

pH-Responsive Aminomethyl functionalized Poly(*p*-xylylene) Coatings by Chemical Vapor Deposition Polymerization

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Abstract

The preparation of stimuli-responsive aminomethyl functionalized poly(*p*-xylylene) coatings by chemical vapor deposition polymerization is reported. Modification of the paracyclophane-precursor with ionizable aminomethyl-groups leads to polymer coatings with pH-responsive swelling properties. The swelling behavior is monitored in situ using spectroscopic ellipsometry and additional streaming potential measurements are performed. With decreasing pH-value, the coating becomes increasingly charged and reversibly swells to several times its dry thickness. The swelling ratio is sensitive to the ionic strength of the solution. By using a mixture of unfunctionalized and functionalized precursors in the chemical vapor deposition process, the number of charges in the polymer layer can be tuned and with it the swelling ratio of the coating. As a proof-of-concept for possible applications, a commercial paper filter is coated. This results in a pH-dependent wetting behavior and pH-dependent transport through the capillaries of the paper.

Keywords: responsive coatings, chemical vapor deposition polymerization, hydrogel coatings, poly(*p*-xylylene)

1 Introduction

For many years, coatings from unsubstituted as well as mono- and dichlorated poly(*p*-xylylene) (PPX) prepared via Chemical Vapor Deposition (CVD) polymerization have been widely used, for instance in the semiconductor industry or in biomedical applications.^{1,2} The main advantages of the CVD coating technique are that the polymer film is deposited from the gas phase without the use of any solvent, catalyst or liquid phase leading to defect-free coatings with low propensity for impurities. Since the polymerization can be directed towards a cooled surface, PPX can be coated uniformly and conformally on structured substrates.^{3,4} Using a great variety of functionalized [2.2]paracyclophane derivatives (PCP) as a precursor material, diverse homopolymer, copolymer or copolymer gradient coatings for the subsequent immobilization of active moieties, such as proteins or signalling molecules, can be produced.⁵⁻⁷ The incorporation of aminomethyl groups into the precursor molecules has been shown to lead to coatings with functional groups reactive to carboxy- or aldehyde-functionalized molecules in post-modification processes.^{8,9}

In 1991, Sochilin et al. reported free-standing sulfated PPX films that exhibit swelling characteristics in aqueous solutions due to the incorporation of sulfo groups.¹⁰ Unfortunately, this behavior was not investigated in detail, although it has to be assumed that the swelling of this kind of coatings is sensitive to the ionic strength of the surrounding solution.

The usage of the CVD of PPX to create stimuli-responsive coatings would offer a versatile way to coat complex substrate geometries, e.g. membranes or microchips, conformally and defect-free in an industrially scalable process for microfluidic lab-on-a-chip systems or sensor applications.¹¹⁻¹³ The swelling behavior of stimuli-sensitive hydrogel coatings, indicating a coating that can swell but not dissolve in water, can be used to control diffusion behavior of molecules through or above the layer, serving as a pump, valve or mixing element, or the swelling can be translated to a measurable macroscopic effect in sensoric devices. For instance, pH-responsive hydrogels demonstrated extraordinary sensitivity as sensing elements, where the swelling was converted to an optical, oscillating or conductimetric signal.¹⁴

In this article, we report the pH-responsive swelling properties of PPX coatings functionalized with amine groups. The swelling was investigated *in situ* using spectroscopic ellipsometry. Additionally, streaming potential measurements were performed. The potential capacity of this modification, e.g. for application in microfluidic devices, was tested in a proof-of-concept experiment: a commercial paper filter was coated with functionalized PPX and the pH-dependent wetting behavior and transport properties through the capillaries were investigated.

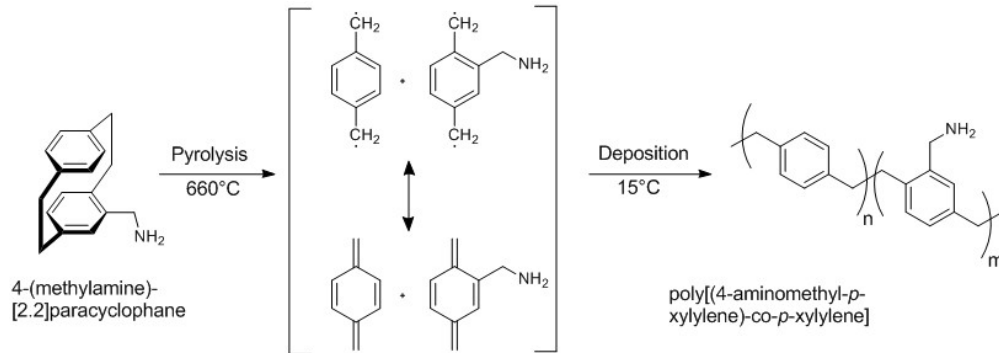


Figure 1: Scheme of the CVD polymerization process of 4-(methylamine)[2.2]paracyclophane.

