Supporting Information

A pH-responsive bio-hybrid carrier material for phenol decontamination in wastewater

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**Synthesis and characterization of the PB-*b*-P2VP diblock copolymer**

Anionic polymerization of the diblock copolymer in THF proceeded without termination. The 1,2-PB precursor (87 mol-% 1,2-addition as determined by ^{1}H-NMR) as well as the diblock copolymer exhibited narrow molecular weight distributions ($Đ = 1.01$, Figure S1A). The number-averaged molecular weight (M_n) of the PB precursor was determined by MALDI-TOF MS to $M_n = 82200$ g mol^{-1} (Figure S1B). To calculate the molecular weight of the synthesized polymer, we used the molecular weight of the PB precursor obtained by MALDI-TOF MS for calibration of ^{1}H-NMR signals. Consequently, the composition of the diblock copolymer was determined to $B_{66}V_{34}{}^{126}$, where the subscripts denote the mass fraction of the respective block and the superscript gives the overall number-averaged molecular weight M_n in kg mol^{-1}.
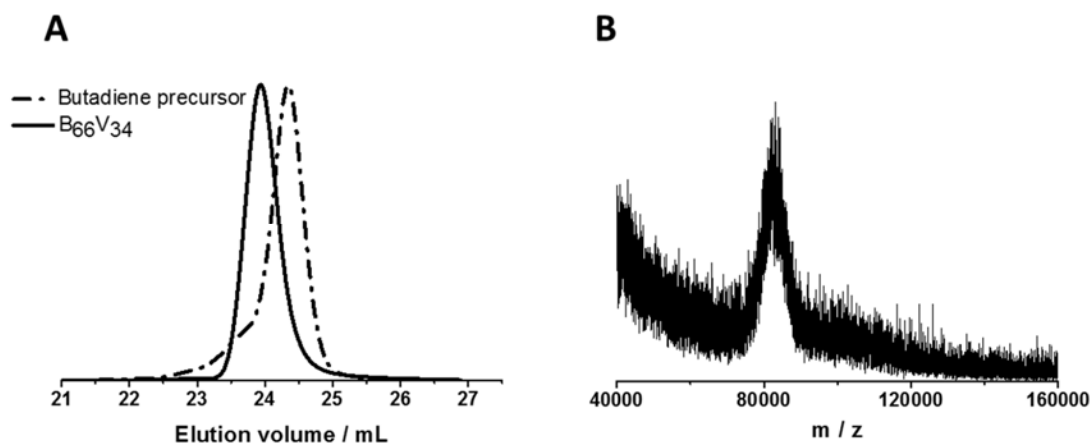
Figure S1. THF-SEC traces of the PB precursor and the $B_{66}V_{34}{}^{126}$ diblock copolymer (A) and MALDI-TOF mass spectrum of the PB precursor (B).

Mechanical properties of crosslinked PB-*b*-P2VP diblock copolymer films and fibers

