Supplementary Information for the Manuscript Entitled

pH-Dependent disruption of giant polymer vesicles: A step forward towards biomimetic membranes

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Supplementary Figures and Tables

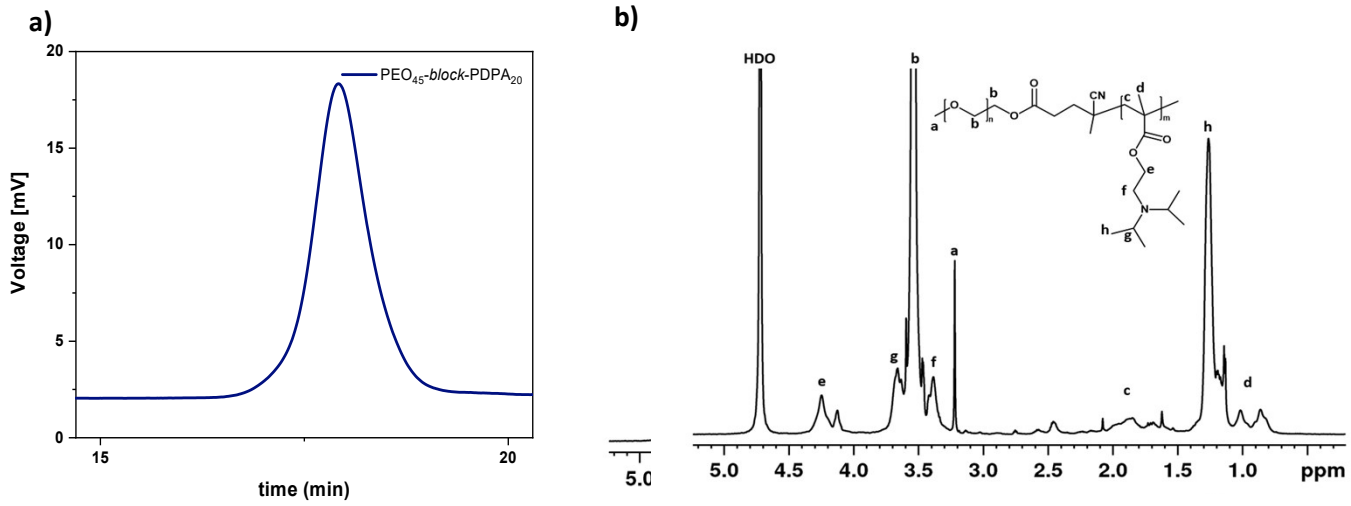

Figure S1. SEC of PEO_{45}-*block*-$PDPA_{20}$ (M_n = 6257 g·mol^{-1}, $Đ$ = 1.11) measured in a mixture of chloroform-triethylamine-isopropanol 94:4:2 (RI detector) (a) and ^{1}H NMR of the copolymer in D_2O/DCl (pH 2.0) (b).

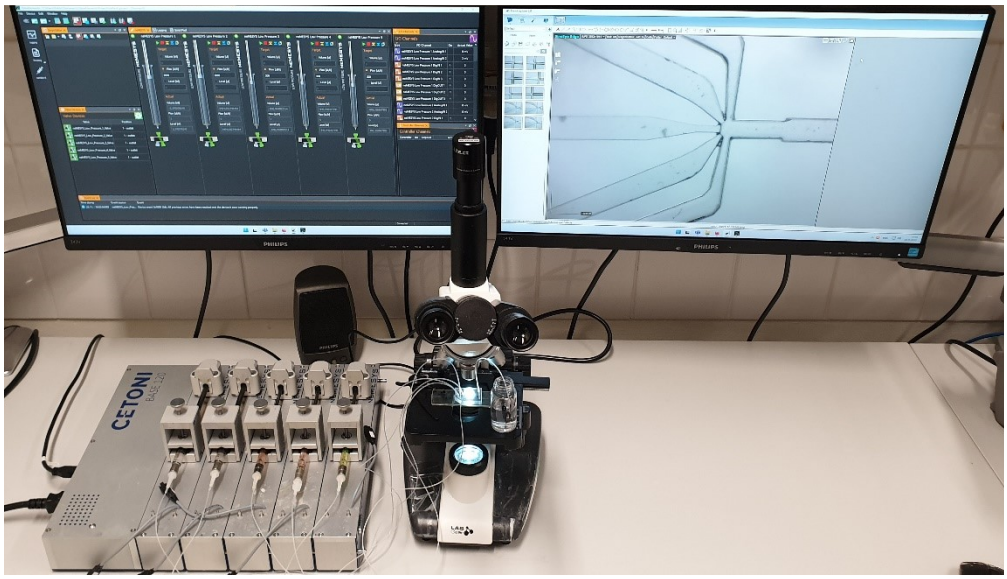

Figure S2. A global picture of the microfluidic setup.