2 Results

Aminomethyl-functionalized poly(*p*-xylylene) films (PPX-AM) were prepared by CVD polymerization of 4-(methylamine)[2.2]paracyclophane (PCP-AM), as depicted in Figure 1. In this process, the functional precursor sublimates under reduced pressure of 0.12 mbar, and is then cleaved at 660 °C into the corresponding quinodimethanes. These quinodimethanes are transported to a substrate, typically silicon wafers, cooled to 15 °C, where they condense on the surface and polymerize spontaneously. By using a defined precursor amount, the thickness d of the coating can be controlled. The thickness of the resulting polymer coating is determined using spectroscopic ellipsometry in dry state. The obtained ellipsometric angles, $\Delta(\lambda)$ and $\Psi(\lambda)$, were evaluated using an optical box model taking into account the silicon substrate with a native oxide layer and an uniaxial Cauchy-layer for the polymer layer.¹⁵

To monitor the pH-dependent swelling in different buffer solutions, spectroscopic ellipsometry was performed with the use of a batch cell. Figure 2 a) displays the thickness and refractive index of the PPX-AM coating compared to PPX-n between pH 4 and pH 8. For PPX-n coatings, no swelling is observed at pH 8 or pH 4. At pH 8, the PPX-AM coating does not swell, as well, the thickness is comparable to the dry state in air (25 nm). With decreasing pH the thickness of the coating increases linearly. Due to incorporation of water molecules in the polymer layer the refractive index (n) simultaneously decreases. This behavior is similar to hydrogel films fabricated from weak polyelectrolytes: below the pK_a value, an increasing amount of the aminomethyl groups on the polymer is protonated with decreasing pH values and thus positively charged.¹⁶ The like-charged groups repel each other causing the polymer film to swell. For PPX-n coatings, on the other hand, no swelling is observed even at pH 4, as it is expected due to the absence of ionizable groups.

Streaming potential measurements were performed to compare the ζ -potential of PPX-AM coatings to

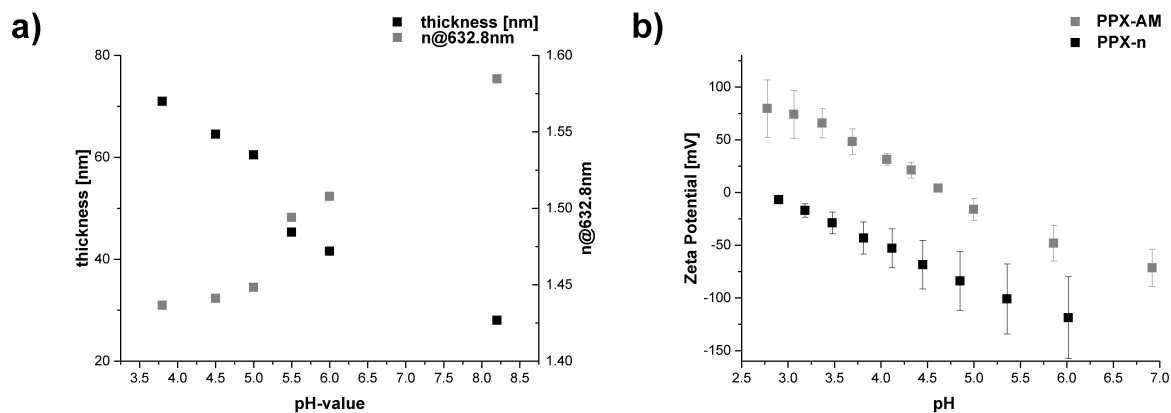


Figure 2: a) pH-dependent thickness and refractive index of a PPX-AM film (dry thickness 25 nm) in 0.1 M sodium acetate buffer as determined by spectroscopic ellipsometry (error bars representing the 90%-confidence values appear smaller than the symbols) and b) streaming potential measurements of a similar PPX-AM film in solutions of varying pH compared to a PPX-n film.

