

Biomimetic Supported Membranes from Amphiphilic Block Copolymers

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Supporting Information

Chemicals. All chemicals and solvents were purchased from Sigma Aldrich or Fluka (Switzerland) with the highest purity grade and, unless otherwise stated, used as received. Tetrahydrofuran (THF) for polymerization and the monomers 1,3-butadiene and ethylene oxide were purified as reported elsewhere.¹ Dichloromethane (DCM) was dried for 12 h over CaH₂ and freshly distilled prior to use.

Polymer Synthesis. Poly(butadiene)-*b*-poly(ethylene oxide) (PB-PEO-OH) block copolymers were synthesized by sequential living anionic polymerization following a procedure utilizing the phosphazene base *t*-BuP₄[‡].^{1, 2} This base prevents the strong association of the living PEO chain ends with the Li⁺ counter-ions from the initiator and therefore allows for a sequential one-step polymerization without intermediate steps. Polymerizations were carried out in a thoroughly flame-dried customized glass vacuum apparatus under inert gas atmosphere. The synthesis was described in detail elsewhere.¹

Polymer Functionalization. Poly(butadiene)-*b*-poly(ethylene oxide) (PB-PEO-OH) were synthesized as described in the supporting information. After purification by repeated

precipitations in cold acetone (-30 °C), the hydroxyl-terminated diblock copolymer was esterified with lipoic acid (LA). LA (269 mg, 1.3 mmol), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC·HCl; 250 mg, 1.3 mmol) and 4-(dimethylamino)pyridine (DMAP; 12 mg, 0.1 mmol) were added to a flame-dried flask. The solids were dried under vacuum for 2 h. The mixture was dissolved in 15 mL absolute DCM. In a second flame-dried flask, PB-PEO-OH (4 g, 1 mmol) was dried under vacuum for 2 h and dissolved in 20 mL absolute DCM. After triethylamine (0.2 mL, 1.4 mmol) was added, the solution was injected into the first flask and the reaction mixture was stirred at room temperature for 72 h. Afterwards, the solution was washed with saturated NaHCO_{3aq}, 10% HCl_{aq}, and distilled water (three times each). The organic phase was dried over MgSO₄, filtered, and the solvent was evaporated.

Polymer Characterization. The molecular weight of the block copolymer was determined by GPC and ¹H-NMR. First, a PB aliquot, drawn prior to the sequential copolymerization, was analyzed by GPC with THF as eluent. Narrow poly(butadiene) standards (PSS Polymer Standards Service, Germany) were used to calculate M_n , M_w , and the polydispersity index (PDI) of the PB block. The number of the ethylene oxide repeating units, thus the molecular weight, was calculated from the integral ratios in the ¹H-NMR spectrum of the block copolymer. The degree of functionalization of the lipoic acid-modified polymer (PB-PEO-LA) was determined by ¹H-NMR. Covalent attachment of the end-group to the polymer was proven by DOSY (diffusion ordered spectroscopy) analysis. Figure S1 shows a GPC chromatogram of PB and the diblock copolymer. A ¹H-NMR spectrum of PB-PEO-LA can be seen in Figure S2.

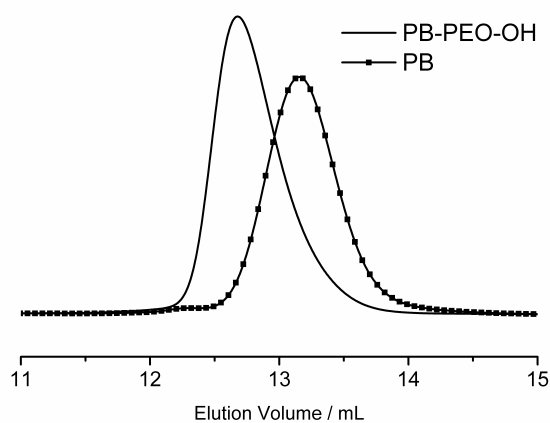


Figure S1 GPC chromatogram of PB and PB-PEO-OH in THF. The PB block consists of 52 repeating units.

