Supporting Information

Tailoring Poly(vinylbenzocyclobutene)-*b*-Poly(4-vinylpyridine) Isoporous Block Copolymer Membranes: Functionalization and Performance Optimization

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***Polymer synthesis**:* The polymers of this work were synthesized via sequential anionic polymerization. The nomenclature followed is $PVBCB_{79}$-*b*-$P4VP_{21}^{108k}$ where the PVBCB is poly(vinylbenzocyclobutene), P4VP abbreviation for poly(4-vinylpyridine), subscripts the weight percentage of each block in the polymer and the Number following is attributed to the total molecular weight in kg/mol. All monomers and solvents were prior purified to reach the standards for anionic polymerization. More specific the monomers vinylbenzocyclobutane (VBCB, Sigma-Aldrich, Schnelldorf, 97%) was twice distilled from di-n-butylmagnesium (Sigma-Aldrich, Schnelldorf, 1.0 M solution in heptane) under high vacuum and 4-Vinylpyridine (4VP) (Sigma-Aldrich, Munich, Germany) was distilled once from calcium hydride and twice from ethyl aluminum dichloride (Sigma-Aldrich, Schnelldorf, 1.0 M in hexanes). The polymerization procedure is conducted polymerization in a Schlenk line apparatus using high vacuum (10^{-7}-10^{-8}mbar) and Argon supply (Argon 7.0, Linde AG, Pullach, Germany) as follows: A 250ml glass reactor was connected on the vacuum line, evacuated to attain high vacuum. Subsequently purified THF was distilled into the reactor and titrated under argon at -80 °C, by a small amount of *sec*- butyllithium (s-BuLi) (Sigma Aldrich, Schnelldorf, Germany, 1.4 M solution in cyclohexane), until a vivid yellow color was observed. Upon the disappearance of the color the reactor was brought again at -80 °C and the first purified monomer 4-vinylbenzocyclobutene (4-VBCB 2.213 g, 0.023 mol) was inserted via a syringe in the reactor, followed by the initiator *s*-BuLi (0.28 M in cyclohexane, 0,08 mL, 0.000022 mol). In the polymerization solution immediately developed a bright orange color indicating the formation of propagating

anion of 4-VBCB and the reaction left to complete for 1h at -80 °C. After the reaction was completed an aliquot was withdrawn and the second purified monomer 4-vinylpyridine (4-VP, 0,539g 0,0056 mol) was inserted in the polymerization reactor. At this point, the solution color changed rapidly in light yellow-green indicating the propagation of the 4VP block. The polymerization completed overnight and on the following day terminated with vacuum-degassed methanol (0.5 mL) The diblock copolymer was recovered by precipitation in hexane and dried under vacuum at 50 °C for 48 h. The yield is 96% (2.75 g). The molecular characteristics of the diblock copolymer derived from the measurements in GPC using as solvent chloroform and PS standards and ^{1}H-NMR in $CDCl_3$. The total molecular weight of the polymer is calculated 108kg/mol and PVBCB block is 79 wt.% and P4VP 21 wt.%.

Molecular Characterization

Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

The synthesized compounds were analyzed by proton nuclear magnetic resonance spectroscopy (NMR). ^{1}H-NMR measurements were performed on a Bruker Ascend 500 NMR spectrometer (500 MHz) using $CDCl_3$ and DMF-*d7* as solvent, at room temperature**.**

P4VP amount was calculated at 21 wt %, P4VCB amount 79 wt%.