that of unfunctionalized PPX-n coatings. Unlike PPX-AM, PPX-n does not contain any ionizable functional groups on the surface. However, for both sets of coatings, an increasing ζ -potential with decreasing pH due to the preferential adsorption of hydroxyl ions (HO^-) at basic pH and hydronium ions (H_3O^+) at acidic pH was observed (Figure 2b)). The preferential adsorption of these ions and resultant displacement of water molecules from a hydrophobic surface can give rise to a pH-dependent zeta potential behavior even if the surface lacks basic or acidic functional groups on the surface. The isoelectric point (IEP) is the pH at which the ζ -potential value reaches zero and subsequently reverses its sign. Since the measurement was done in the asymmetric mode against a polypropylene sample, we solely focus on the comparison of the basic or acidic character of the surfaces relative to each other. Employing the IEP as a measure of acidity or basicity of a surface (analogous to pK_a), it can be seen that PPX-AM (IEP=4.7) has a higher IEP than PPX-n (IEP=2.7), indicating higher basicity. Thus, the modification of the PPX backbone with aminomethyl groups renders the surface more positively charged. These ζ -potential results confirm the assumption that increased charging causes the pH-dependent swelling of PPX-AM below its IEP as measured by spectroscopic ellipsometry.

Besides the pH, the counter ion concentration also determines the charging of the polyelectrolyte surface. Swelling measurements were performed with additional sodium chloride in the acetate buffer solution (Figure 3). With increasing concentration of sodium chloride, the swelling ratio ($d(\text{pH } 4)/d(\text{dry})$) is gradually reduced. This can be explained by an increased shielding of the charges on the polymer chains in the presence of additional counter ions, which results in deswelling of the polymer layer.

To test the reversibility of the swelling effect, the coating was alternately treated with solutions of pH 4

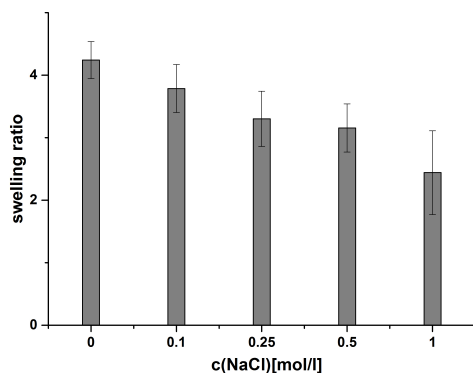


Figure 3: Swelling ratio ($d(\text{pH } 4)/d(\text{dry})$) of a PPX-AM film in 0.1M sodium acetate buffer with additional sodium chloride as determined by spectroscopic ellipsometry. Values are given as the average of three different samples, where the error bars represent the standard deviation.

and pH 8 (Figure 4). Probably due to buffer ions remaining in the polymer layer after the first treatment with pH 4, the polymer layer does not deswell to its initial dry thickness upon treatment with pH 8, even after washing with MilliQ water. However, the polymer layer can be switched repeatedly between a swollen and deswollen state.

After the in situ measurements, the samples were measured again in dry state. No change in thickness compared to the original state was observed, indicating that the polymer layer swells, but does not dissolve. Corley et al.¹⁷ took similar observations as an indication that the PPX film does not solely consist of linear chains but contains some crosslinking points, probably due to chain transfer processes occurring in the growing polymer film.

Replacing the aminomethyl groups with amine groups results in a different swelling behavior. Figure 5 displays the swelling of poly[(4-amino-*p*-xylylene)-*co*-(*p*-xylylene)] (PPX-NH₂) in comparison to PPX-AM and PPX-n. Almost no swelling of PPX-NH₂ could be measured at pH 4 by spectroscopic ellipsometry. In addition, PPX-NH₂ expresses a lower zeta potential than PPX-AM for each pH value. However, the IEP of PPX-NH₂, while higher than that of PPX-n, still falls below the IEP of PPX-AM. In PPX-NH₂, the basicity of the amine groups is considerably reduced due to the greater proximity to the aromatic ring and its electron-withdrawing effects. Thus the protonation of PPX-NH₂, and with it, the onset of swelling are both shifted out of the pH range monitored by spectroscopic ellipsometry.