A homogeneous deformation without necking or cold-drawing was observed for the prepared fibers, which typically indicates a rubber-like state of the polymer (Figure S2A). This type of behavior was expected, due to the high PB content in the diblock copolymer. Moreover, the elongations at break using thin films and nonwovens were in the range of 100-200%. In the case of electrospun nonwovens, slightly higher elongation at break values were obtained. Furthermore, the Young´s modulus and tensile strength (Figure S2B) were as well similar for film and electrospun samples. These results indicate similar mechanical properties of PB-*b*-P2VP as polymeric material when prepared as thin film or nonwoven.
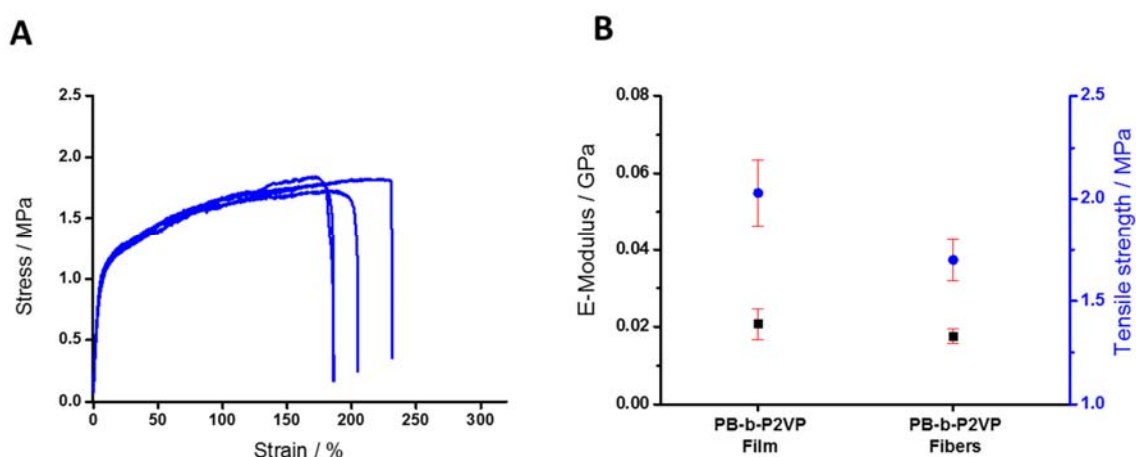
Figure S2. Stress-strain curves for crosslinked PB-*b*-P2VP electrospun nonwovens (A) and comparison of Young´s modulus and tensile strength for crosslinked PB-*b*-P2VP films and nonwovens (B).

Atomic Force Microscopy
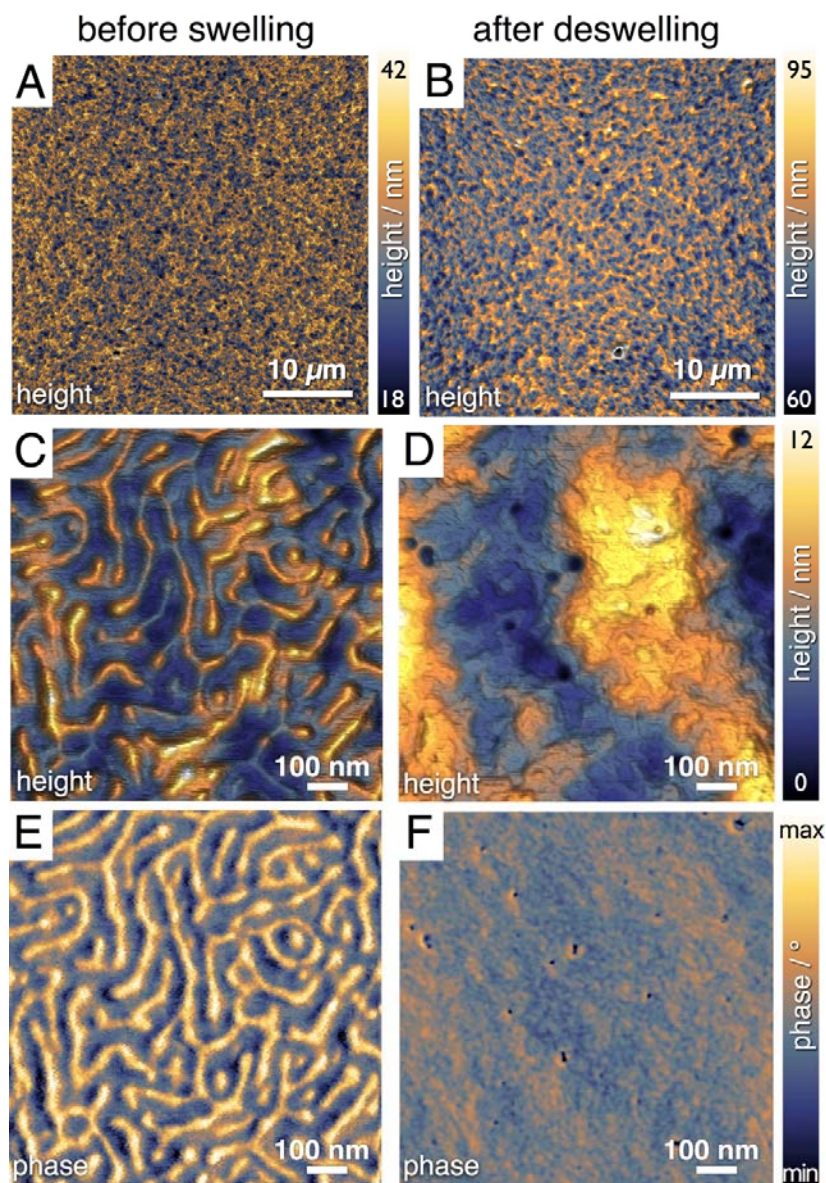
Figure S3. AFM topography and phase images of the PB-*b*-P2VP films before and after pH-responsive swelling/deswelling: Overview (A, B; 40 x 40 µm^2) and detail scans (C - F, 1 x 1 µm^2). The PB-*b*-P2VP film (thickness: 162 nm) was prepared by spin coating from THF solution onto silicon wafers and exhibited an initial surface roughness of 3.4 nm (RMS). After swelling/deswelling the microphase separation in the top layer of the film was not observable anymore.