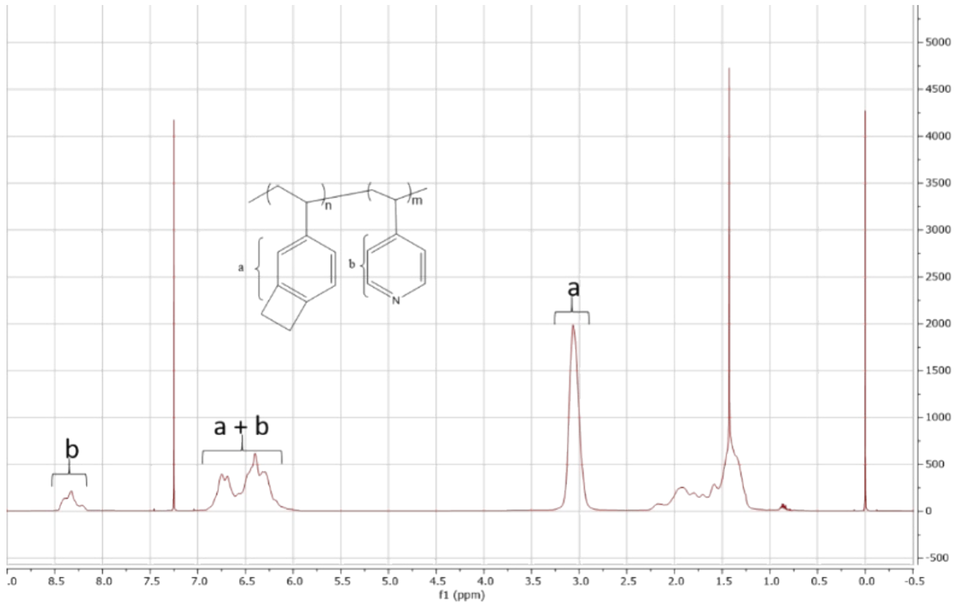

Figure S1: ^{1}H-NMR spectrum of the PVBCB$_{79}$-b-P4VP$_{21}$^{108k} block copolymer

Gel Permeation chromatography (GPC)

The molecular weights of the polystyrene-precursor and molecular weight distribution of the block copolymer were determined by gel permeation chromatography calibrated with PS standards. The measurements were performed at 30 °C in chloroform using PSS GRAM columns [GRAM precolumn (dimension 8·50 mm), GRAM column (porosity 3000 A, dimension 8·300 mm, particle size 10 µm) and GRAM column (porosity 1000 A, dimension 8·300 mm, particle size 10 µm)], at a flow rate of 1.0 mL min^{-1} (VWR-Hitachi 2130 pump). A Shodex RI-101 refractive index detector with a polystyrene calibration was used. P4VP, due to its polar nature, has been reported to occasionally exhibit interactions with the stationary phase. Therefore, interactions of these solutes are exhibited asadsorption (retardation in retention time) led to misleading results concerning the actual molecular weight of the second block. For this reason, GPC results from the precursor PVBCB block (Figure S1 green line) were evaluated with the weight average results for each block derived from ^{1}H-NMR to reveal the final molecular weight of the block polymer. For the above-mentioned reason the Figure S1 chromatograms are representative for the successful synthesis of a monodispersed homopolymer ((Figure S1 green line) and diblock copolymer polymer (Figure S1 blue line) but in the case of the diblock copolymer not representative total molecular weight.

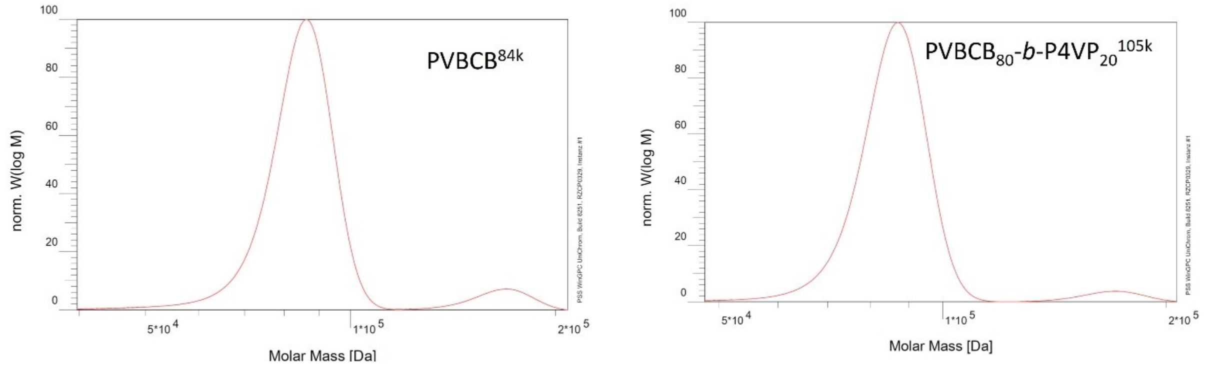

Figure S2: Chromatograms of the PVBCB precursor homopolymer and the final diblock copolymer PVBCB-b-P4VP in CHCl$_3$. The line is attributed to the RI detector signal.

