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Double Stimuli-Responsive Isoporous Membranes via Post-Modification of pH-Sensitive Self-Assembled Diblock Copolymer Membranes

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Double stimuli-responsive membranes are prepared by modification of pH-sensitive integral asymmetric polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer membranes with temperature-responsive poly(*N*-isopropylacrylamide) (pNIPAM) by a surface linking reaction. PS-*b*-P4VP membranes are first functionalized with a mild mussel-inspired polydopamine coating and then reacted via Michael addition with an amine-terminated pNIPAM-NH_2 under slightly basic conditions. The membranes are thoroughly characterized by nuclear magnetic resonance (^1H-NMR), Fourier transform infrared spectroscopy and X-ray-induced photoelectron spectroscopy. Additionally dynamic contact angle measurements are performed comparing the sinking rate of water droplets at different temperatures. The pH- and thermo-double sensitivities of the modified membranes are proven by determining the water flux under different temperature and pH conditions.

1. Introduction

Over the last decade amphiphilic membranes made by self-assembly from block copolymers have attracted great scientific interest. The formation of the porous structure of these membranes is based on the interplay between microphase separation of the block copolymer and the macrophase separation during solvent–non-solvent exchange induced by the phase-inversion process during membrane casting.[1]

In order to use these membranes for the filtration of aqueous solutions, additional functional groups inside the pores and on the surface of the membrane may give the opportunity for various applications. Functional molecules may be attached to corresponding functional sites of the block copolymer via supramolecular interactions or covalent bonds. Furthermore the block copolymer membrane can be coated by another thin polymer layer. Different approaches to achieve the surface modification of membranes are described in the literature.[2] These include the blending of polymers with defined functional groups,[3] composite materials,[4] chemical modification of the membrane[5] or the membrane polymer,[6] copolymerization[7] or grafting,[8] electron-beam based functionalization,[9] and coating.[10] In the last couple of years, polydopamine, a mussel-inspired mild polymer coating based on catecholic chemistry, has attracted a lot of interest in the field of modification by coating.[11] For the formation of the polydopamine layer, dopamine undergoes an oxidative polymerization in slightly basic solution (**Figure 1**a) and forms interactions with the surface of many different substrates.[11a,12] The mechanism of this reaction is still not completely understood. The interactions between the dopamine monomers were first postulated to be covalent aryl-aryl linkages (Figure 1a).[11a,13] Freeman et al. proposed that polydopamine is a supramolecular aggregate held together by hydrogen bonding, π-stacking, and charge transfer interactions (Figure 1b).[14] In a recent paper, the existence of trimers during the polydopamine preparation was proposed.[15]

However, the interactions in polydopamine aggregates are stable between pH 2–11 and in a large temperature range.[16] Membranes modified with polydopamine enhance the water flux due to the increased hydrophilicity caused by the hydroxyl-groups on their surfaces.[11e] Postmodifications of polydopamine surfaces are possible via Schiff base or Michael addition reaction which offers the opportunity to attach amine or thiol containing compounds.[11c]

We envisaged to use polydopamine as an interlayer for the functionalization of integral asymmetric polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer membranes with an amino terminated polymer poly(*N*-isopropylacrylamide) (pNIPAM-NH_2) which may undergo the above mentioned reaction. Poly(*N*-isopropylacrylamide) (pNIPAM) is a well-studied temperature-responsive polymer which undergoes a coil-globule transition around its lower critical solution temperature (LCST) at 32 °C.[17] In general membranes are modified with pNIPAM, for instance, by plasma induced grafting polymerization,[18]

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DOI: 10.1002/adfm.201202015

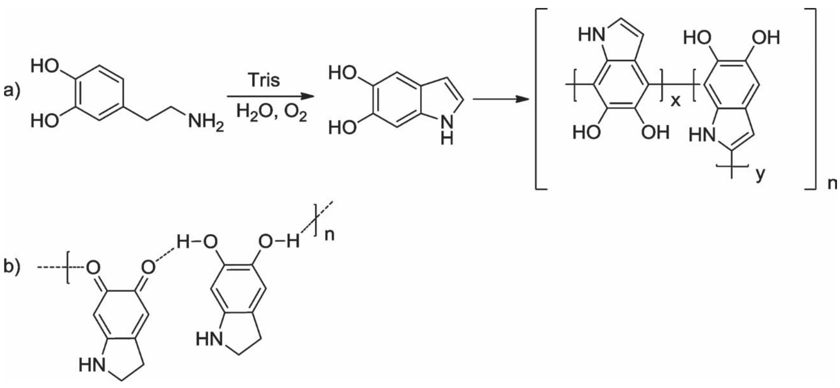

Figure 1. Polydopamine: a) synthesis and structure of polydopamine as proposed by Messersmith et al.;[13] b) new structural model of polydopamine as proposed by Freeman et al.[14]

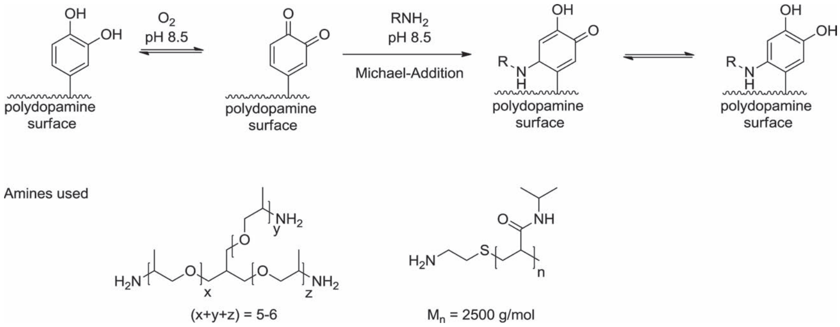

Figure 2. Michael-Addition on polydopamine coated membranes.

