Applicability of Vapor-Deposited Thermoresponsive Hydrogel Thin Films in Ultrafast Humidity Sensors/Actuators

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Supporting Information

ABSTRACT: Thermoresponsive polymers reversibly react to changes in temperature and water content of their environment (i.e., relative humidity, RH). In the present contribution, the thermoresponsiveness of poly(N-vinylcaprolactam) thin films cross-linked by di(ethylene glycol) divinyl ether deposited by initiated chemical vapor deposition are investigated to assess their applicability to sensor and actuator setups. A lower critical solution temperature (LCST) is observed at around 16 °C in aqueous environment, associated with a dramatic change in film thickness (e.g., 200% increase at low temperatures) and refractive index, while only thermal expansion of the polymeric system is found, when ramping the temperature in dry atmosphere. In humid environment, we observed a significant response occurring in low RH (already below 5% RH), with the moisture swelling the thin film (up to 4%), but mainly replacing air in the polymeric structure up to ~40% RH. Non-temperature-dependent swelling is observed up to 80% RH. Above that, thermoresponsive behavior is also demonstrated to be present in humid environment for the first time, whereas toward 100% RH, film thickness and index appear to approach the values obtained in water at the respective temperatures. The response times are similar in a large range of RH and are faster than the ones of the reference humidity sensor used (i.e., seconds). A sensor/actuator hygromorphic device was built by coating a thin flower-shaped poly(dimethylsiloxane) (PDMS) substrate with the thermoresponsive polymer. The large swelling due to water uptake upon exposure to humid environment at temperatures below the LCST caused the petals to bend, mimicking the capability of plants to respond to environmental stimuli via reversible mechanical motion.

KEYWORDS: iCVD, pNVCL, smart polymer, thin film, humidity, sensor, actuator

INTRODUCTION

Stimuli-responsive swelling is a property of smart hydrogel materials, which makes them suitable for a plethora of sensor and actuator setups. A variety of materials have been developed exhibiting a specific water uptake behavior depending on external stimuli including temperature, pH, magnetic/electric fields, or concentrations of specific chemical species (e.g., glucose). Such hydrogels, as networks of hydrophilic polymer chains, can swell to up to a multiple of their dry size; they react reversibly by taking up or repelling out water upon changing the environment (i.e., the magnitude of the external stimulus).

This water exchange occurs diffusion-based and is, hence, time-limited by water diffusivity. To achieve fast response times and, as a result, optimal device performance, thin polymeric films are employed. Furthermore, device setups often require the coating of delicate surfaces (e.g., drugs, flexible substrates), exhibiting sophisticated nanostructure. In this contribution, initiated chemical vapor deposition (iCVD) was adopted to meet these specific requirements. This solvent-free technique enables the conformal thin film deposition of a plethora of chemical species and compositions from the vapor-phase similar to free radical polymerization processes. The mild processing conditions employed allow for full retention of delicate functional groups, such as the adopted thermoresponsive units, upon deposition. A variety of process parameters (e.g., flow rates, pressure, filament temperature) can be utilized to tune the properties of the deposited thin films in a large range of directions (e.g., composition, morphology, molecular weight).

During swelling, the resulting smart hydrogel thin films undergo rearrangements of polymer chains that impose stress on the thin films, possibly eventuating in poor adhesion or mechanical failure. To increase the thin films’ mechanical stability, a second monomer, working as a cross-linker, can be copolymerized. As the cross-linking agent binds two separate polymer chains, the cross-linked hydrogel can be viewed as a polymer network (with a certain mesh size), able to take up a specific maximum amount of water.

