (2) and OH457 (3), and the liquid PDMS before cross-linking (4). Indices correspond to the beads (a) and bulk samples (b).

Table SI-1 – Glass transition temperatures and cross-linking degree values calculated from DSC curves of obtained silicone materials.

	Bulk samples				Beads		
	Non-porous	Silube	OH457		Non-porous	Silube	OH457
$T_g$	167.5 K	163.8 K	163.8 K		167.8 K	163.5 K	162.8 K
$X_c$	0.094	0.04	0.04	$X_c$	0.1	0.034	0.023

## References:

<sup>1</sup> Shefert, A.; Gottlieb, M. Effect of cross-links on the glass transition temperature of end-linked elastomers. *Macromolecules* **1992**, 25, 4036-4042.

<sup>2</sup> Stutz, H.; Illem, K. H.; Mertes, J. A generalized theory for the glass transition temperature of crosslinked and uncrosslinked polymers. *J. Polym. Sci.* **1990**, 28,1483.