by ATRP,[19] by spin coating of pNIPAM containing triblocks on PAN membranes[20] and by blending.[21] To the best of our knowledge the use of pNIPAM-NH_2 to modify polydopamine coated membranes has not been reported yet. However, with respect to polydopamine, pNIPAM was polymerized on a polydopamine containing macroinitiator by ATRP.[22] In another paper, dopamine was functionalized with pNIPAM before the polymerization on nanodiamond particles.[23]

In this work, we prepared double stimuli-responsive membranes by modification of PS-*b*-P4VP diblock copolymer membranes. Therefore, the pH-sensitive PS-*b*-P4VP membranes were first coated with polydopamine as an interlayer. In order to determine whether a Michael addition on the polydopamine surface (**Figure 2**) is possible in our special case, Jeffamine T403 was reacted with the membrane under slightly basic conditions.

In a further experiment, the polydopamine coated membrane was reacted with pNIPAM-NH_2 to introduce the thermo-responsive unit. **Figure 3** demonstrates the concept to introduce the thermo-responsive polymer on our PS-*b*-P4VP membranes by the use of polydopamine as an interlayer. The modified membranes were characterized by ^{1}H-NMR, ATR-FTIR, and XPS. In case of the pNIPAM modified membrane dynamic contact angle and water flux measurements indicate the changes of the pore size at different temperatures.

The PS-*b*-P4VP membranes used in this work have an important property in water flux measurements: they are able to close their pores while lowering the pH value by swelling of the P4VP block, whereas an increase in pH leads to a reversible opening of the pores. In order to test if this property remains after the modification with polydopamine and pNIPAM-NH_2, pH-dependent water fluxes were measured at five different temperatures (25–45 °C) including the LCST of pNIPAM.

2. Results and Discussion

2.1. Deposition of Polydopamine

An indication of the polydopamine thickness on a substrate is given by the darkening color with growth time due to the strong broad band UV-visible absorption.[24] In order to analyze the uniform distribution of phenol groups, which are part of the polydopamine structure on the surface, the membranes were colored by iron(III) chloride, as shown in **Figure 4**.[25] We concluded a 60 min dopamine coating to be sufficient for our purpose since we were looking for the lowest as possible but still uniform polydopamine coating.

2.2. SEM of the Modified Membranes

Figure 5 depicts the SEM of the surface of the PS-*b*-P4VP membrane (Figure 5a) and the modified membrane with polydopamine and pNIPAM-NH_2 (Figure 5b). As expected, the pores are smaller in case of the modified membranes which may be noticed in the cross-section of the unmodified (Figure 5c) and the modified (Figure 5d) membranes as well.

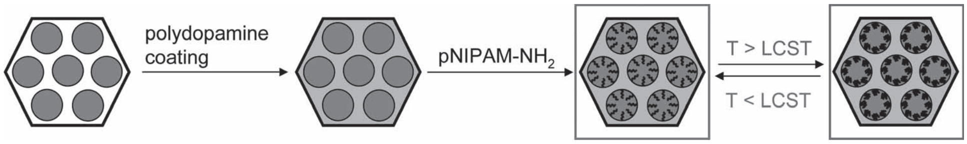

Figure 3. Schematic illustration of the modification of PS-*b*-P4VP membranes.

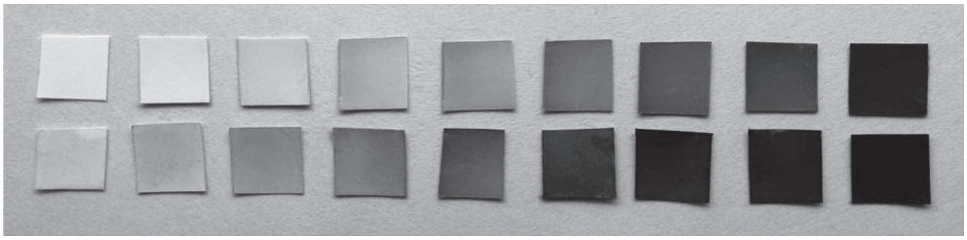

Figure 4. Time dependent polydopamine coating; left to right: pure membrane, 20, 40, 60, 80, 240, 360, and 480 min, and 26 h of coating; at the bottom: after treatment with $FeCl_3$ solution.