The swelling of the PPX-AM coatings can be tuned by adjusting the number of functional groups in the film. To this end, the PCP-AM precursor was mixed with unmodified [2.2]paracyclophane (PCP-n)

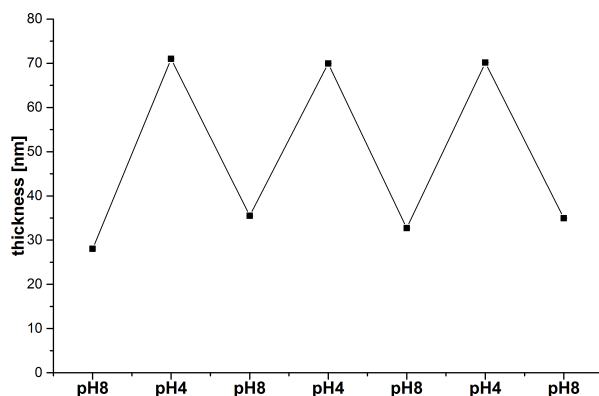


Figure 4: Reversible swelling in pH8 and pH4 of a PPX-AM film in 0.1M sodium acetate buffer as determined by spectroscopic ellipsometry (error bars representing the 90%-confidence values appear smaller than the symbols).

in different ratios. X-ray Photoelectron spectroscopy (XPS) measurements were performed to measure the resulting nitrogen content on the surface (Figure 6a). The N 1s peak can be deconvoluted into two components: a main peak at 399.6 eV is observed and attributed to the amine groups.¹⁸ An additional peak of weak intensity at 401.5 eV is detected due to the presence of protonated amine. Comparing the experimental with the theoretical values, the nitrogen content is higher than expected. This could be explained by the lower sticking coefficient of the unfunctionalized quinodimethane moiety. Figure 6 displays the swelling ratio of PPX-AM coatings with varying number of aminomethyl-groups, as measured by XPS. With decreasing number of protonable groups, the swelling ratio decreases.

Since the coating of PPX is an industrially established process, the findings presented in this report show promise for the usage of PPX-AM as active layers on rough and structured samples. For instance such a layer can act as responsive barrier in microfluidic systems or membranes, which opens at low and closes at neutral or higher pH-values (Figure 7a)). To show this potential application, commercial paper filters were coated with a thin layer of PPX-AM. Due to the intrinsic properties of the process, CVD is well suited for the coating of paper, for instance in order to protect documents or for the fabrication of paper-based microfluidic devices.¹⁹⁻²²

Due to the high roughness and low reflectivity of the paper, the thickness of the coating cannot be measured directly using spectroscopic ellipsometry. On a silicon wafer coated together with the paper in the same run, the thickness of the PPX-AM film was 15 nm. The morphology of the samples was investigated by Scanning Electron Microscopy (see Supporting Information). No change in morphology could be observed

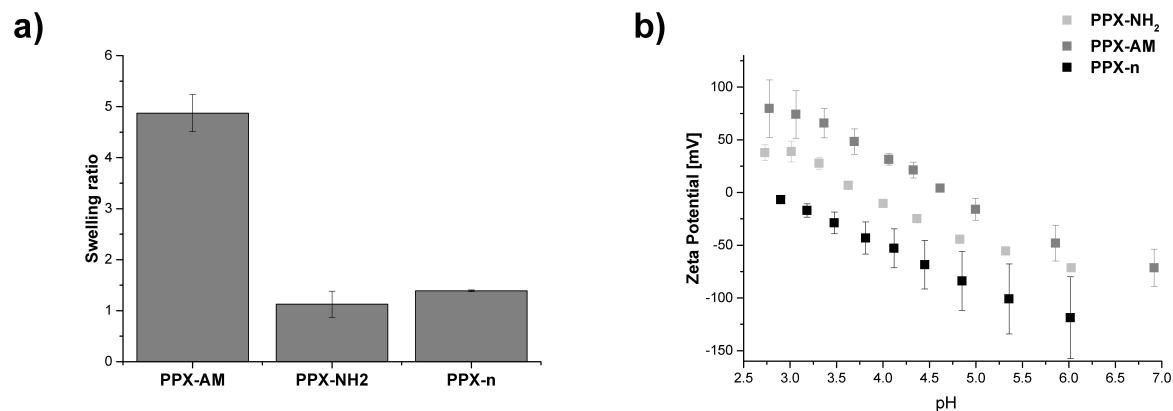


Figure 5: Comparison between the swelling of PPX-AM, PPX-NH₂ and PPX-n films: (a) Swelling ratio measured by spectroscopic ellipsometry (The error bars represent the 90%-confidence values), (b) streaming potential measurements.