Figure S3: Chromatograms of the PVBCB precursor homopolymer and the final diblock copolymer PVBCB-b-P4VP in $CHCl_3$. The line is attributed to the RI detector signal.

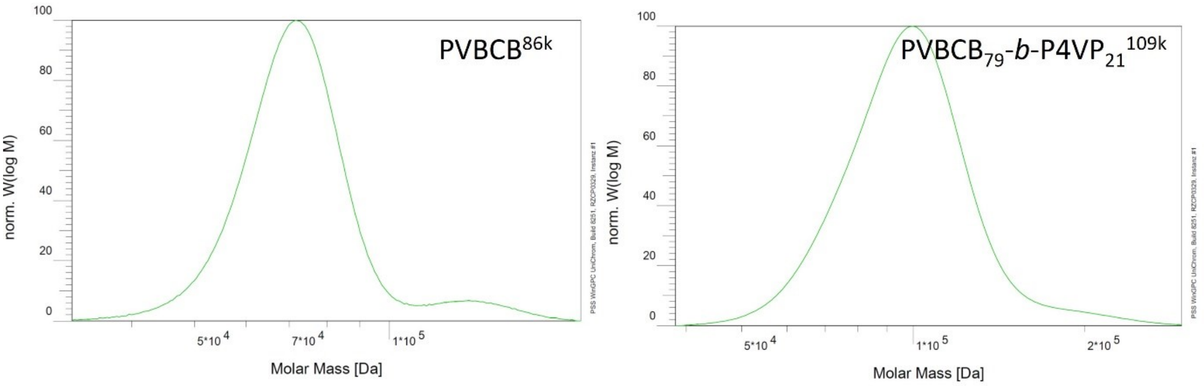

Figure S4: Chromatograms of the PVBCB precursor homopolymer and the final diblock copolymer PVBCB-b-P4VP in $CHCl_3$. The line is attributed to the RI detector signal.

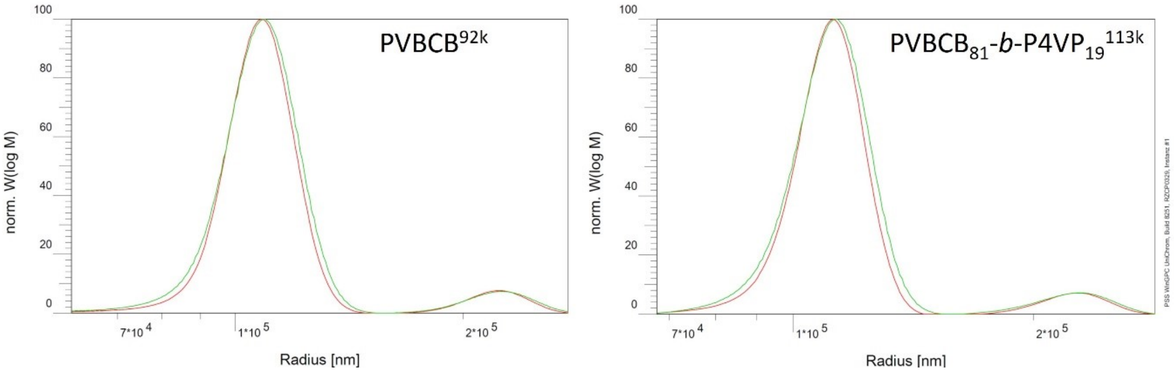

Figure S5: Chromatograms of the PVBCB precursor homopolymer and the final diblock copolymer PVBCB-b-P4VP in $CHCl_3$. The green line is attributed to the RI detector signal and the red is attributed to the UV detector signal.

Figure S6: Chromatograms of the PVBCB precursor homopolymer and the final diblock copolymer PVBCB-b-P4VP in $CHCl_3$. The line attributed to the RI detector signal.