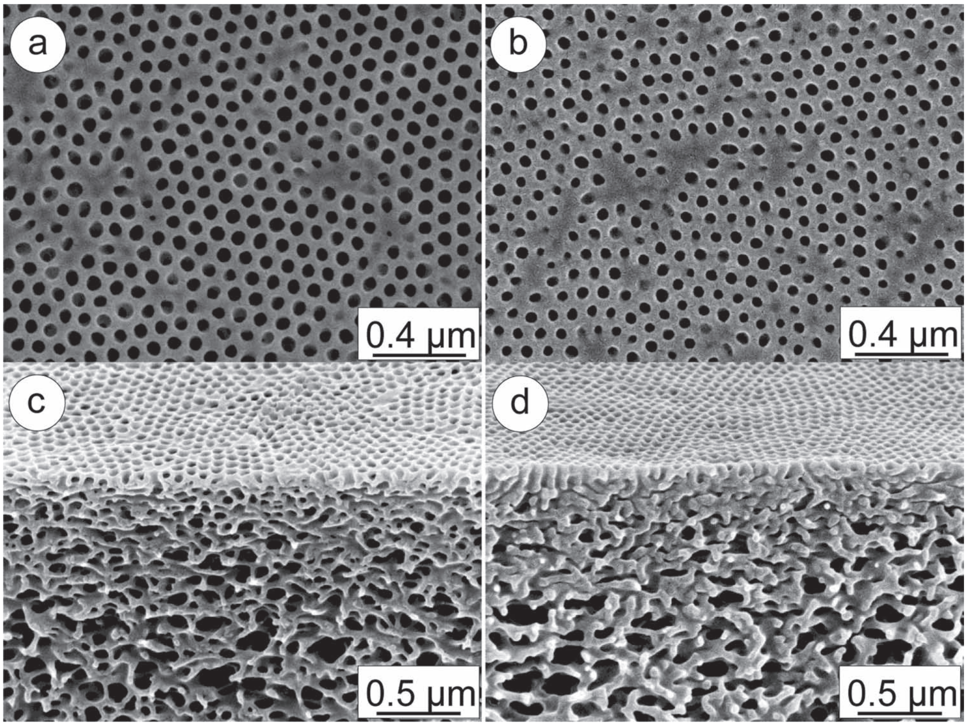

Figure 5. SEM images: surfaces of (a) the bare PS-*b*-P4VP membrane and (b) the PS-*b*-P4VP membrane modified with polydopamine and pNIPAM-NH_2, and cross-sections of (c) the bare PS-*b*-P4VP membrane and (d) the PS-*b*-P4VP membrane modified with polydopamine and pNIPAM-NH_2.

2.3. ATR-FTIR of Modified Membranes

The unmodified membrane, the membrane coated with polydopamine, and the membrane after further reactions with Jeffamine T403 and pNIPAM-NH_2 were analyzed by ATR-FTIR. The results are presented in **Figure 6**. No significant difference between the spectra of the raw membrane and the dopamine coated membrane was detected. The IR spectrum of the membrane modified with Jeffamine T403 (Figure 6, curve c) shows a small shoulder at 1110 cm^{-1} arising from C–O–C stretching vibration in polyethers.

In the IR spectra of the membrane modified with pNIPAM (Figure 6, curve d), we clearly observe characteristic peaks for secondary amide C=O stretching and the in plane N–H bending vibration (amide I and II) at 1650 and 1550 cm^{-1}, respectively. A broad signal from 3600–3200 cm^{-1} was found due to the N–H stretching vibration of the secondary amide group. The small peaks at 1369 and 1388 cm^{-1} are characteristic deformation vibration peaks of the C–H bond in isopropyl group of NIPAM.

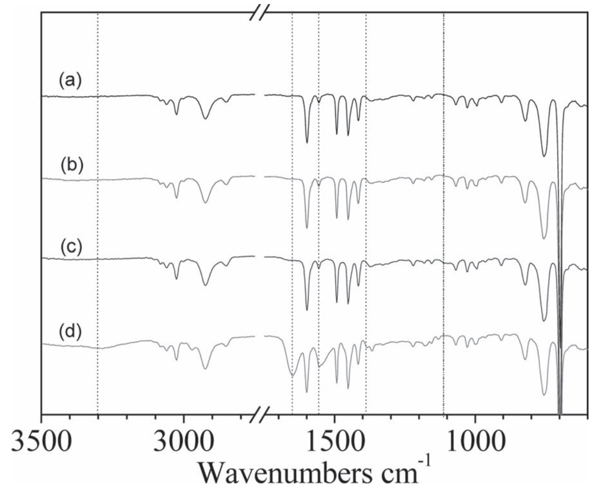

Figure 6. ATR-FTIR spectra: a) PS-*b*-P4VP membrane, b) membrane after 60 min of polydopamine coating, c) dopamine coated membrane after reaction with Jeffamnie T403, and d) dopamine coated membrane after reaction with pNIPAM-NH_2.