Determination of the film thickness and water content

For the determination of the film thickness, the polymer layer was modeled as a transparent Cauchy layer, *i.e.*, homogeneous layer of thickness d with an index of refraction n in the form of $n(\lambda) = n_0 + n_1 \lambda^{-2} + n_2 \lambda^{-4}$ and no absorption $k = 0$ on a silicon wafer (Fig. S4A). First, the thickness of the native oxide layer of the silicon wafer (without the polymer layer) was determined ($d = 2.0 \pm 0.1$ nm). Then, the polymer layer was applied and measured in dry state to obtain its initial optical properties (n_0, n_1, n_2), using AFM measurements as a reference for d. The swelling experiments were performed using a home-built liquid cell with glass windows in 65° reflection geometry, which was placed into the optical path of the ellipsometer.[1]
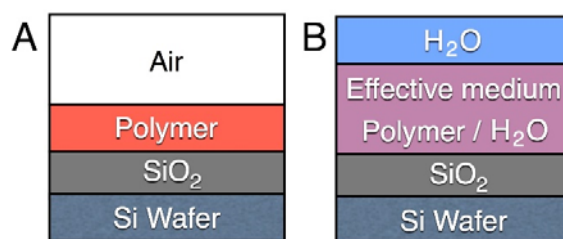
Figure S4. Schematic representation of the layer models used for (A) dry state and (B) *in-situ* measurements in liquid.

The swelling and deswelling of the polymer film was monitored for stepwise changes of the swelling medium. The change in thickness upon uptake of water was modeled by a simple multilayer model (Fig. S4B). For this purpose, the Cauchy layer of polymer was substituted by an effective medium layer based on a Maxwell-Garnett homogenization of the optical properties of the (dry) polymer film and water ($n = 1.333$, $k = 0$). This approximation yields an effective refractive index n_{eff} of a host medium with inclusions of a second medium of volume fraction ϕ.[2]

$$n_{\text{eff}} = n_{\text{host}} \sqrt{\frac{2\left(1-\phi\right)n_{\text{host}}^2 + \left(1+2\phi\right)n_{\text{inclusion}}^2}{\left(2+\phi\right)n_{\text{inclusion}}^2 + \left(1-\phi\right)n_{\text{inclusion}}^2}}$$

<div align="right">Eq. S1</div>

Following Eq. S1, the ellipsometric data in liquid state were evaluated by numerical fitting for the layer thickness and water content.