The responsiveness to water and to the other external stimuli can be tailored via the chemical nature of monomer and cross-linker. In case of thermoresponsive hydrogels, e.g., the most prominent example poly(N-isopropylacrylamide) (pNIPAAm) exhibits hydrophilic groups (i.e., amide) that are able to bind water molecules via hydrogen-bonds; antagonistically, the polymeric mesh shows the potential for attractive...
intrachain interactions leading to polymer collapse at higher temperatures.\(^8\) The combination of such specific properties result in the material exhibiting a lower critical solution temperature (LCST).\(^8\) In aqueous environment, below the LCST, the polymer exhibits a hydrated swollen state and a transition to a dehydrated shrunken state, when the temperature is increased. Recently, another temperature-responsive polymer, namely poly(N-vinylcaprolactam) (pNVCL), was synthesized by iCVD for the first time.\(^7\) Its nontoxicity and biocompatibility make it promising for biomedical applications.\(^10\) Its specific chemical structure facilitates a typical Flory–Huggins demixing behavior with water, which is, for example, different from the miscibility of pNIPAAm.\(^11\) Our group provided further evidence of such behavior by showcasing the tunability of the thermoresponsiveness of pNVCL-based copolymer thin films via molecular weight (i.e., chain length) by varying the filament temperature during iCVD.\(^12\) Mechanical stabilization and further tailoring of the LCST were demonstrated by copolymerizing a cross-linking agent, namely di(ethylene glycol) divinyl ether (DEGDVE), together with pNVCL, as described elsewhere.\(^12\) DEGDVE has been previously shown to allow for tuning of the temperature-responsiveness in pNIPAAm- and pNVCL-based copolymers by our group.\(^12\) We also aimed at shedding light onto the thermoresponsive behavior of the polymer in humid environment. Kinetic swelling data is collected to gain information about the applicability of these systems as fast-responding thin films in sensor and actuator setups in humid environment as well as when water-immersed. The swelling behavior of simple polymeric systems in humidity has been investigated within few studies previously. For instance, Serce and Nolte measured the response of single-component polyelectrolyte thin films in controlled humid environment by reflectometry.\(^15\) They report on swelling curves of these thin films similar to results of our group published in previous contributions.\(^14,16\) However, the literature is lacking clear, systematic studies. Furthermore, the swelling behavior of more complex systems like temperature-responsive hydrogels is not very well documented. Thijs et al., for instance, measured the weight change of two macroscopic temperature-responsive hydrogel powders (pNIPAam, poly[(dimethylamino)ethyl methacrylate]—PDMAEMA), while introducing water vapor into these systems up to 90% RH.\(^17\) They report on the weight gain being a function of temperature in the whole range of investigated humidity values (up to 90% RH). Preliminary measurements on cross-linked pNIPAAm thin films contradict this observation. For such thin films, our group reported on the temperature-responsive transition not being present as a change in film thickness in nitrogen environment, but being tunable by cross-linking, when immersing the samples in liquid water.\(^14\) In humid environment now, we employed cross-linked pNVCL thin films due to their great tunability in thermoresponsiveness, as demonstrated by us recently.\(^12\) Instead of weight gain, we aim at measuring the change in film thickness in situ by spectroscopic ellipsometry (SE), upon introducing water vapor into the system, while it is held at certain temperatures below and above the LCST. The sharp temperature-dependent transition observed in pNVCL-based systems in water facilitates the described experimental determination of the thermoresponsiveness in RH-dependent swelling. Further-

more, it yields great potential for the applicability of the investigated systems in device setups.

To provide a proof-of-concept sensor/actuator device based on the fast and large swelling response and thermoresponsiveness of the pNVCL thin films, we fabricated a bilayer hygromorphic system, inspired by Taccola et al.\(^18\) A pNVCL-based polymer layer was deposited onto a thin polydimethylsiloxane (PDMS) substrate and subsequently laser-cut into flower shapes. In such double-layered structure, the PDMS acted as an elastic, mechanically passive layer, not being swollen by humidity. The swelling of the pNVCL layer caused a macroscopic, fast and reversible bending of the petals upon changes in the environment (i.e., temperature, RH). While previous studies focused on actuation of responsive hydrogels immersed in water,\(^19\)–\(^21\) we provide a first demonstration of macroscopic humidity-driven actuation with temperature-responsive tuning/switching.

### EXPERIMENTAL SECTION

**Thin Film Synthesis.** Poly(N-vinylcaprolactam-co-di(ethylene glycol) divinyl ether) thin films were synthesized by initiated chemical vapor deposition. The depositions were run in a custom-built iCVD reactor, as described elsewhere.\(^17\) N-Vinylcaprolactam (NVCL, 98%; Aldrich, Germany) is used as monomer and di(ethylene glycol) divinyl ether (DEGDVE, 99%; Aldrich, Germany) as cross-linker. NVCL and DEGDVE are kept in their individual glass jars at 78 and 70 °C, respectively. The monomer and cross-linker flow rates are both set to 0.2 sccm. Nitrogen is used as a carrier gas at a flow rate of 1.8 sccm. The corresponding values of the ratio between the monomer partial pressure and the saturation pressure at the substrate temperature \(\left(p_{\text{M}}/p_{\text{sat}}\right)\) are 0.063 and 0.018, for monomer and cross-linker, respectively. In this range of \(p_{\text{M}}/p_{\text{sat}}\) values, a linear relation to the surface concentration of the chemical species has been reported.\(^12\) The applied flow rates yield polymer layers of p(NVCL-co-DEGDVE) with nominal cross-linking of 20%. To monitor the deposited thickness, \(\text{in situ}\) laser interferometry with a He–Ne laser (4 mW, 633 nm; Thorlabs, USA) is performed through a removable quartz glass lid. Several samples exhibiting film thickness values of \((50 \pm 5)\) nm have been synthesized and investigated in terms of their swelling behavior in different environmental conditions. Directly after deposition, the thin film samples were rinsed for 30 s with deionized water for equilibration reasons, as reported earlier.\(^14,16,23\)