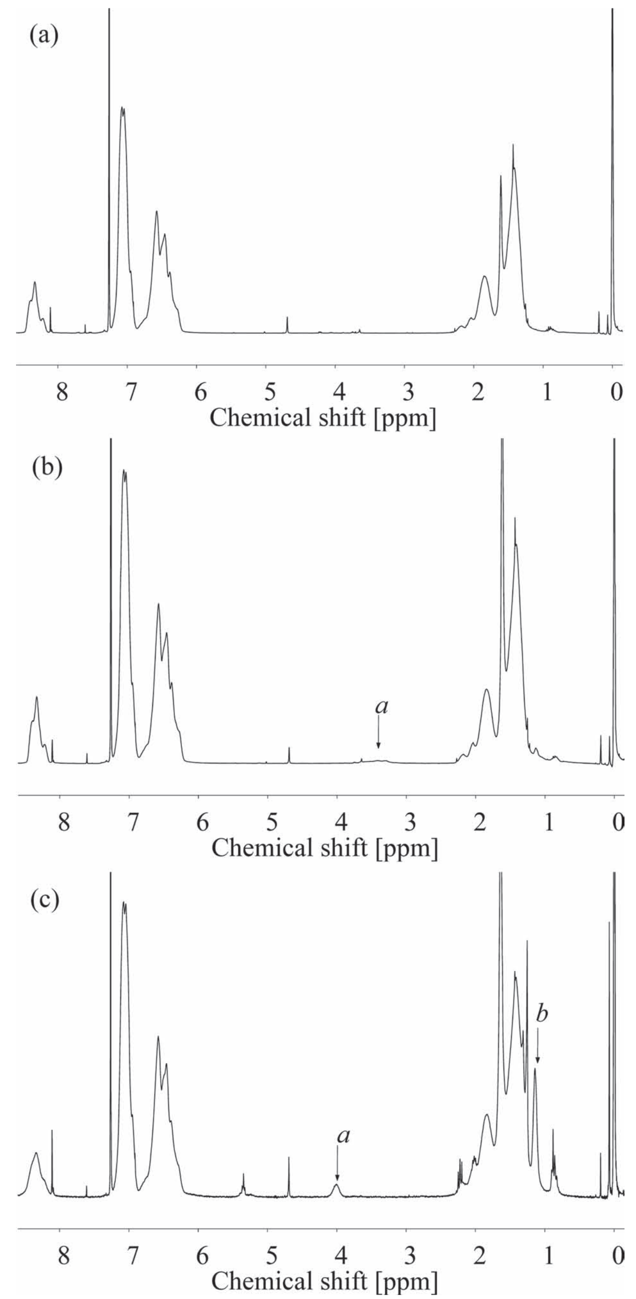

Figure 7. ^1H NMR spectra of: a) the PS-*b*-P4VP membrane after polydopamine coating, b) the PS-*b*-P4VP membrane modified with Jeffamine T403 after polydopamine coating, and c) the PS-*b*-P4VP modified with pNIPAM-NH_2 after polydopamine coating.

2.4. NMR of the Modified Membranes

The modified membranes were characterized by ^1H-NMR spectroscopy. In order to ensure that the modification with Jeffamine T403 and pNIPAM-NH_2 is covalently bonded to the polydopamine surface and not just attached via hydrogen bonding, the membranes were rinsed with 500 mL of water in a water flux measurement system. **Figure 7** shows the ^1H NMR in $CDCl_3$ of the polydopamine coated membrane (Figure 7a) after further modification with Jeffamine T403 (Figure 7b) and after further modification with pNIPAM-NH_2 (Figure 7c). The broad multiplet in the range of 3.2–3.7 ppm (*a* in Figure 7b) is attributable to the methylene protons of Jeffamine T403. In Figure 7c the chemical shift at 4.0 (*a* in Figure 7c) and 1.1 ppm (*b* in Figure 7c) are assigned to the isopropyl group of pNIPAM.

2.5. Dynamic Contact Angle Measurement

Figure 8 shows the snapshots of the dynamic contact angle measurement of 5 μL water droplets onto the surface of the PS-*b*-P4VP membrane at 22 °C (Figure 8a), the polydopamine coated PS-*b*-P4VP membrane at 22 °C (Figure 8b), and the polydopamine coated PS-*b*-P4VP membrane after further reaction with pNIPAM-NH2 at 22 °C and 40 °C (Figure 8c,d, respectively). The water contact angle of the raw membrane becomes zero after 30 s. In case of the slightly more hydrophilic polydopamine coated membrane the droplet is totally sunk into the membrane already after 23 s. The pNIPAM is swollen at ambient temperature which is below the LCST and reduces the pore size of the membrane. This behavior results in a much slower droplet sinking in case of the pNIPAM modified membrane at 22 °C (Figure 8c) after 70 s compared to Figure 8b. At 40 °C (above the LCST) the pNIPAM chains collapse resulting in an opening of the pores and a faster water subsidence after 50 s (Figure 8d).

2.6. XPS of the Modified Membranes

In order to provide information about the chemical compositions of the modified membranes they were analyzed by XPS. For the evaluation of the data Kratos sense factors and a Gauss Lorentz fit GL(30) algorithm with Shirley background was used. As expected, the ratio of nitrogen and oxygen increased after coating with polydopamine compared to the raw membrane. Further reactions with Jeffamine T403 and pNIPAM-NH_2 leads to a rise up of the nitrogen and oxygen contents as shown in more detail in **Table 1**. The N1s signal was evaluated with respect to chemical bonding shifts due to the film coating processes. **Figure 9** shows deconvoluted N1s excitations for various treatment steps. On top, the bare PS-*b*-P4VP membrane reveals the pyridine signal at 399.3 eV.[26] After deposition of PDA the pyrollic peak of polydopamine became visible at 399.7 eV,[27] in comparison to the spectrum in Figure 9b. Since the film thickness is very low (below ca. 3 nm) convolution of different polymer bonds takes place. Further reaction with pNIPAM-NH_2 showed the amide formation above 400 eV as shown in Figure 9c.[28] After the reaction with Jeffamine T403 a strong signal occurs at 399.2 eV assigned to the NH_2 bonds of Jeffamine.

The strongest signal C1s was not fully evaluated. Due to the high amount of complex carbon bonds and its signal convolution a physical correct evaluation is not possible. This becomes even more complicated by the CO_2 adsorption especially of amines.