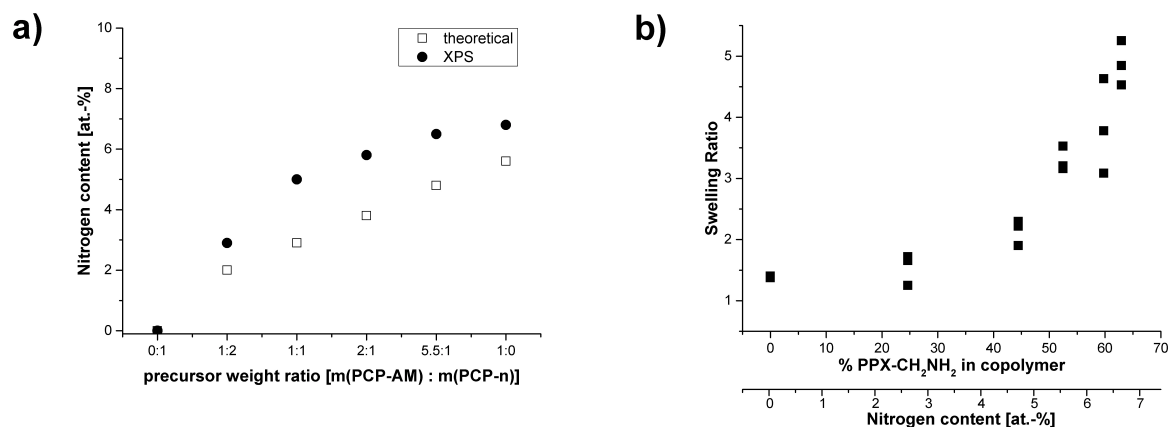


Figure 6: a) Nitrogen-content in PPX-AM films with varying density of functional groups, and b) Effect of percentage of aminomethyl functionalization on the swelling ratio ($d(\text{pH } 4)/d(\text{dry})$) of PPX-AM.

upon coating. However, the wetting behavior was found to become dependent on the pH value (Figure 7b)). A constant contact angle of about 110° was found for pH 7.2 phosphate buffer, while a fast drop in contact angle was observed for pH 4 acetate buffer, reaching complete wetting after two to three minutes. Without PPX-AM immediate wetting was observed (see Supporting Information).

To further visualize the influence of the PPX-AM coating on the transport properties through the paper filter, a strip of the sample was marked with a felt-tip pen and placed with one end in a beaker of buffer solution. On uncoated samples, the solution wets the fibres of the paper independent of pH and transports the dye upwards via capillary forces. Upon coating with PPX-AM, no transport of the dye can be observed after placement into a phosphate buffer solution at pH 7.2, since the coating forms a hydrophobic barrier on

the fibres. Exchange of the solution to acetate buffer at pH 4, results in swelling of the PPX-AM coating, thus opening the way for the transport of water and dye through the capillaries of the paper (Figure 7c). Opening and closing of the barrier coating could be demonstrated upon cycling between solutions of different pH (see video in supporting information).