**Characterization and Investigation.** Spectroscopic ellipsometry (SE) in a wavelength range of 370–1000 nm (M-2000S, J. A. Woollam, USA) was applied to determine film thickness and optical properties of the thin films in the different environmental conditions. Swelling experiments in deionized water were performed in a temperature controlled liquid stage (J. A. Woollam, USA). The recorded data was evaluated with an optical model consisting of a c-Si semi-infinite layer on the bottom (temperature dependent), a 1.6 nm thick native SiO\(_2\) layer in the middle and the polymer film on top, modeled as a Cauchy function with an Urbach tail accounting for adsorption in the low wavelength region. \(\text{H}_2\text{O}\) with temperature-dependent optical properties was set as the surrounding medium. For the temperature-dependent swelling experiments, the liquid stage and the mounted sample (already exposed to deionized water) were precooled to 10 °C. The respective signal was then recorded while applying a temperature ramp from 10 to 50 °C (also the limitations of the temperature stage) at a heating rate of 0.5 °C/min. Similar heating rates have previously been shown to allow the temperature-responsive material to equilibrate during deswelling and hence yield an “equilibrium swelling behavior”.\(^24\) For thermal equilibrium reasons reported earlier,\(^14,16\) the temperature-dependent swelling behavior and the LCST of the iCVD thin films in water were evaluated from the third heating experiment. All subsequent measurements yielded similar curves and consistent results.

The spectroscopic ellipsometry measurements in controlled humid environment were performed in a THMS600 temperature stage
polystyrene (PS) disks for 60 s at a speed of 650 rpm and then cured with the base and curing agent, Dow Corning Corp.) was spin coated onto a substrate with an SPTT 15 humidity sensor (Sensirion, Switzerland). To measure the response of the film as a function of RH at a constant substrate temperature, the humidity was increased from 0% RH up to the point where condensation occurs on the sample surface. With the temperature and RH value measured at the sensor (T\(_{\text{sensor}}\)) and at the substrate temperature (T\(_{\text{sub}}\)) were calculated with the help of the Arden–Buck equation (eq 1):

\[
P_{\text{sat}} = 0.61121 \times \exp \left( \frac{17.368 \times T}{T + 238.88} \right)
\]

(1)

The relative humidity at the substrate level (RH\(_{\text{sub}}\)), that the sample is effectively exposed to, was then calculated as the product of the relative humidity measured at the sensor (RH\(_{\text{sensor}}\)) and the ratio of the saturation vapor pressure values at the sensor temperature and at the substrate temperature (Equation 2):

\[
\text{RH}_{\text{sub}} = \frac{\text{RH}_{\text{sensor}} \times P_{\text{sat,sensor}}}{P_{\text{sat,sub}}}
\]

(2)

The point of condensation could be taken as a reference for the validity of this calculation and could successfully be estimated by ±2% RH, which is within the uncertainty of the RH sensor used. To evaluate the film thickness and refractive index of the sample, the same optical model as in the liquid case has been used to fit the recorded data, but with the ambient material being set to air (n ≈ 1). Thickness and refractive index were monitored at each humidity step and read out after several minutes of equilibration, so that the observed film thickness would not vary for more than 1% in 2 min.

The transition temperature of the deposited systems has been evaluated from the optical thin film properties recorded by spectroscopic ellipsometry during swelling experiments in water while increasing the temperature from 10 to 50 °C.

Additionally, kinetic measurements were performed in situ while applying water or a certain amount of humidity onto the thin film samples. The same optical models as in the temperature-dependent measurements (liquid and humid environment, respectively) were employed for fitting the data.

Fabrication and Testing of Hygromorphic Devices. To fabricate hygromorphic actuator/sensor devices that respond to changes in the environment (i.e., temperature, RH), thin poly(dimethylsiloxane) (PDMS) substrates were prepared. PDMS (10:1 ratio of base elastomer to curing agent; Sylgard 184 silicone elastomer base and curing agent, Dow Corning Corp.) was spin coated onto polystyrene (PS) disks for 60 s at a speed of 650 rpm and then cured at T = 80 °C for 3 h in an oven. The PDMS film had a thickness of \(t_{\text{PDMS}} = (55 ± 4) \mu\text{m}\), as determined by stylus profilometry (Alpha Step D-500 Profiler, KLA Tencor, USA). PDMS substrates, still supported by PS, were then coated with 300 nm of the 20% cross-linked p(NVCL-co-DEGDV) film with the iCVD process as described above. After iCVD, the bilayer system was laser-cut into a flower shape (see design and schematics of bilayer actuators in Figure S1, Supporting Information), with a direct-write CO2 laser (VLS 2.30, Universal Laser Systems, Inc., USA) equipped with a 30 W source. Power, speed, and resolution were tuned to optimize sharp cutting of PDMS with negligible damage to the underlying PS support.