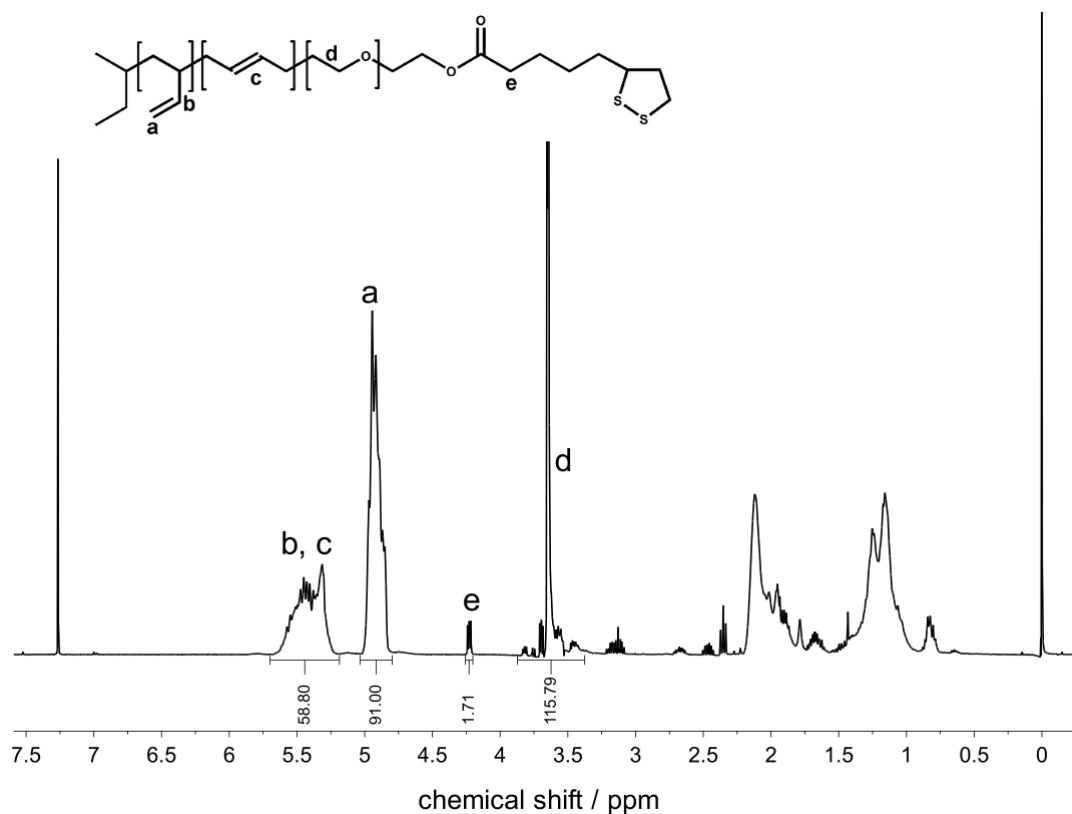


Figure S2 ¹H-NMR spectrum of PB-PEO-LA. Since the number of repeating units of the PB precursor is known from GPC, the repeating units of the PEO block, thus the overall molecular weight, could be determined. Furthermore, the 1.2- to 1.4-isomer ratio could be calculated to 0.87:0.13. The yield of the functionalization with lipoic acid is approximately 86%.

Surface plasmon resonance (SPR) spectroscopy measurements were performed using a home-built setup in Kretschmann configuration with a He/Ne laser ($\lambda = 633$ nm) which is described in literature in detail.^{3, 4} In scan mode, reflectivity is monitored as a function of the incident angle and with the aid of a photodiode. To achieve the high in-plane wave vectors of the exciting light at moderate coupling angles, the microscope slide (microcrown glass; Menzel, Germany) was attached to a LaSFN9 Prism ($n=1.845$; Schott, Germany).