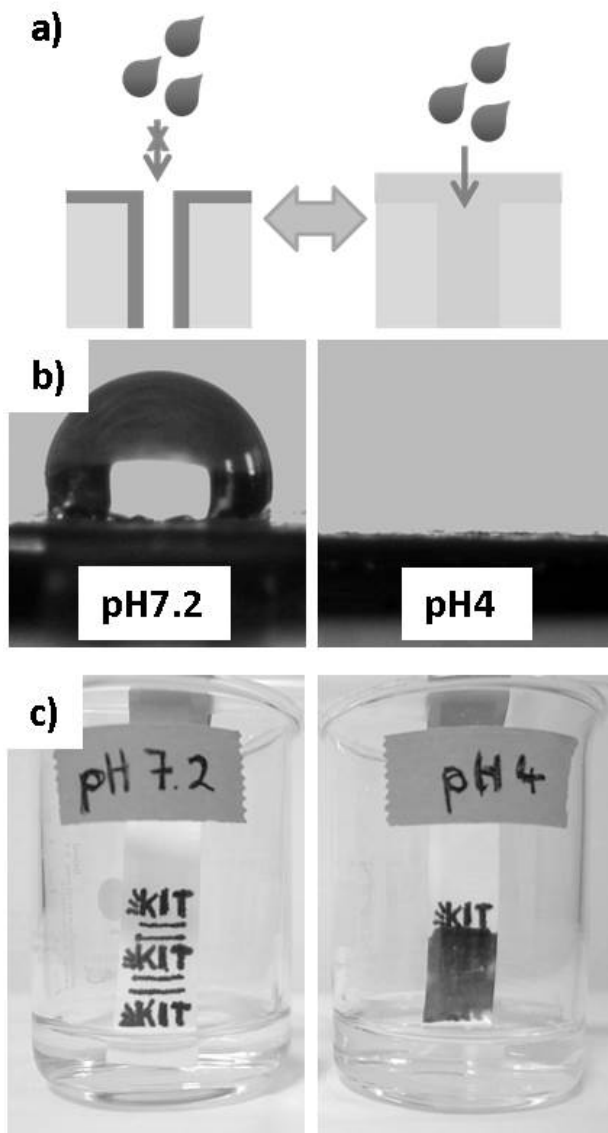


Figure 7: a) Scheme of PPX-AM acting as active barrier layer, b) wetting behavior of filter paper coated with PPX-AM (image was taken 3 min after placement of droplet) and c) transport properties through paper capillaries after 20 min in pH 7.2 phosphate buffer and after 6 min in pH 4 acetate buffer.

3 Conclusions

In summary, we herein present the feasibility to impart PPX with stimuli-responsive properties by the incorporation of functional groups. The modification of the paracyclophane-precursor with aminomethyl-groups results in PPX coatings with pH-responsive properties. Due to charging of the functional groups at acidic pH-values, the polymer coating swells reversibly to several times its dry thickness, as measured by spectroscopic ellipsometry. The swelling increases with decreasing pH. Streaming potential measurements confirmed the charging of the polymer chains. Additionally, the swelling ratio was shown to be sensitive to the ionic strength of the ambient solution and the density of the functional groups. The latter can be tuned by mixing of functionalized and unfunctionalized precursor in the CVD process. As a proof-of-concept, PPX-AM was coated on filter paper. pH-dependent transport properties through the fibres of the paper could be shown. This demonstrates the applicability of this type of coating as active barriers in responsive devices.

4 Experimental Section

Chemical Vapor Deposition Polymerization The precursor 4-methylamine-[2.2]paracyclophane (PCP-AM) was synthesized from [2.2]paracyclophane (Curtiss Wright Surface Technologies, Galway, Ireland) in a three-step synthesis. The starting material, 4-(hydroxymethyl)[2.2]paracyclophane, for the last step was synthesized using a previously reported synthetic route.²³ For the synthesis of PCP-AM a Gabriel-synthesis was performed. First, the functional hydroxyl-group was transferred into a bromide. Under an argon atmosphere, 4-(hydroxymethyl)[2.2]paracyclophane (3.00 g, 12.60 mmol, 1.00 eq.) was dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C. Then PBr_3 (1.50 mL, 15.75 mmol, 1.25 eq.) was added dropwise and the mixture was stirred for 3 h. The reaction was hydrolyzed by the addition of water (50 mL) and the phases were separated. The organic layer was washed with aqueous HCl (50 mL, 1 M), sat. NaHCO_3 solution (50 mL) and sat. NaCl solution (50 mL). The organic phase was dried over MgSO_4 , filtrated and the solvent was removed in vacuo. The residue, 4-bromomethyl[2.2]paracyclophane* (3.40 g, 11.2 mmol, 1.00 eq.*) and potassium phthalimide (2.18 g, 11.8 mmol, 1.05 eq.*) were dissolved in DMF (50 mL) and heated to 90 °C for one hour. After removal of the solvent the crude product was taken up in CH_2Cl_2 (200 mL) and water (200 mL). After phase separation, the organic phase was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic phases were dried over MgSO_4 . After removal of the solvent, the crude imide was dissolved in MeOH (150 mL) and hydrazine hydrate (8.00 mL) was added and the mixture was heated to 60 °C for one hour. The solid was

filtered off and rinsed with MeOH. After removal of the solvent, the crude product is purified by column chromatography (eluent: $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 1:1 +5 Vol-% NEt_3) to yield the product as an off-white solid (2.22 g, 84%). ^1H NMR (500 MHz, CDCl_3): 6.60 (dd, $J = 7.8$ Hz, 1.9 Hz, 1H, aromatic), 6.53 (dd, $J = 7.8$ Hz, 1.8 Hz, 1H, aromatic), 6.49-6.43 (m, 3H, aromatic), 6.40 (dd, $J = 7.9$ Hz, 1.8 Hz, 1H, aromatic), 6.32 (bs, 1H, aromatic), 3.87 (d, $J = 14.3$ Hz, 1H, NCH_2), 3.52 (d, $J = 14.3$ Hz, 1H, NCH_2), 3.36 (ddd, $J = 13.4$ Hz, 10.2 Hz, 2.1 Hz, 1H, CH_2) ppm, 3.17-2.95 (m, 6H, CH_2), 2.84 (ddd, $J = 13.6$ Hz, 6.1 Hz, 1H, CH_2) ppm.