For investigating the response to RH, a flower-shaped device was peeled off from the PS support and placed on a paper rod support, with the thermoresponsive layer pointing upward. After placing it in a cuboid (8 × 8 × 8 cm\(^3\)) to constrain the gas exchange with the environment, the different levels of humidity were supplied at 25 °C by a gas stream flowing in from top, using the same mixing setup as described above. To investigate the response to temperature, the device was placed onto the temperature stage with the thermoresponsive layer being in direct contact with the sample table (i.e., pointing downward). The RH of the environment was measured to be 35% at 25 °C.

### RESULTS AND DISCUSSION

Thermoresponsiveness in Water and Dry Atmosphere. Effective sensors are characterized by a fast and large amplitude response. In a previous contribution, we demonstrated that the cross-linker amount largely affects the amplitude of the response in thermoresponsive films deposited by iCVD; together with employing distinct amounts of cross-linking, utilizing the knob of the filament temperature makes it possible to tune the LCST in the range 16–40 °C.\(^{12}\) For the present study, we synthesized p(NVCL-co-DEGDV) thin films by initiated chemical vapor deposition with a minimal nominal amount of cross-linking of 20% to ensure the films' stability in water. We use a model system with an LCST of about 16 °C (cf. Figure 1). From ellipsometric measurements,

![Figure 1](image-url)

Figure 1. (a) Film thickness normalized by the dry thickness (\(d/d_{\text{dry}}\)) and refractive index (\(n\)) measured during swelling of a nominally 20% cross-linked 50 nm p(NVCL-co-DEGDV) thin film in water while heating from 10 to 50 °C, with dry thickness measured in N2 atmosphere at 10 °C and transition temperature between swollen and collapsed state (as mean value of points of inflection of thickness and index curves) indicated with a vertical line at 16.1 °C. (b) \(d/d_{\text{dry}}\) and \(n\) measured during temperature ramps between 10 and 50 °C (10 min ramp; 5 min wait at max/min T) of the thin film in nitrogen atmosphere.

the thickness and refractive index of the thin films in water have been evaluated via fitting the measurement data; they are plotted in Figure 1a as a function of temperature.

From the measurement data represented in Figure 1a, the transition temperature could be determined as the mean value of the points of inflection of the temperature-dependent thickness and refractive index curves, as already described elsewhere.\(^{13}\) This gives an LCST value of 16.1 °C. The temperature-dependent swelling curves show an increase of the film thickness compared to the dry one of more than 250% at temperatures below the LCST. A strong transition between a
swollen state with large film thickness and low refractive index below the LCST, and a collapsed state with smaller film thickness and higher refractive index above the LCST is observed. At temperatures above the LCST, the film thickness reaches values of ~1.5 times the dry film thickness, hinting toward a significant amount of water being retained in the polymeric structure also above the transition temperature, as already reported before. Furthermore, at temperatures above ~40 °C, the refractive index appears to decrease, while the film thickness increases again. From 35 to 50 °C, the hydrogel film thickness increases by ~8%, while the refractive index decreases by ~0.012. Hypothetically, this can be attributed to thermal expansion at temperatures above the LCST, at which the transition is completely finished and the polymeric system appears in the collapsed state. However, the increase in film thickness and the decrease in refractive index seem unusually large.

To investigate this effect further, the thermal expansion of the hydrogel thin films in a dry environment (i.e., N₂ atmosphere) has been investigated by ramping the temperature from 10 to 50 °C and vice versa; ramping times of 10 min and wait times of 5 min were used, while recording the optical response of the material by spectroscopic ellipsometry. The film thickness normalized by the thickness obtained at 10 °C and the refractive index gained from the respective experiment are plotted in Figure 1b as a function of temperature. Interestingly, the hydrogel thin film does not exhibit a temperature-responsive behavior without the presence of water (in N₂ atmosphere). Hence, the (linear) thermal expansion of the polymeric material can be estimated. For comparison, from 35 to 50 °C, the film thickness is observed to increase by ~0.5% and the refractive index is observed to decrease by ~0.005. At the respective temperatures (above the LCST), the increase in film thickness in water appears to be larger than the one observed in N₂ atmosphere by 1 order of magnitude. Hypothetically, the water retained in the polymeric system in the collapsed state decreases the attractive interaction of polymeric structures. This promotes the entire polymeric system to expand more easily and would explain the higher thermal expansion in water.