Determination of *C. glutamicum* leakage from PB-*b*-P2VP electrospun fibers

Bacterial leakage from the prepared electrospun fibers for water decontamination needs to be avoided. Therefore, the incubation media was tested for bacteria growth on agar plates after incubation for 7 days at 30 °C with PB-*b*-P2VP fibers containing the immobilized *C. glutamicum*. Figure S5 shows that no bacteria colonies grew after 72 h at 30 °C from the incubated media at pH = 7. In the case of incubation at pH = 4, similar results were obtained, as free bacteria do not tolerate acidic conditions.

Incubation media containing immobilized
C. glutamicum at pH 7

No bacteria growth after streaking on an agar plate
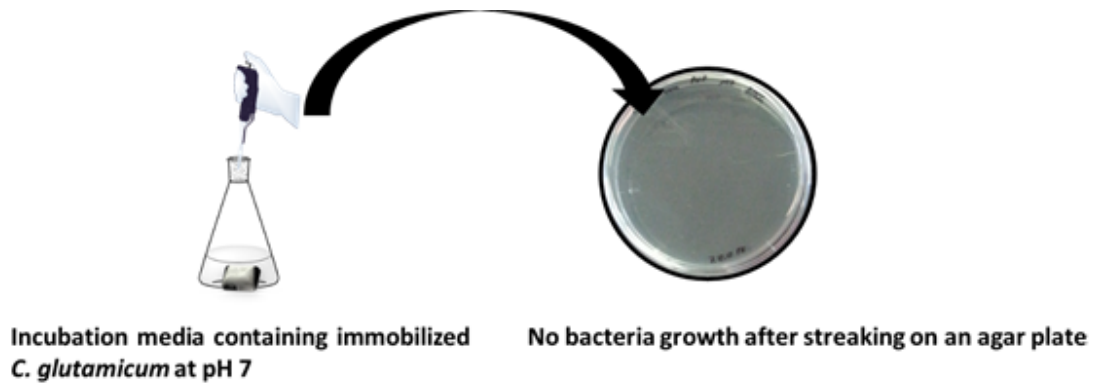
Figure S5. Agar plate after incubation of the growth media (pH = 7) containing immobilized *C. glutamicum* in PB-*b*-P2VP fibers.

Blank test with PB-*b*-P2VP nonwoven without encapsulated bacteria

Figure S6 reveals that the phenol concentrations stay constant for the nonwoven without encapsulated bacteria. This clearly shows the necessity of encapsulated *C. glutamicum* inside the electrospun nonwoven for phenol degradation.
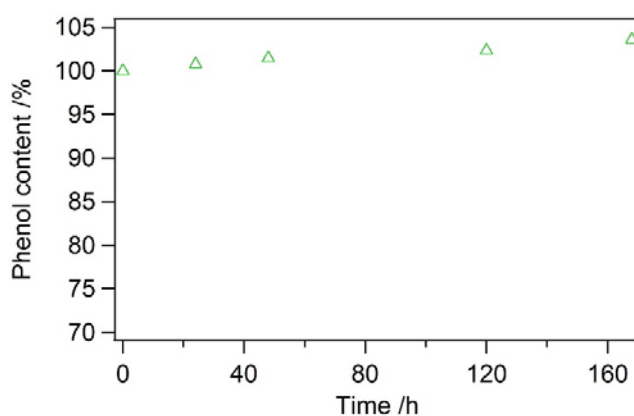

Figure S6: Blank test with a cross-linked PB-*b*-P2VP nonwoven.

References

(1) Elbs, H.; Krausch, G. Ellipsometric determination of Flory-Huggins interaction parameters in solution. *Polymer* **2004**, *45*, 7935–7942.

(2) Garnett, J. C. M., Philos. T. Colours in Metal Glasses and in Metallic Films. *Roy. Soc. A.* **1904**, *203*, 385–420.