A custom-built setup was used for the CVD process. In this setup, the precursor is sublimated under a reduced pressure (0.12 mbar) at a temperature close to 100°C . Then, it enters the pyrolysis furnace, heated to 660°C , with the help of an argon carrier gas stream (20 sccm). Quinodimethane intermediates are formed and spontaneously polymerize on the substrates, cooled to 15°C on the sample holder, located in the deposition chamber. A slow deposition rate (close to $0.2 \text{ \AA}/\text{s}$), monitored by a quartz crystal microbalance located in the deposition chamber, was maintained. As substrates silicon wafers with a native oxide layer (Siegert Wafer GmbH, Aachen, Germany) or filter paper (VWR Grade 413 Filter Paper, VWR International GmbH, Darmstadt Germany) were used.

Spectroscopic Ellipsometry Spectroscopic ellipsometry measurements were performed with a M2000 (Woollam Co., Inc., Lincoln NE, USA). Samples were analyzed within 24 hours of CVD polymerization to minimize aging effects. All measurements were performed in the spectral region of 370-900 nm at an angle of incidence of 75° . For in situ measurements a home-built batch cell made from Teflon was used. Glass cover slides are used as window material. The inner volume of the cell is approximately 50 mL. To evaluate the experimental data, an optical box model was used. Silicon substrates were fitted with database values for Si and SiO_2 .²⁴ The optical properties of the polymer were fitted by an uniaxial Cauchy-layer.¹⁵

Streaming Potential Measurements For measuring the ζ -potential as a function of pH, polymer coatings were prepared directly on treated polystyrene slides (Ted Pella, Inc., Redding, CA, USA) using the CVD polymerization processes described above. The clamping cell of an electrokinetic analyzer SurPASS (Anton Paar GmbH, Graz, Österreich) was used in asymmetric mode to acquire ζ -potential values of the samples across a pH range of 3 to 6. Polypropylene foil was used as the reference. For each sample, titration was performed from the neutral to the acidic range using 0.1 M hydrochloric acid as the titrant and 0.001 M potassium chloride as the electrolyte. The pH-value was controlled using an automated titration unit, which effected pH changes in increments of 0.3, while the electrolyte solution was stirred continuously. The electrolyte solution was purged continuously with nitrogen to prevent carbon dioxide dissolution and unintended

changes in pH. Streaming current was measured using Ag/AgCl electrodes and the Helmholtz-Smoluchowski equation was applied to compute the ζ -potentials. Flow rates of 50-70 mL/min were observed at a pressure of 400 mbar and a gap of 100-120 μm was maintained between the sample and the polypropylene reference standard. Samples were rinsed for 3 minutes before each measurement to equilibrate the surface against the electrolyte solution. Samples were analyzed within 24 hours of CVD polymerization to minimize aging effects.

X-Ray Photoelectron Spectroscopy XPS measurements were performed using a K-Alpha⁺ XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK). Data acquisition and processing using the Thermo Advantage software as described elsewhere.²⁵ All thin films were analyzed using a microfocused, monochromated Al K α X-ray source (400 μm spot size). The kinetic energy of the electrons was measured by a 180° hemispherical energy analyzer operated in the constant analyzer energy mode (CAE) at 50 eV pass energy for elemental spectra. The K-Alpha⁺ charge compensation system was employed during analysis, using electrons of 8 eV energy, and low-energy argon ions to prevent any localized charge build-up. The spectra were fitted with one or more Voigt profiles (binding energy uncertainty: ± 0.2 eV) and Scofield sensitivity factors were applied for quantification.²⁶ All spectra were referenced to the C 1s peak (C-C, C-H) at 285.0 eV binding energy controlled by means of the well known photoelectron peaks of metallic Cu, Ag, and Au, respectively.