**Swelling in Humid Environment.** Overall, the magnitude of the observed swelling and temperature-dependent response in water make the material promising for sensor and actuator systems. To investigate the applicability of the synthesized hydrogel thin films in humid environment, we probed the thermoresponsive thin films in terms of swelling in RH below and above the transition temperature of 16.1 °C by SE. For that, we monitored the film thickness and the refractive index, while introducing controlled amounts of water vapor into the nitrogen filled system. As described before, these experiments were performed at various substrate temperatures between 10 and 24 °C, measuring the response of the thin films at temperatures below and above the LCST, respectively (Figure 2). As shown later, the response of the thin films investigated is in the order of seconds. To ensure measuring a reliable thickness value, the values were read out after several minutes of equilibration, so that the observed film thickness would not vary for more than 1% in 2 min.

The SE measurements of p(NVCL-co-DEGDVE) thin films in humid environment at different temperatures (see Figure 2) show swelling of the thin films already occurring at humidity levels of below 5% RH for all the investigated substrate temperatures. The measurements performed at different substrate temperatures yield similar swelling-vs-RH curves up to a humidity level of approximately 80% RH (see inset of Figure 2). Above 80% RH, the thermoresponsiveness of the thin film samples, apparent when studied immersed in water, can also be observed in humid environment. In this region, the degree of swelling is a function of the substrate temperature and approaches the values observed in water at humidity levels close to 100% RH. Even though the uncertainty of fitting the optical measurement data increases at humidity levels above 90% RH, the difference between the recorded measurement points at the different temperatures is clear and distinct.

Secrist and Nolte’s measurements15 of the response of non-thermoresponsive single-component polyelectrolyte thin films in controlled humid environment by reflectometry yield comparable results to the swelling-vs-RH-curves presented in Figure 2. Thijs et al.17 also report on the weight change of macroscopic hydrogel powders, exposing non-thermoresponsive hydrogels (pHEMA) to up to 90% RH; they observed similar swelling behavior as well. However, for thermoresponsive hydrogels investigated in the mentioned study,17 only the trends of water uptake reported for temperatures below the LCST appear to be comparable to the ones reported in the present contribution. As described earlier, the cited publication reports on the weight gain being a function of temperature in the whole range of investigated humidity levels (measured up to 90% RH). Counterintuitively, even a negative weight change was reported for the measurements performed at elevated temperatures (above the LCST) as a function of RH.

The different results either arise from the different sample morphologies (macroscopic pNIPAAm powder vs cross-linked pNVCL-based thin film) or stem from the different measurement setups. In either way, temperature gradients are nearly unavoidable to measure thermoresponsive properties, but can be problematic in studying and interpreting the response of such a material in humid environment. In a more recent case, further pNIPAAm-based hydrogels were investigated in terms of moisture uptake from a humid environment.25 Again, the weight change was reported to be a function of temperature in the whole range of investigated humidity levels; however, the resulting swelling-curves are different from the ones reported.
by Thijs et al.\textsuperscript{17} gained from similar measurements. The results at temperatures below the LCST, again, appear to be comparable to the trends reported in Figure 2. However, the data suggest that the systems have not been investigated at temperatures above the LCST at the same humidity levels as below the LCST. For example, the amount of adsorbed moisture reported for a temperature of 20 °C at 30% RH compares well to the one reported for 90% RH at 40 °C;\textsuperscript{25} as a matter of fact, generating a humidity of 90% RH at 20 °C translates to a humidity of \(~30\)% at 40 °C (cf. eqs 2 and 1 and Figure 3). Figure 3 should serve as an illustration for the relative humidity changing with temperature.

Overall, several studies report on data at a specific relative humidity, varying the temperature. However, they appear to disregard that changing the temperature also changes the relative humidity drastically; for example, a humidity of 90% RH generated at 20 °C increases by \(~5.6\)% for an object that is exposed to this very humidity, but is held at 1 °C lower (i.e., 19 °C) (cf. eqs 2 and 1). To avoid such problems in the experiments performed for the present contribution, the humidity was varied while keeping the temperature constant.