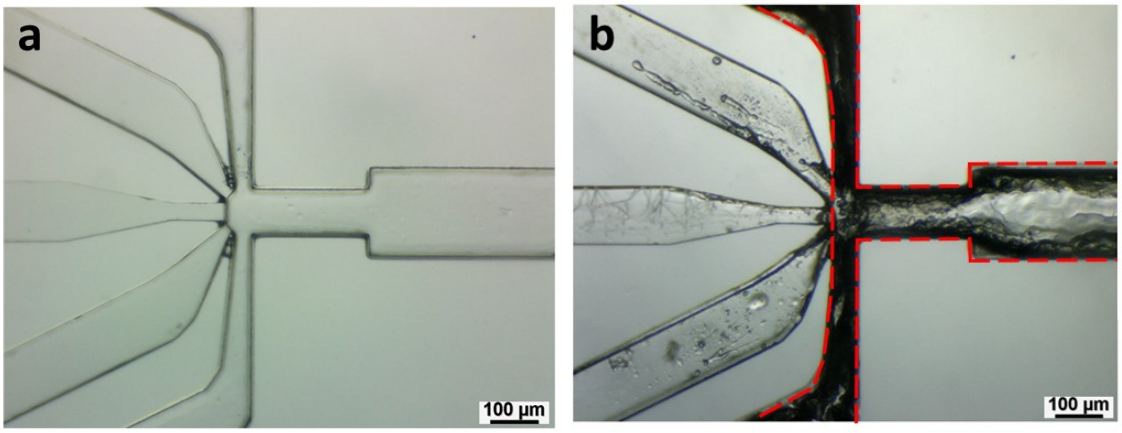

Figure S3. Bright-field microscope images of microfluidics channels before (a) and after (b) coverage with glass (all channels) and poly(ethylene oxide) (only in the selected channels marked in red).

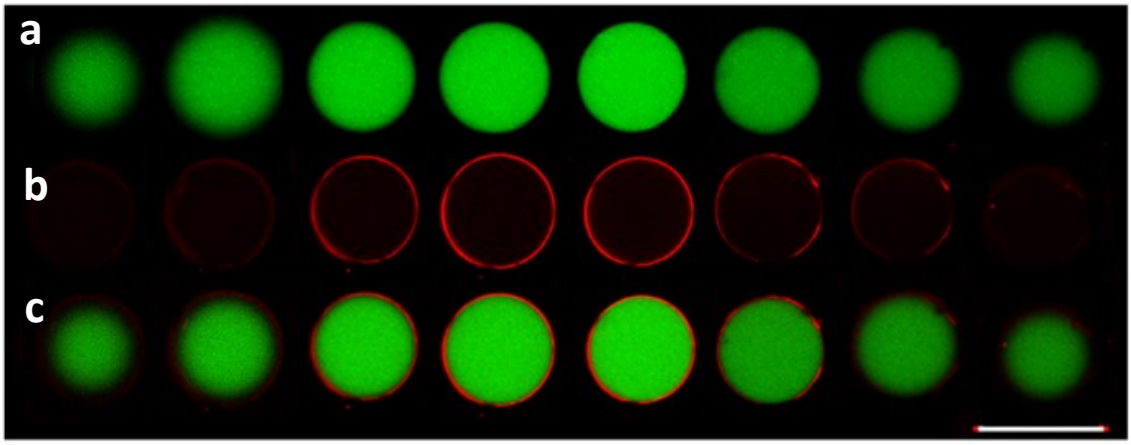

Figure S4. Z-stacks series of images taken at different z-planes for a single GUPV (a) using only the fluorescent excitation/emission range of calcein (λex = 488 nm; λem = 510-545 nm), (b) using only the excitation/emission range of Nile red (λex = 635 nm; λem = 645-665 nm) (c) using the excitation/emission ranges of both Nile red and calcein. Z-stack step size is 10 µm and the scale bar denotes 100 µm.