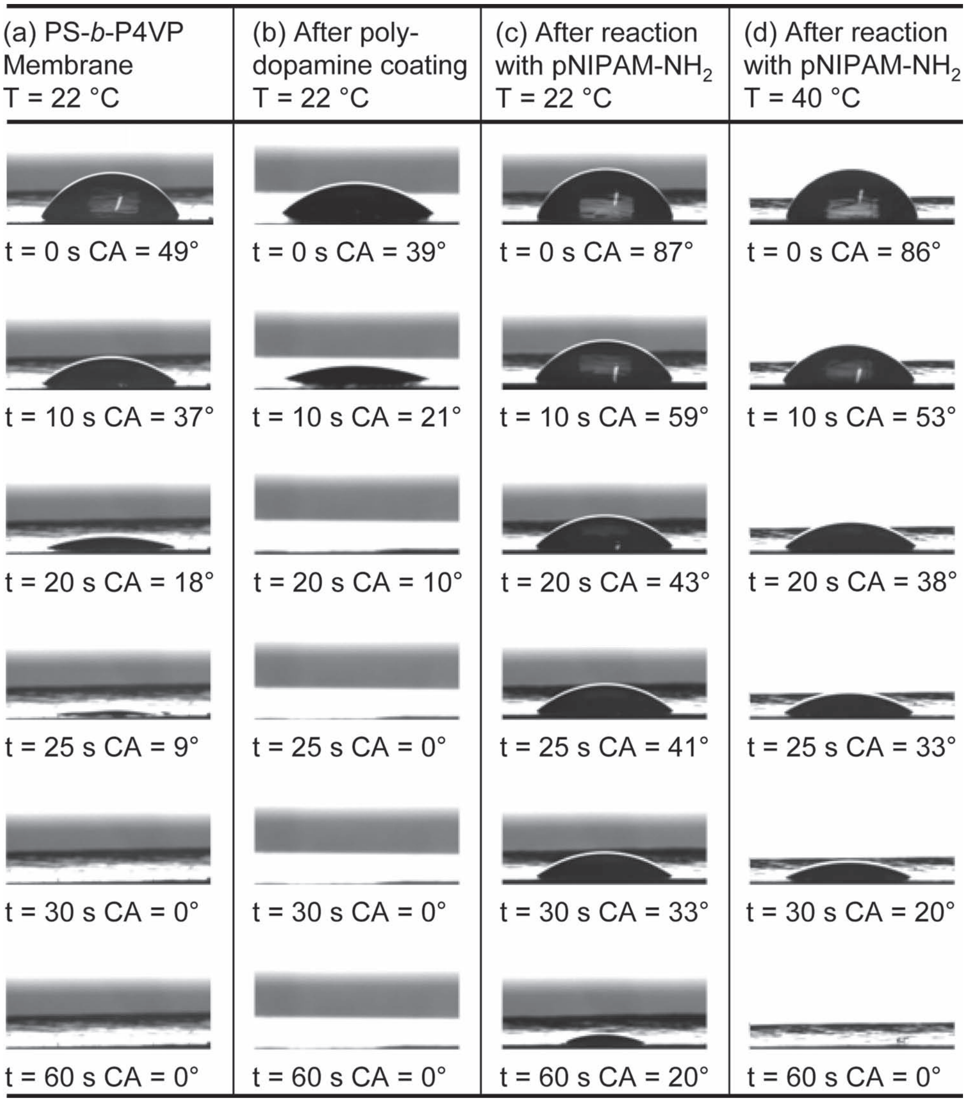

Figure 8. Snapshots of dynamic contact angle measurement of water droplets (5 µL) onto different membrane surfaces. a) PS-*b*-P4VP membrane, b) PS-*b*-P4VP membrane after polydopamine coating, c,d) PS-*b*-P4VP membrane after polydopamine coating and reaction with pNIPAM-NH_2 at 22 and 40 °C (CA = contact angle).

Table 1. Results from XPS - C1s, N1s and O1s peak evaluation of PS-*b*-P4VP membrane before and after modification.

	C [at%]	N [at%]	O [at%]
PS-*b*-P4VP membrane	91.5	6.1	2.4
PS-*b*-P4VP membrane after coating with polydopamine	90.0	5.6	4.4
PS-*b*-P4VP membrane after coating with polydopamine and further reaction with pNIPAM-NH_2	79.9	9.9	10.2
PS-*b*-P4VP membrane after coating with polydopamine and further reaction with Jeffamine T403	82.7	8.2	9.1

2.7. pH and Thermo Sensitivity

The water fluxes of the membranes were measured at different pH values and different temperatures. The water flux measurement from 3 to 45 °C are shown in **Figure 10**a,b for the PS-*b*-P4VP membrane (curve a), the polydopamine coated membrane (curve b) and the latter one after further reaction with pNIPAM (curve c), showing a steady increase of the water flux with temperature correlating to the regular increased permeability with the temperature. However, the water flux of the polydopamine coated membrane is slightly higher above 20 °C compared to the base membrane due to the increasing hydrophilicity. The effect of the pNIPAM is shown in (curve c) where the water flux strongly decreases below and increases