To give further insight into the experimental setup, the humidity (up to 100% RH) is generated by bubbling nitrogen through water (at 70 °C), air filtering and mixing it with pure nitrogen to be able to control the humidity level. This mixture is then flown into the measurement chamber via a 1-m tube to avoid fluctuations in temperature. In the chamber, a humidity sensor measures the RH approximately at room temperature. Only the substrate is cooled to temperatures below room temperature to prevent condensation happening anywhere else before 100% RH are reached at the substrate level. From the RH measured at room temperature right next to the substrate, as described earlier, the real RH that the sample is exposed to at the substrate temperature can be calculated via eqs 2 and 1. As stated above, temperature gradients need to be addressed with care. However, we believe this procedure leads to reliable RH values, as supported by the fact that the point of condensation could be estimated by \(\pm 2\)% RH, so within the error of the humidity sensor used in all the investigated temperatures.

A more systematic and detailed view on the swelling behavior of the hydrogel thin films investigated in humid environment is given in Figure 4; there, the normalized film thickness (\(d/d_{\text{dry}}\) in part a)) and the refractive index (\(n\) in part b)) are plotted as a function of the relative humidity as obtained from SE measurements, while increasing the RH from 0 to almost 100% at 20 °C substrate temperature. From this data, the response behavior of the hydrogel thin film to relative humidity can be divided into three different regions (boxes in Figure 4): First, after starting off in dry atmosphere (0% RH), up to \(~40\)% RH, the film thickness increases only slightly (by \(~4\)%), whereas the refractive index also increases with respect to the dry state. This phenomenon occurred in all the temperatures investigated. The peak in refractive index appears at very similar values within the \(~5\)% resolution arising from the RH increase steps (data not shown). This can be viewed, primarily, as filling of voids in the polymeric structure with water, as the refractive index of water (\(~1.33\)) is higher than that of air (\(~1.0\)). For comparison, the investigated polymer exhibits a refractive index of \(~1.52\) in the dry state (see Figure 4). Second, from 40% up to \(~80\)% RH, the film thickness increases fairly linearly to \(~15\)% when compared to the dry state. In this region, the thin film starts to incorporate water into its polymeric structure, which can be observed as a decrease of the system’s refractive index. However, the response is still small compared to the swelling in water at the specific temperature. Third, above \(~80\)% RH, the film thickness increases in a highly nonlinear manner, approaching the film thickness of the system observed in water at the corresponding temperature. The observed refractive index trend in the mentioned region above \(~80\)% RH exhibits the corresponding behavior.

The monotonous proportionality of the film thickness to the relative humidity at a certain temperature can directly be used in sensor and actuator setups (as shown below). The refractive index cannot be utilized in the whole range of RH due to its non-monotonous behavior. However, two regions can be
identified with respect to $n$: Up to 40% RH, the response is small, but monotone; above 40%, the response is larger and also monotone. For example, in optical systems for RH determination, the refractive index can, thus, be employed in applications, where the environment remains within one of these mentioned ranges.

**Kinetics in Water.** As, especially, the response characteristics of the film thickness of the presented system to various environmental conditions are promising, to test its applicability to sensors and actuators, also the kinetic response behavior was experimentally probed. First of all, the kinetic swelling of the synthesized layers when flooded with water after being in dry atmosphere has been investigated by *in situ* SE measurements (see Figure 5). The fast response of the film was shown, as the film thickness did not change for more than 1% already ~30s after the water exposure had started. Anymore, the behavior cannot be further resolved by SE because it takes time to fill the entire measurement chamber (5 mL) with water and align the sample, during which it is not possible to record meaningful data due to multiple gas–liquid interfaces interfering with the measurement. However, these measurements allow to yield stable thickness values already within seconds of water exposure, perfectly in agreement with the values obtained from the temperature-dependent SE measurements in water (cf. Figure 1a).

**Kinetics in Humid Environment.** As the response to water appears to be promisingly fast, also the kinetic behavior of the hydrogel thin film in humid environment was investigated. At a constant temperature (24 °C), the humid environment in the measurement chamber of the ellipsometer was changed by controlling the flow rates of humid and dry nitrogen vapors; the RH was measured *in situ* in the chamber. Relative humidity levels of below 20%, around 50% and above 80% were introduced to investigate the applicability in different humid environments. The evident response in thickness was utilized to calculate directly back to an RH value via the $d/d_{dry}$-vs-RH plots measured for the respective temperature (cf. Figure 2). For that, a triple-exponential function was used to interpolate the data. The respective responses of the investigated layers in RH together with the measurements of the reference sensor can be found in Figure 6.