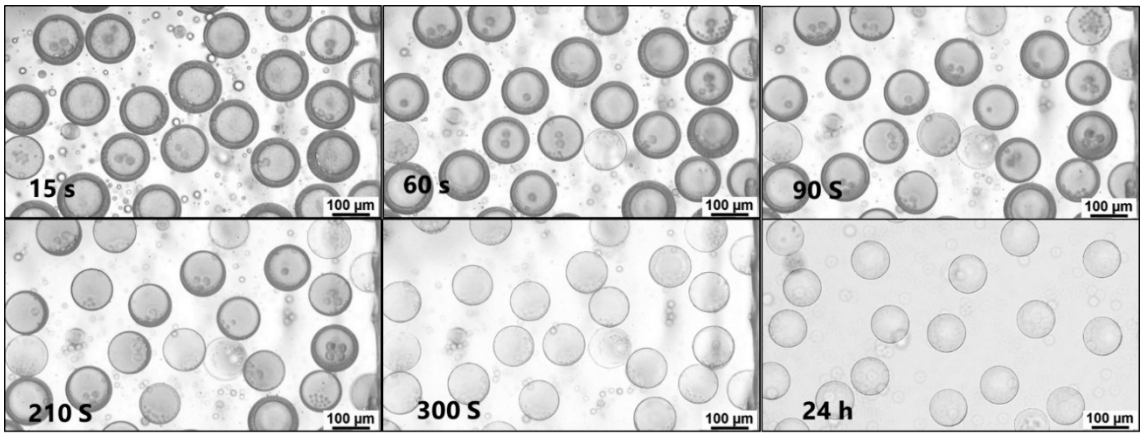

Figure S5. Bright-field microscope images of double emulsion droplets showing the dewetting process as a function of time. The double emulsion drop consists of an aqueous drop surrounded by a shell of PEO_{34}-*b*-PBD_{46} (7.14 mg·mL^{-1}) with PEO_{45}-*b*-$PDPA_{20}$ (0.28 mg·mL^{-1}) diblock copolymer dissolved in toluene. The last image of the GUVs after complete evaporation of toluene after 24 hours is shown as comparison.

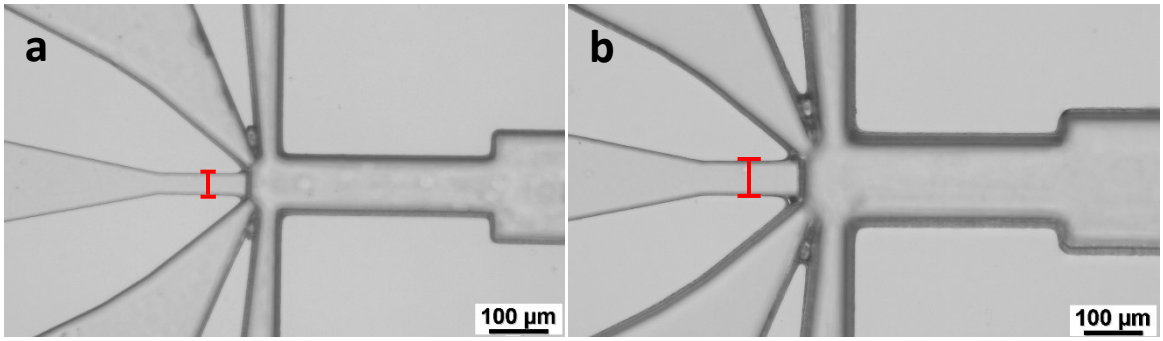

Figure S6. Optical microscopy images of microfluidic channels with distinct dimensions. (a) IA with channel dimension of 35 µm and (b) with channels dimension of 65 µm.