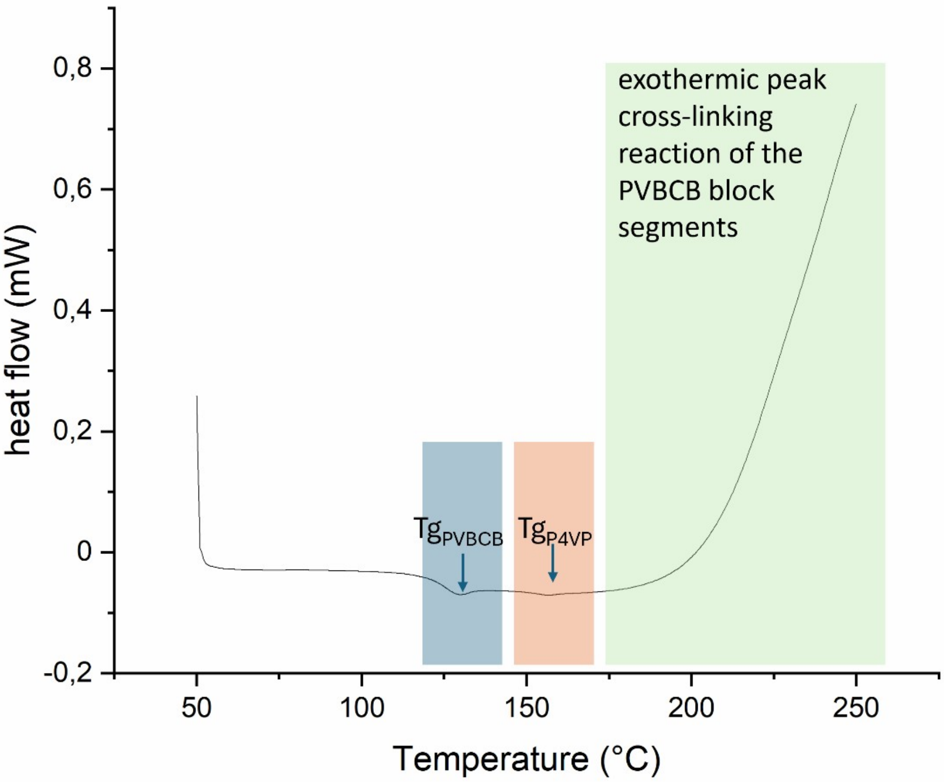

Figure S7: DSC measurements for block copolymer PVBCB$_{81}$-b-P4VPq$_{19}^{113k}$ used in this work revealed one visible glass transition temperature at 125 °C, which can be assigned to the PVBCB block segments (blue area). A second glass transition temperature is indicated at around 145 °C and can be assigned to the P4VP block segments (orange area). A strong exothermic peak starting at 180 °C and showing a maximum at 280 °C (green area). This strong exothermic peak can be assigned to the thermal cross-linking reaction of the PVBCB block segments. During the heating process, the benzocyclobutene moieties can transform into o-xylene units.