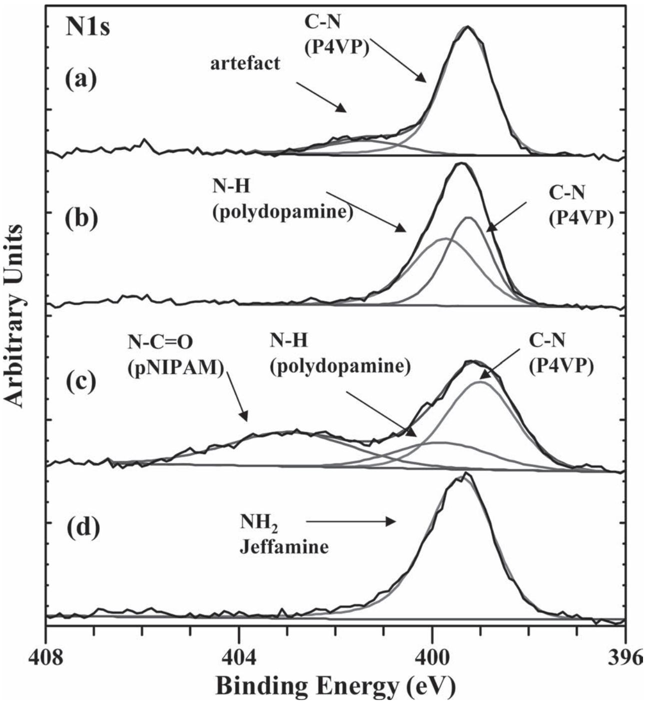

Figure 9. High resolution XPS spectra of N1s excitations: a) PS-*b*-P4VP membrane, b) PS-*b*-P4VP membrane after polydopamine coating, c) PS-*b*-P4VP membrane modified with pNIPAM-NH$_2$ after polydopamine coating, and d) PS-*b*-P4VP modified with Jeffamine T403 after polydopamine coating. The artifact is caused by impurities.

above the LCST (LCST of pNIPAM: 30–35 °C). Above 40 °C we observed again the regular increase of the water flux as for the membranes that are not functionalized with pNIPAM-NH$_2$, (curve a and curve b).

In order to determine whether the modified PS-*b*-P4VP membrane still remained sensitive to pH, pH dependent water fluxes were measured at five different temperatures (25–45 °C) and the results are depicted in **Figure 11**. At all temperatures there is a decrease of the water flux between pH 3.8–3.4. The lower the temperature the smaller is the change in the flux due to the swelling of the pNIPAM and decreasing of the pore size at low temperature.

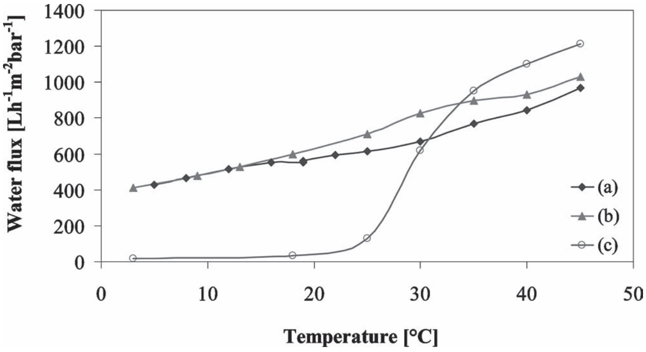

Figure 10. Temperature dependent water flux measurement: the PS-*b*-P4VP membrane (curve a), the PS-*b*-P4VP membrane after coating with polydopamine (curve b), and the PS-*b*-P4VP membrane after coating with polydopamine and further reaction with pNIPAM-NH$_2$ (curve c).

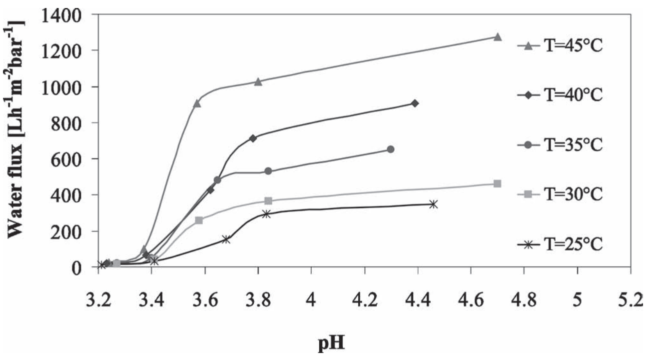

Figure 11. pH dependent water flux at different temperatures (25, 30, 35, 40, and 45 °C) for the PS-*b*-P4VP membrane after coating with polydopamine and further reaction with pNIPAM-NH$_2$.

3. Conclusion

This study proposed an approach to functionalize membranes under mild conditions with the temperature-responsive polymer, pNIPAM, leading to a double stimuli-responsive membrane. Therefore, a pH-sensitive PS-*b*-P4VP membrane was coated with polydopamine as an interlayer and further modified with pNIPAM-NH$_2$. The pH- and thermo-double sensitivities of the modified membranes were proved by determining the water flux under different temperature and pH conditions. In dynamic contact angle measurements the sinking rate of water droplets was investigated at different temperatures. For further investigation a variation of the polydopamine thickness before grafting with pNIPAM may change the permeability of the membranes. Therefore, the density of the pNIPAM chains will be estimated in the future. In order to stabilize the membrane against organic solvents it is envisaged to test cross-linking reactions by electron beam experiments. The double stimuli-responsive property of these membranes offer promising applications such as biomolecule separations that will be investigated in the future.

4. Experimental Section

Membranes: Membranes used in this work were prepared by the phase inversion process. Therefore PS-*b*-P4VP diblock copolymers synthesized by anionic living polymerization were dissolved in a solvent mixture of THF and DMF. The solutions were cast on a polyester nonwoven support using a casting machine. The membrane casting machine allows a continuously casting of the polymer solution onto a substrate, e.g., nonwoven, on rolls up to 30 cm width. The gap height of the doctor blade is variable for adjusting the casting thickness as well as the speed of the take-up reel in order to control the evaporation time before immersing into the non-solvent bath. The films were left for a certain time on air before immersing them in water. The membranes were dried at 60 °C under reduced pressure before using for further modification. The molecular characteristics of the polymers used for the membranes discussed in this work are summarized in **Table 2**.