The film thickness and, hence, the calculated RH follow the signal of the relative humidity as measured by the reference sensor and also stabilize, when a constant humidity is reached. The data suggest a faster response of the investigated layer compared to the signal of the reference sensor for all humidity levels employed. From the response curves over time, the respective time constants ($\tau$) could be extracted from fitting double-exponential functions to the measured data. The time constants of the p(NVCL-co-DEGDVE) were evaluated to be $\tau_{iCVD,20\%} = (5.3 \pm 0.6)$ s, $\tau_{iCVD,50\%} = (5.1 \pm 0.3)$ s, and $\tau_{iCVD,80\%} = (4.9 \pm 0.2)$ s. It should be noted that the measurement time of the ellipsometer was set to 2 s. The time constants determined from the response of the reference sensor are $\tau_{ref,20\%} = (14.4 \pm 0.4)$ s, $\tau_{ref,50\%} = (8.8 \pm 0.1)$ s, and $\tau_{ref,80\%} = (7.6 \pm 0.1)$ s. A secondary time constant of about 1 min was evaluated to be present for all the data sets for both the responses of the investigated layer and the reference sensor, suggesting that the corresponding “long-term” response stems from the experimental setup. Hence, the primary time constants evaluated from all the measurements yield information about the kinetics of the response of the investigated systems. Also for these primary time constants, the kinetics of the visible/extracted responses of both the investigated layer and the reference sensor ($\tau$, as given above) are, most probably, a convolution of the real response of the sensing system (i.e., water uptake behavior, $\tau_{real}$) and the time it takes to fill the measurement chamber experimentally with a certain relative humidity ($\tau_{setup}$); thus, $\tau = \tau_{real} + \tau_{setup}$.

Overall, the response of the 50 nm p(NVCL-co-DEGDVE) layer determined from the increase in thickness upon humidity exposure appears to be about twice as fast as the response of the reference sensor. For decreasing the RH toward dry $N_2$ atmosphere, similar results were obtained; also when investigating the response at 10 °C, the p(NVCL-co-DEGDVE) film was observed to respond faster than the reference sensor, but the experimental setup at lower temperatures appears to stabilize slower as temperature gradients are involved (data not shown). In the data sheet of the reference sensor, a response time of 8 s is given; the response of the sensor to RH levels above 50% is comparable. At lower RH, the apparent larger time constant determined from the response of the sensor suggests a strong contribution from the experimental setup. For the reference sensor and the investigated polymer layer, the time constants appear to be lower (and, thus, the responses faster) for higher RH. Intuitively, the opposite would be expected, as it takes more time to experimentally reach a higher level of RH after starting out in dry nitrogen environment. However, the different flow rates of dry $N_2$ and a certain level of humidity (as controlled by

![Figure 5](image1.png)

*Figure 5.* Thickness normalized by the dry thickness measured in nitrogen atmosphere ($d/d_{dry}$) obtained from spectroscopic ellipsometry measurements as a function of time while exposing a p(NVCL-co-DEGDVE) sample (50 nm dry thickness) to water after starting off the measurement in dry atmosphere; the dashed lines give interpolated data during flooding and aligning of the liquid cell of the ellipsometer.

![Figure 6](image2.png)

*Figure 6.* Relative humidity (RH) as evaluated from the response of the sensor layers (cf. Figure 2) and from the reference sensor during RH exposure at different levels over time at 25 °C.
the needle valves experimentally) could interfere with this consideration. As a consequence, it is not clear how much the experimental filling process \( t_{\text{setup}} \) contributes to the evaluated time constants; in general, it seems to be plausible to assume a filling time in the order of seconds. Regardless, the developed sensing layer is at least as fast as evident from the derived response times or, most probably, faster.

The similar time constants at different levels of RH are, especially, promising for applications of the layers in humidity sensors, where operation over a wide range of humidity is needed. The observed fast responses make the layers appealing for applications, where changes in the RH need to be resolved in the order of seconds or below. An example of a fast sensor device based on such stimuli-responsive hydrogels is presented in Buchberger et al.\textsuperscript{26}

**Testing of the Sensor/Actuator Hygromorphic Device.** The thermoresponsive swelling at high RH could be interesting for actuator setups, where two stimuli, T and RH, are used to obtain a mechanical deformation of the system. Hygromorphs, as objects responding to environmental humidity by changing their shape, show striking examples in nature (especially in plants, such as in pine cones)\textsuperscript{27} and they have recently gained much interest for the development of biomimetic artificial structures for sensing and soft robotics.\textsuperscript{18,28} To the author’s knowledge, this is one of the first examples of a fast, humidity-driven and temperature-controlled actuator with a bilayered structure involving hydrogel thin films.