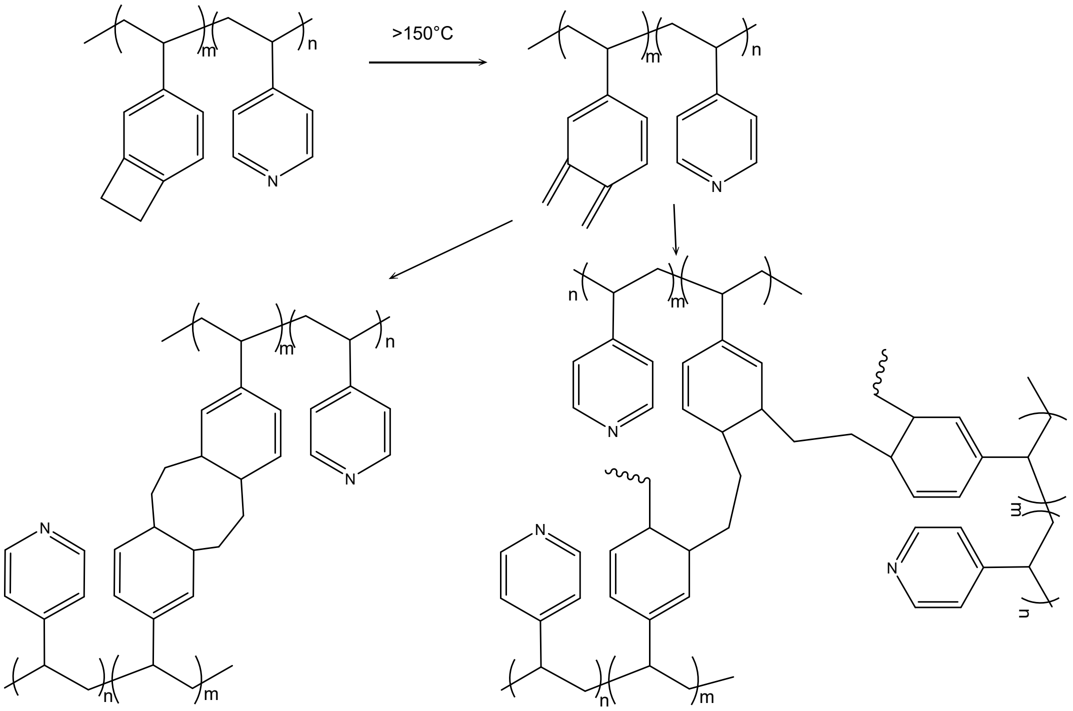

Figure S8: Thermal crosslinking procedure of PVBCB-b-P4VP diblock copolymers.

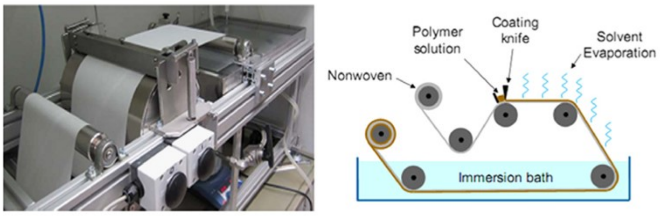

Figure S9. Photo of laboratory-size casting machine (left) and schematic presentation of the casting process (right) (Reprinted with permission from Ref.9)

Table S1. Molecular characteristics of the PVBCB-*b*-P4VP block copolymers, casting conditions for membrane formation by SNIPS process and average pore diameters shown in Figure 4.

	Polymer	Mn$^{a)}$ (kg mol^{-1})	Mn, P4VP$^{b)}$ (kg mol^{-1})	wt% P4VP	c$_{BCP}$ (wt%)	DMF/ THF/ DIOX	dpore (nm)
a	PVBCB$_{80}$-*b*-P4VP$_{20}$^{105k}	105	21	20	20	45/10/45	27
b	PVBCB$_{79}$-*b*-P4VP$_{21}$^{109k}	109	23	21	20	45/10/45	31
c	PVBCB$_{79}$-*b*-P4VP$_{21}$^{118k}	118	25	21	17	45/10/45	35
d	PVBCB$_{80}$-*b*-P4VP$_{20}$^{138k}	138	28	20	14	45/10/45	39

$^{a)}$ molecular weight determined by combination of SEC measurements and ^{1}H NMR spectroscopy, $^{b)}$ molecular weight determined by ^{1}H NMR spectroscopy.

In FigureS10 the pore diameters of the membranes are plotted against the molecular weight of the P4VP block segments of the corresponding block copolymers.