Table 2. Composition of the polymers used for the membrane preparation.

	PS [wt%]	P4VP [wt%]	M_n [g/mol]
PS-*b*-P4VP membrane used for XPS, NMR, IR	74.8	25.2	300000
PS-*b*-P4VP membrane used for water flux, contact angle measurements and SEM	79.8	20.2	252000

Polydopamine Deposition: Block copolymer membranes (ca. 4 cm × 4 cm) were dipped into a solution of dopamine hydrochloride (2 mg/mL) dissolved in 15 mM Tris-buffer (pH 8.5–8.8, ultrapure water). The reaction vessel was placed on a shaker and the membranes were coated for 60 min. The membranes were rinsed three times with 50 mL of ultrapure water for 30 min and dried at 60 °C under reduced pressure before using for further reactions.

Conjugation of Amines to Polydopamine Grafted Membranes: Polydopamine coated membranes were dipped into a solution of the corresponding amine (0.3–0.5 mg/mL) dissolved in 15 mM Tris-buffer (pH = 8.5–8.8, ultrapure water). The reaction vessel was placed on a shaker and heated to 60 °C for 3 h. After cooling down to room temperature the membranes were shaken for additional 16 h, rinsed three times with 50 mL of ultrapure water for 30 min and dried at 60 °C before characterization. Poly(*N*-isopropylacrylamine), amine terminated (average M_n: 2500 g/mol, Sigma Aldrich) and Jeffamine T403 (average M_n: 440 g/mol, Huntsman Trading Corp.) were used without further purification.

Characterization: Scanning electron microscopy (SEM) was carried out on a LEO Gemini 1550 VP at a voltage of 3 kV. The samples were coated with 2.0 nm Pd. The cross-sections of the membrane were embedded in epoxy resin and thin sections (thickness 50–100 nm) were cut using a Leica ultramicrotome equipped with a diamond knife. All ^{1}H NMR measurements were performed on a Bruker Advance 300 NMR spectrometer at 300 MHz with internal standard [tetramethylsilane (TMS)] using chloroform ($CDCl_3$) as a solvent. Fourier transform infrared spectroscopy (FTIR) was conducted using a Bruker alpha-P, platinum ATR equipped with-diamond ATR (Bruker Corporation, Alexandria, New South Wales, Australia). Dynamic contact angles were measured on a KRUESS Drop Shape Analysis System DSA 100. In order to heat the membrane to 40 °C a heater was placed on this system and the temperature was measured briefly before the droplet was set on the membrane. Water flux experiments were performed using a dead end filtration setup at a transmembrane pressure up to 2.2 bar with the use of demineralized water with a electrical conductivity of ≈0.055 μS cm^{-1}. X-ray-induced photoelectron spectroscopy (XPS) experiments were carried out on a Kratos Axis Ultra DLD system attached with a 15 kV X-ray gun using monochromatic Al-K_α radiation. After outgasing the membranes were placed on a bar and positioned in the UHV chamber. The analyzed area size was 700 μm × 300 μm, and the pass energy was set to 160 eV for survey measurements. High resolution spectra were measured using 20 eV pass energy. In order to avoid charging effects a neutralizer (1.66 V) was applied. Due to physical limits, the information depth is limited to approximately 5–10 nm.

Acknowledgements

The authors thank Sabrina Bolmer and Anne Schroeder for their help in SEM investigations, Silvio Neumann and Mona Wambach for the NMR measurements, Brigitte Lademann for the synthesis of the polymers, Petra Merten for her help with the flux measurements and Sergey Shishatskiy for the photograph and Nico Scharnagl for his help with evaluation of the XPS data. This work is financially supported by FP7 EU-project SELFMEM under grant agreement NMP3-SL-2009-228652.

Received: July 18, 2012
Published online: September 18, 2012

[1] a) K. V. Peinemann, V. Abetz, P. F. Simon, *Nat. Mater.* **2007**, *6*, 992–996; b) S. P. Nunes, A. R. Behzad, B. Hooghan, R. Sougrat, M. Karunakaran, N. Pradeep, U. Vainio, K. V. Peinemann, *ACS Nano* **2011**, *5*, 3516–3522; c) A. Jung, S. Rangou, C. Abetz, V. Filiz, V. Abetz, *Macromol. Mater. Eng.* **2012**, *297*, 790–798 .

[2] N. Nady, M. C. R. Franssen, H. Zuilhof, M. S. M. Eldin, R. Boom, K. Schroën, *Desalination* **2011**, *275*, 1–9.

[3] a) A.-S. Jönsson, B. Jönsson, *J. Membr. Sci.* **1991**, *56*, 49–76; b) Y.-q. Wang, T. Wang, Y.-l. Su, F.-b. Peng, H. Wu, Z.-y. Jiang, *J. Membr. Sci.* **2006**, *270*, 108–114; c) Y. Su, C. Li, W. Zhao, Q. Shi, H. Wang, Z. Jiang, S. Zhu, *J. Membr. Sci.* **2008**, *322*, 171–177.

[4] a) Z.-P. Zhao, Z. Wang, S.-C. Wang, *J. Membr. Sci.* **2003**, *217*, 151–158; b) G. S. Gohil, R. K. Nagarale, V. V. Binsu, V. K. Shahi, *J. Colloid Interface Sci.* **2006**, *298*, 845–853; c) Z. Zhao, Z. Wang, N. Ye, S. Wang, *Desalination* **2002**, *144*, 35–39.