To investigate this potential application and provide a first proof of concept, a flower-shaped hygromorphic sensor/actuator system was fabricated (the schematics/design are provided in Figure S1, Supporting Information) based on a bilayer of PDMS/p(NVCL-co-DEGDVE). In such bilayer, the PDMS substrate (55 \( \mu \text{m} \) thick) is acting as a mechanically passive and elastic foundation, while the pNVCL coating (just 300 nm thick) is providing the capability to be swollen upon water uptake and thermoresponsiveness. Each petal of the flower structure can thus act as a simple unimorph actuator (bending beam geometry) upon uptake/release of water from the environment, as schematized in Figure S1. The double-layered device setup was tested upon changing the relative humidity and the substrate temperature. Movies (see Supporting Information) and pictures (see Figure 7) were taken during these tests. The flower-shaped devices reacted to the stimuli by bending of their petals due to swelling/deswelling of the p(NVCL-co-DEGDVE). As can be appreciated in the pictures and videos, the device is able to act against gravity upon deswelling (RH-response, Figure 7a) and upon swelling (in the experiment to probe its temperature-response, Figure 7b). The (unbent) reference state of the flower was retrieved by lowering the RH (Figure 7a). Alternatively, the humidity-driven swelling/deswelling could be triggered by temperature, given the thermoresponsiveness of the active layer (Figure 7b). Again, the kinetics of the mechanical response appear to be very fast (i.e., in the order of seconds) and mostly limited by the kinetics of the external stimuli applied: The temperature ramp was applied with cooling/heating rates of 60 °C/min. In case of RH, with the flows supplied, it takes about 10 s to reach the respective maximal/minimal values. The bending radius of the petals is unequivocally set by a specific couple of temperature/humidity values; this fact makes the system interesting for further investigation to obtain reliable and fully reversible actuation.

Remarkably, the bending motion is obtained despite the low thickness of the pNVCL layer (i.e., 300 nm) compared to the PDMS foundation (around 150 times thinner) and compared to similar test devices (e.g., millimeters in thickness,\textsuperscript{19,21} or hydrogel films of tens of micrometers thickness\textsuperscript{20}). Such results support our hypothesis that the large and fast response of the pNVCL layers can be used for fast and integrated humidity—temperature actuators and sensors.

**CONCLUSIONS**

Thermoresponsive p(NVCL-co-DEGDVE) thin films were successfully synthesized via iCVD and probed in terms of response behavior to temperature and different environments (i.e., water, humidity, \( \text{N}_2 \)). This study revealed that in water, the layer swells to up to 250% of its dry thickness below the transition temperature and repels out water upon undergoing a phase transition toward a shrunk state at elevated temperatures. In nitrogen atmosphere, only thermal expansion (∼1.5% thickness increase) is observed upon heating the samples in a similar temperature range as in water (10 to 50 °C). In humid environment, a first detailed study on the swelling behavior of hydrogel thin films shows that the layer monotonously swells with increasing the RH. To the author’s knowledge, with the described measurement setup, this is also the first contribution in which thermoresponsive hydrogel thin films are investigated at humidity levels above 80% RH below and above their LCST. This is why this is also the first contribution in which the thermoresponsiveness of hydrogel thin films is genuinely proved to occur as a change in film thickness and refractive index at different temperatures (also) in humid environment. We show that the thermoresponsive transition (in film thickness and refractive index) only occurs at humidity levels above 80% RH for the investigated system. Toward 100% RH, the film thickness approaches the values observed in water at the respective temperatures. We also observed a significant response in low RH (already below 5% RH), with the moisture swelling the thin film (up to 4%), but mainly replacing air in the polymeric structure up to ∼40% RH.

Kinetically, the investigated p(NVCL-co-DEGDVE) thin films were found to respond quickly to changes in the
environment (i.e., water and different levels of humidity). With the help of calibrating the system by measuring a thickness-vs-
RH curve, in subsequent measurements, the RH was directly
the help of calibrating the system by measuring a thickness-vs-

The response in differently humid environments was about twice as fast as the one of the market-available reference sensor used.

The fast response together with the similar time constants measured for differently humid environments make the investigated system particularly interesting for its application in sensor and actuator setups. Such applicability was successfully demonstrated in flower-shaped double-layered hygromorphic devices. The artificial petals bend due to a humidity-driven and temperature-tunable actuation mechanism, showcasing also a fast mechanical response against gravity in both swelling and deswelling.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.9b00957.

Sketch of the design and schematics of the bilaayered hygromorphic actuators and the full captions for the videos (PDF)

Video of the hygromorphic actuator while changing the relative humidity (Video S1) (MOV)

Video of the hygromorphic actuator while changing the temperature (Video S2) (MOV)

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Notes

The authors declare no competing financial interest.

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