Acknowledgements

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

S1: AFM image of PPX-AM coating, S2: XPS spectra of PPX-n and PPX-AM; S3: SEM of paper filter;
S4: Contact Angle measurements on paper filter; Videos of transport properties through paper filter

References

- [1] W. F. Gorham, *J. Polym. Sci. Part A: Polym. Chem.* **1966**, *4*, 3027–3039.
- [2] M. E. Alf, A. Asatekin, M. C. Barr, S. H. Baxamusa, H. Chelawat, G. Ozaydin-Ince, C. D. Petruczok, R. Sreenivasan, W. E. Tenhaeff, N. J. Trujillo, S. Vaddiraju, J. Xu, K. K. Gleason, *Adv. Mater.* **2010**, *22*, 1993–2027.
- [3] H.-Y. Chen, Y. Elkasabi, J. Lahann, *J. Am. Chem. Soc.* **2006**, *128*, 374–380.
- [4] E. M. Tolstopyatov, *J. Phys. D: Appl. Phys.* **2002**, *35*, 1516–1525.
- [5] J. Lahann, *Polym. Int.* **2006**, *55*, 1361–1370.
- [6] A. Ross, H. Durmaz, K. Cheng, X. Deng, Y. Liu, J. Oh, Z. Chen, J. Lahann, *Langmuir* **2015**, *31*, 5123–5129.
- [7] Y. Elkasabi, J. Lahann, *Macromol. Rapid Commun.* **2009**, *30*, 57–63.
- [8] H.-Y. Chen, A. A. McClelland, Z. Chen, J. Lahann, *Anal. Chem.* **2008**, *80*, 4119–4124.
- [9] Y. Elkasabi, H. Y. Chen, J. Lahann, *Adv. Mater.* **2006**, *18*, 1521–1526.
- [10] V. A. Sochilin, A. V. Pebalk, V. I. Semenov, I. Y. Kardash, *Vysokomol. Soedin. A* **1991**, *33*, 1536–1542.
- [11] D. Buenger, F. Topuz, J. Groll, *Prog. Polym. Sci.* **2012**, *37*, 1678–1719.
- [12] D. H. Kang, S. M. Kim, B. Lee, H. Yoon, K.-Y. Suh, *Analyst* **2013**, *138*, 6230–6242.
- [13] G. Ozaydin-Ince, A. M. Coclite, K. K. Gleason, *Rep. Prog. Phys.* **2012**, *75*, 016501.
- [14] A. Richter, S. Howitz, D. Kuckling, K.-F. Arndt, *Sensor. Actuat. B-Chem.* **2004**, *99*, 451–458.
- [15] J. J. Senkevich, S. B. Desu, *Polymer* **1999**, *40*, 5751–5759.

- [16] I. Tokarev, S. Minko, *Soft Matter* **2009**, *5*, 511–524.
- [17] R. S. Corley, H. C. HAAS, M. W. Kane, Di Livingston, *J. Polym. Sci.* **1954**, *13*, 137–156.
- [18] J. E. Baio, T. Weidner, J. Brison, D. J. Graham, L. J. Gamble, D. G. Castner, *J. Electron. Spectros. Relat. Phenom.* **2009**, *172*, 2–8.
- [19] B. J. Humphrey, *Studies in Conservation* **1984**, *29*, 117–123.
- [20] S. A. Dobroussina, T. D. Velikova, O. V. Rybalchenko, *Restaurator* **1996**, *17*, 75–85.
- [21] P. Kwong, M. Gupta, *Anal. Chem.* **2012**, *84*, 10129–10135.
- [22] G. Demirel, E. Babur, *Analyst* **2014**, *139*, 2326–2331.
- [23] J. Lahann, D. Klee, H. Höcker, *Macromol. Rapid Commun.* **1998**, *19*, 441–445.
- [24] *Handbook of optical constants of solids*, (Ed.: E. D. Palik), Academic Press, London, **1997**.
- [25] K. L. Parry, A. G. Shard, R. D. Short, R. G. White, J. D. Whittle, A. Wright, *Surf. Interface Anal.* **2006**, *38*, 1497–1504.
- [26] J. H. Scofield, *J. Electron. Spectros. Relat. Phenom.* **1976**, *8*, 129–137.

Table of contents entry

The preparation of a pH-responsive poly(*p*-xylylene) derivative via Chemical Vapor Deposition Polymerization can be achieved by modification of the paracyclophane-precursor with ionizable aminomethyl groups. The swelling behavior is investigated using spectroscopic ellipsometry and streaming potential measurements. The capacity regarding the coating of complex substrates with stimuli-responsive films is demonstrated coating filter paper.

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