[5] B. Van der Bruggen, *J. Appl. Polym. Sci.* **2009**, *114*, 630–642.

[6] L. Breitbach, E. Hinke, E. Staude, *Angew. Makromol. Chem.* **1991**, *184*, 183–196.

[7] Y. Tsujii, K. Ohno, S. Yamamoto, A. Goto, T. Fukuda, *Adv. Polym. Sci* **2006**, *197*, 1–45.

[8] a) M. Ulbricht, G. Belfort, *J. Appl. Polym. Sci.* **1995**, *56*, 325–343; b) M. Ulbricht, M. Riedel, U. Marx, *J. Membr. Sci.* **1996**, *120*, 239–259.

[9] a) A. Schulze, B. Marquardt, S. Kaczmarek, R. Schubert, A. Prager, M. R. Buchmeiser, *Macromol. Rapid Commun.* **2010**, *31*, 467–472; b) A. Schulze, B. Marquardt, M. Went, A. Prager, M. R. Buchmeiser, *Water Sci. Technol.* **2012**, *65*, 574–580.

[10] a) M. Nyström, *J. Membr. Sci.* **1989**, *44*, 183–196; b) F. F. Stengaard, *Desalination* **1988**, *70*, 207–224.

[11] a) H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007**, *318*, 426–430; b) M. E. Lynge, R. van der Westen, A. Postma, B. Stadler, *Nanoscale* **2011**, *3*, 4916–4928; c) J. H. Waite, *Nat. Mater.* **2008**, *7*, 8–9; d) B. D. McCloskey, H. B. Park, H. Ju, B. W. Rowe, D. J. Miller, B. J. Chun, K. Kin, B. D. Freeman, *Polymer* **2010**, *51*, 3472–3485; e) J. T. Arena, B. McCloskey, B. D. Freeman, J. R. McCutcheon, *J. Membr. Sci.* **2011**, *375*, 55–62; f) Q. Ye, F. Zhou, W. Liu, *Chem. Soc. Rev.* **2011**, *40*, 4244–4258; g) B. Li, W. Liu, Z. Jiang, X. Dong, B. Wang, Y. Zhong, *Langmuir* **2009**, *25*, 7368–7374.

[12] a) M. G. Peter, *Angew. Chem.* **1989**, *101*, 572–587; b) L.-P. Z. Jin-Hong Jiang, Li-Jing Zhu, Bao-Ku Zhu, You-Yi Xu, *Langmuir* **2011**, *27*, 14180–14187.

[13] H. Lee, J. Rho, P. B. Messersmith, *Adv. Mater.* **2009**, *21*, 431–434.

[14] D. R. Dreyer, D. J. Miller, B. D. Freeman, D. R. Paul, C. W. Bielawski, *Langmuir* **2012**, *28*, 6428–6435.

[15] S. Hong, Y. S. Na, S. Choi, I. T. Song, W. Y. Kim, H. Lee, *Adv. Funct. Mater.* **2012**, DOI: 10.1002/adfm.201201156.

[16] B. Yu, D. A. Wang, Q. Ye, F. Zhou, W. Liu, *Chem. Commun.* **2009**, *44*, 6789–6791.

[17] X. Yin, A. S. Hoffman, P. S. Stayton, *Biomacromolecules* **2006**, *7*, 1381–1385.

[18] a) M. Yang, R. Xie, J.-Y. Wang, X.-J. Ju, L. Yang, L.-Y. Chu, *J. Membr. Sci.* **2010**, *355*, 142–150; b) T. Meng, R. Xie, Y.-C. Chen, C.-J. Cheng, P.-F. Li, X.-J. Ju, L.-Y. Chu, *J. Membr. Sci.* **2010**, *349*, 258–267.

[19] P.-F. Li, R. Xie, J.-C. Jiang, T. Meng, M. Yang, X.-J. Ju, L. Yang, L.-Y. Chu, *J. Membr. Sci.* **2009**, *337*, 310–317.

[20] A. Nykänen, M. Nuopponen, A. Laukkanen, S.-P. Hirvonen, M. Rytelä, O. Turunen, H. Tenhu, R. Mezzenga, O. Ikkala, J. Ruokolainen, *Macromolecules* **2007**, *40*, 5827–5834.
[21] G.-Q. Zhai, L. Ying, E. T. Kang, K. G. Neoh, *Surf. Interface Anal.* **2004**, *36*, 1048–1051.
[22] X. Wang, Q. Ye, T. Gao, J. Liu, F. Zhou, *Langmuir* **2012**, *28*, 2574–2581.
[23] A. Barras, J. Lyskawa, S. Szunerits, P. Woisel, R. Boukherroub, *Langmuir* **2011**, *27*, 12451–12457.
[24] F. Bernsmann, A. Ponche, C. Ringwald, J. Hemmerlé, J. Raya, B. Bechinger, J.-C. Voegel, P. Schaaf, V. Ball, *J. Phys. Chem. C* **2009**, *113*, 8234–8242.
[25] G. Ackermann, D. Hesse, *Z. Anorg. Allg. Chem.* **1970**, *375*, 77–86.
[26] X. Li, S. H. Goh, Y. H. Lai, A. T. S. Wee, *Polymer* **2000**, *41*, 6563–6571.
[27] X. Chen, L. Hong, X. Chen, W. H. A. Yeong, W. K. I. Chan, *J. Membr. Sci.* **2011**, *379*, 353–360.
[28] D. Cimen, T. Caykara, *J. Mater. Chem.* **2012**, *22*, 13231.