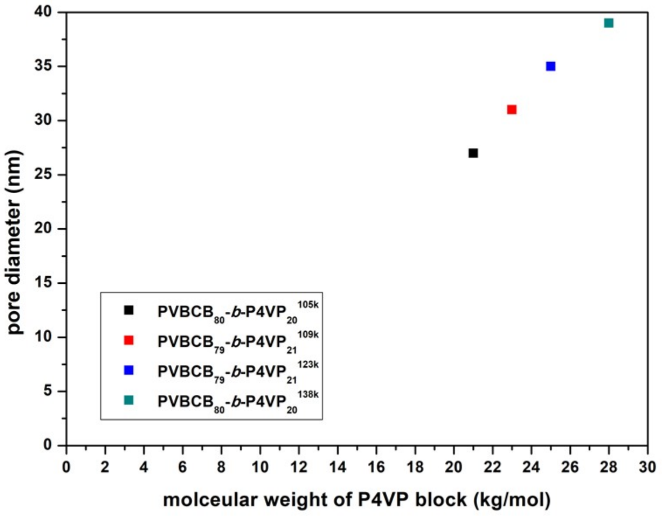

Figure S10. Plot of the average pore diameter versus the molecular weight of the P4VP block segments of the Corresponding block copolymers $PVBCB_{80}$-b-$P4VP_{20}^{105k}$ (black), $PVBCB_{80}$-b-$P4VP_{20}^{109k}$ (red), $PVBCB_{79}$-b-$P4VP_{21}^{118k}$ (blue) and $PVBCB_{80}$-b-$P4VP_{20}^{138k}$ (green).

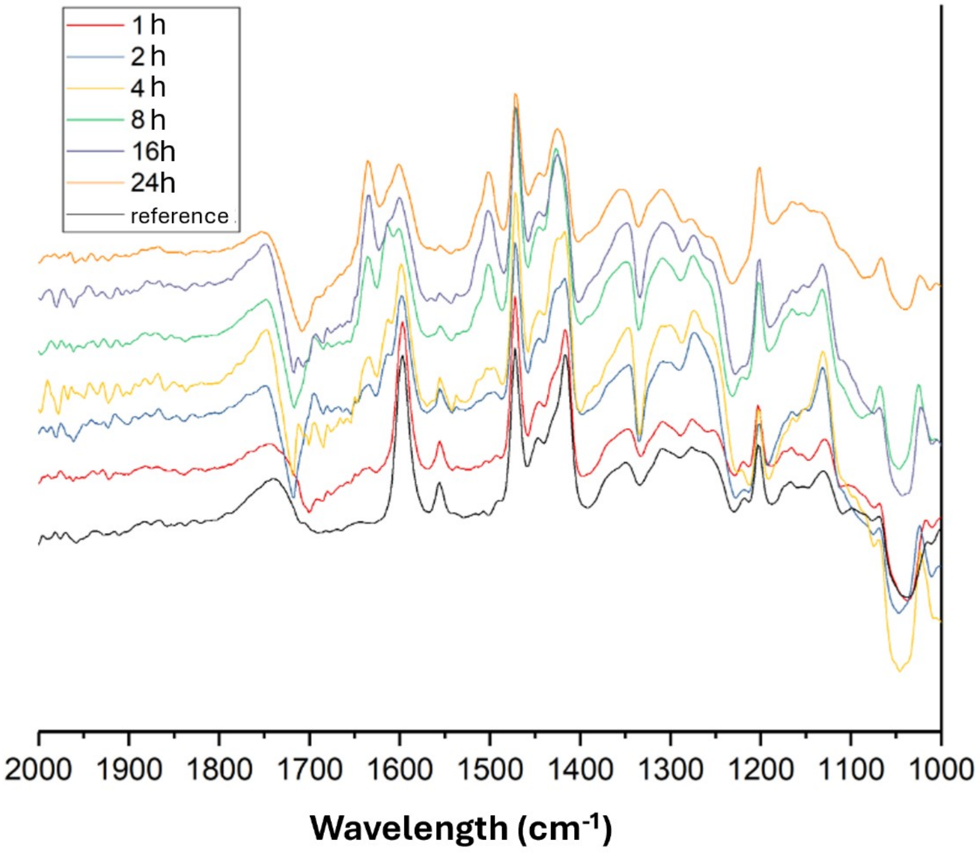

Figure S11: IR spectra from functionalized PVBCB81-b-P4VPq19113k membranes in the range of 1350-1700 cm^{-1}. $PVBCB_{81}$-b-$P4VPq_{19}^{113k}$ membranes after 1h (red line), 2h (red dotted line), 4h (grey line), 8h (grey dotted line), 16h (dark grey line) and 24h (dark grey dotted line) of functionalization with octylbromide as well as the pristine $PVBCB_{81}$-b-$P4VP_{19}^{113k}$ membrane (black) are shown