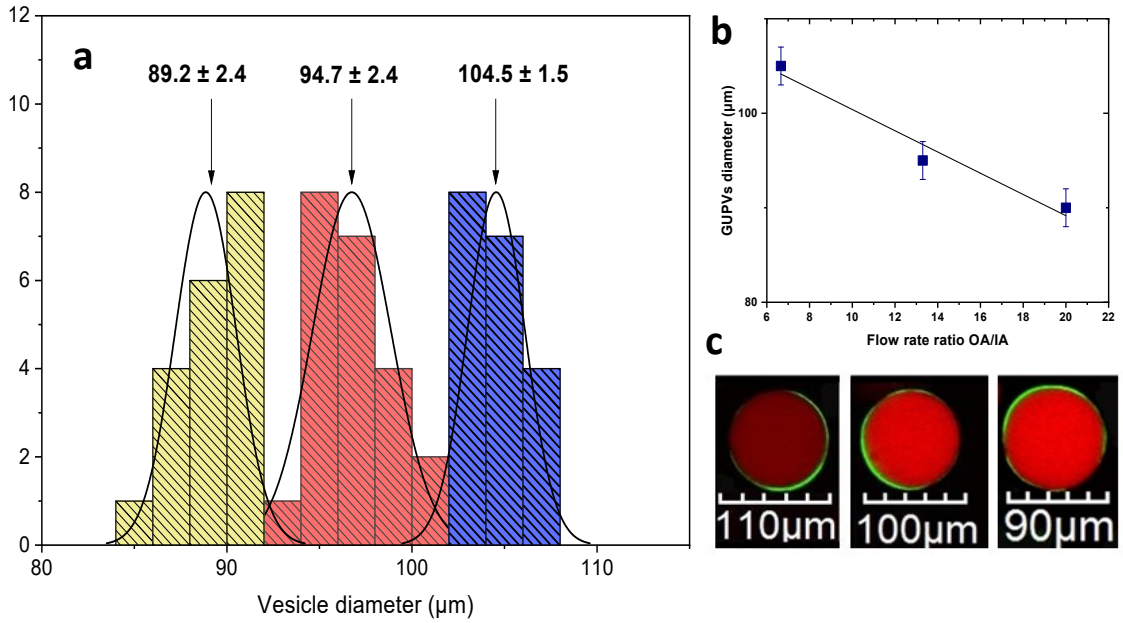

Figure S7. (a) Frequency histograms of GUPVs in the size range of interest (89-110 µm) with highly monodisperse (1.4 to 2.8 %) populations (n ≥ 200 particles). Gaussian fits represent in solid lines, arrows point to the mean diameters and the standard deviations (89.2 ± 2.4, 94.7 ± 2.4, 104.5 ± 1.5 µm). (b) GUPVs diameter as a function of flow rate ratio of OA/IA produced using the chip with IA channel dimension of 65 µm. (c) CSLM images of GUPVs using the fluorescent excitation/emission ranges of calcein (λ_{ex} = 488 nm; λ_{em} = 510-545 nm) and Nile red (λ_{ex} = 635 nm; λ_{em} = 645-685 nm).

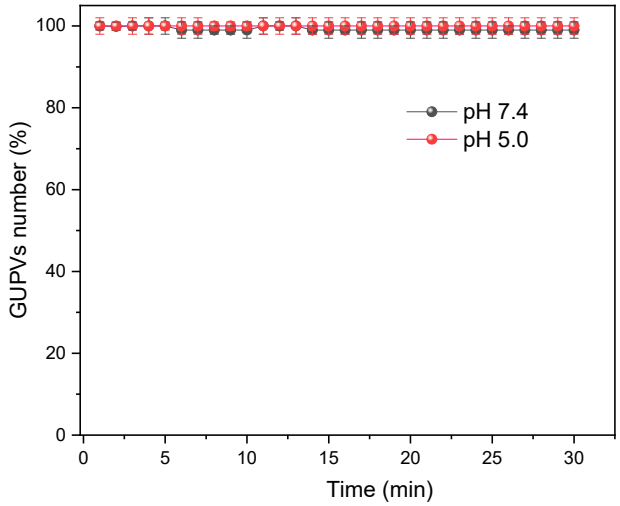

Figure S8. Number percentage of non-responsive GUPVs as a function of time after exposure to different pH.

Detailed photo- and soft lithographical microchip fabrication

The whole preparation process of polydimethylsiloxane (PDMS) microfluidic devices is shown in Fig. S9. The first step contains the photolithography which is performed in a clean room by spin-coating (Cee 200X, Brewer Science Inc.) a negative photoresist (SU-8 50, Microchem Corp.) onto a 3" silicon wafer, as visible in Fig. S9A. If a so-called 2D-chip design for 2D-focusing is prepared, just one layer of photo resist SU8-50 is spin-coated to build up a channel structure of 100 µm height. For producing a 3D-focusing chip design, two layers about 50 µm and 100 µm as well as two