Data evaluation was done using the free program WINSPALL which was developed at the MPI for Polymer Research. The analysis is based on a model calculation of the reflectivity $R(\theta)$ from the multilayer system deposited on the prism base. Layer parameters are obtained from a least-squares fit to the data. The calculations are based on Fresnel equations and are done with a transfer-matrix approach described in detail by Yeh.⁵ For each layer, a thickness d and a constant dielectric response $\epsilon = \epsilon' + i\epsilon''$ can be attributed, the latter may be complex-valued. For the dielectric film either the d or ϵ has to be known to determine the other parameter respectively. In our case ϵ -values were taken from literature. First the pure gold layer was measured as a reference and the dielectric constants and thicknesses obtained from fitting were kept constant for the following polymer film evaluation. Starting values for gold are found in literature.⁶ Spectra of films were fitted using a four layer model including the prism, gold, mono- or bilayer, and the surrounding medium (water or air). A refractive index $n = 1.5$ ($\epsilon' = 2.25$) was assumed for both, mono- and bilayer⁷ so that film thicknesses were obtained from the fit.

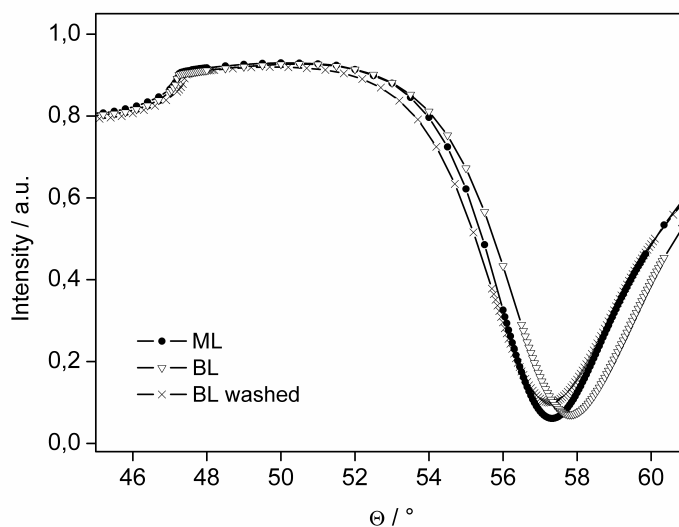


Figure S3 Angular SPR spectrum measured in ultrapure water. After the bilayer (BL) was washed with a good solvent such as THF or chloroform, the reflectivity minimum returned to the one obtained for a monolayer (ML).

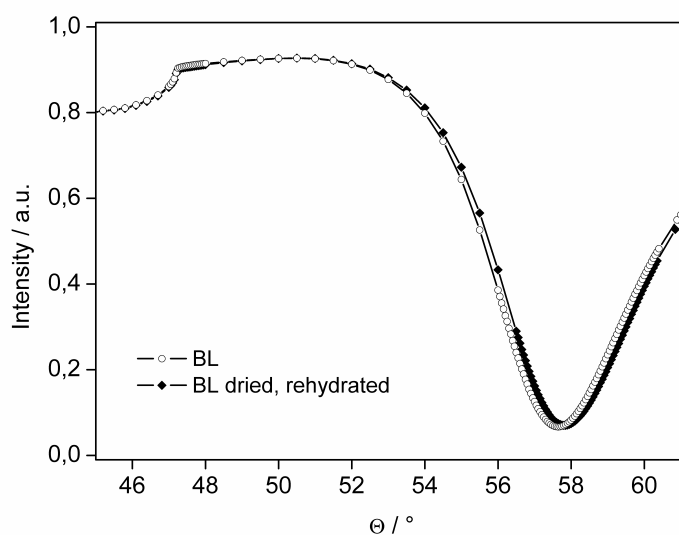


Figure S4 Angular SPR spectrum measured in ultrapure water. A bilayer (BL) was dried under a stream of nitrogen and left dry for 2 h prior to rehydration. There is hardly a minimum shift noticeable.

‡. IUPAC name: 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2Λ⁵,4Λ⁵-catenadi(phosphazene).

References

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