chip parts with channel structures are necessary to finally receive a higher channel height for the two side channels of 250 µm in comparison to the middle channel with 50 µm. The microchannel structures are imparted to the photoresist using a mask aligner (MJB4, SÜSS MicroTec SE). The uncured photoresist is removed in the subsequent development process which yields a one-layered respectively two-layered master. All detailed geometric design parameters of the sinusoidal and linear microchannels are shown in the main publication. The second part of the fabrication process, the soft lithography1 , continues under dust-free conditions by replicating the micro structured master using polydimethylsiloxane (PDMS, Sylgard 184 kit, Dow Corning Corp.) and curing it for t = 1.5 h atT = 75 °C, as visible in Fig. S9B. The PDMS replica is removed from the master and inlet ports are punched into the polymer using home-made punch needles with an outer diameter of d = 1 mm. The PDMS is cut into smaller pieces for better handling whereby the channel design allows preparing several microchannels simultaneously. The final microfluidic device is created by bonding the PDMS replica for a 2D-chip onto a glass slide and the two structured PDMS chip halves to each other for a 3D-device. This is achieved by activating the PDMS and glass surface using air plasma (MiniFlecto-PC-MFC, Gala Instrumente GmbH), respectively the two PDMS chip halves by adding a little drop of pure water (0.2 µm-filtered Millipore) for initially aligning and finally drying at T = 30 °C for about t = 1 h. The use of a microscope helps during the alignment step and in addition to it the integrated orientation structures of the multi-layer design will snap in and align the microstructures automatically with high precision.

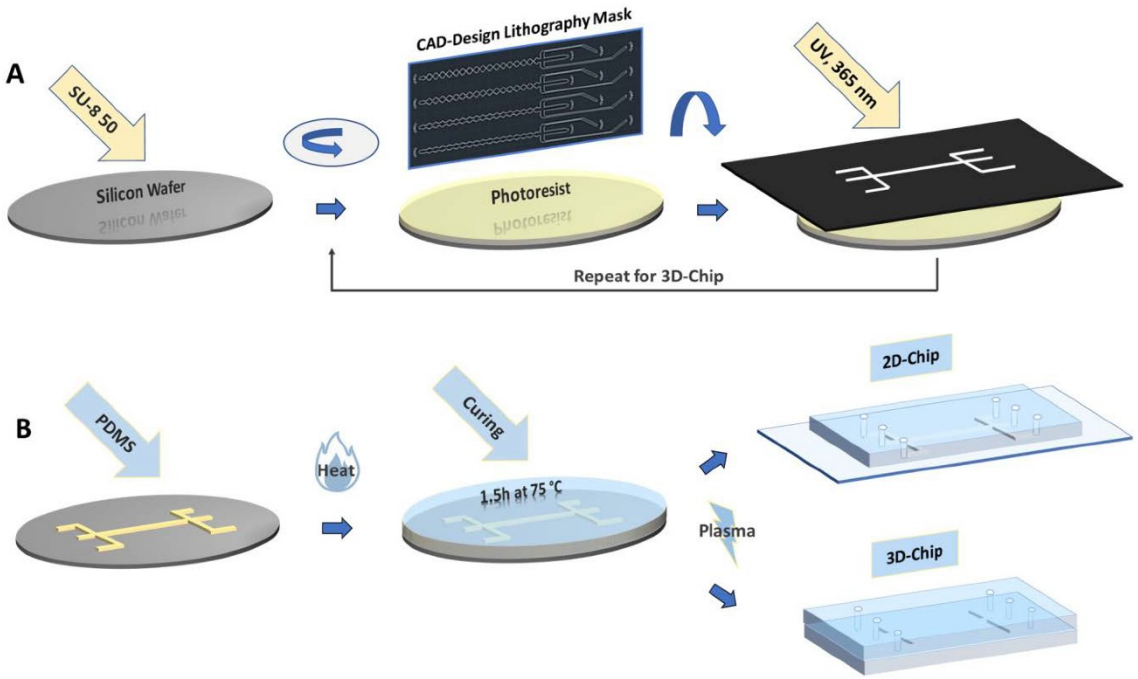

Figure S9. Fabrication of microfluidic devices made of PDMS. (A) Master device fabrication based on SU-8 50 photoresist using photolithography with UV-exposure whereby the photolithographic master for 3D-chips involves one repeating step to build up a multilayered microstructure. After development, the uncured photoresist is removed. (B) The resulting 2D- respectively 3D-microchannel template is replicated by using soft lithography1. Therefore, the PDMS is poured onto the master device and cured for t = 1.5 h at T = 75 °C. Afterwards, the PDMS replica is peeled off the master device, cut into the chip parts and inlet ports for fluids are added. After plasma treatment of the two PDMS halves respectively the glass surface for a 2D-chip, the device is sealed using air plasma treatment.