

# Deposition of Thermoresponsive Plasma Polymer Films from *N*-Isopropylacrylamide Using Dielectric Barrier Discharge at Atmospheric Pressure

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**ABSTRACT:** Thermoresponsive polymers are of great interest as functional coatings in biomedical applications. Poly-*N*-isopropylacrylamide (NiPAAm) is a widely used compound that switches its surface properties from hydrophilic to hydrophobic by passing the lower critical solution temperature of 32°C. This study investigated plasma polymerization of NiPAAm (pp-NiPAAm) using a dielectric barrier discharge. The films' chemical composition, thermoresponsive behavior, and stability in water were analyzed. Small effects with regard to thermoresponsive behavior were observed for films with high retention of the monomer structure. Unfortunately, however, these films were not stable in water, so plasma copolymerization was performed to improve film stability. Two different monomers were chosen: vinyltrimethoxysilane and glycidyl methacrylate. Thin films of pp-NiPAAM-co-glycidyl methacrylate show thermoresponsive behavior. While stability in water was improved significantly, the responsive behavior was lost after storing these films in water. Future work to ensure the long-term stability of pp-NiPAAm films, particularly in an aqueous environment, has to be done.

**KEY WORDS:** dielectric barrier discharge, plasma polymerization, thermoresponsive polymer, *N*-isopropylacrylamide

## I. INTRODUCTION

Stimuli-responsive polymers are of great interest in the field of biomedical applications, such as in drug release, chromatography, or controlled cell detachment.<sup>1–6</sup> A review by Kumar et al.<sup>7</sup> gives an overview of different applications. Stimuli-responsive polymers can be characterized as described by de Neindre and Cancouet:<sup>8</sup> “they react with a great change of one of their physical or chemical properties on a small external stimulus, which can be given by a temperature or a pH shift, by changing the electric or magnetic field or the ionic strength of a solution.” The addition of certain metabolic chemicals or of an oppositely charged polymer can also induce changes in the properties of “smart” polymers.

One prominent example of a thermoresponsive polymer is poly-*N*-isopropylacrylamide (PNiPAAm), which in its linear form has a lower critical solution temperature

(LCST) of 32°C, that is, below 32°C hydrogels of PNiPAAm are highly swollen and highly soluble in water. Upon increasing the temperature above the LCST, the polymer undergoes a conformational change, and water is repelled from the polymeric network; the polymer shrinks because of phase separation. Substrates coated with PNiPAAm show hydrophilic behavior at temperatures below the LCST. For films consisting of linear polymerized PNiPAAm, a sharp increase in the water contact angle is observed, leading to reduced wettability with water at temperatures above the LCST.<sup>9–11</sup>

Different methods to create PNiPAAm surfaces are described in the literature. A suitable technique is grafting irradiation-induced surface<sup>12</sup> onto polymers. Radicals are created on the surface by ultraviolet light or gamma irradiation. Afterward, PNiPAAm is grafted onto the surface by radical polymerization from aqueous solutions at elevated temperature. Moreover, Wang et al.<sup>13</sup> described plasma-induced surface grafting in an aqueous environment; plasma was activated in argon at low pressure. Liang et al.,<sup>2</sup> Pan et al.,<sup>14</sup> and Chen et al.<sup>15</sup> describe deposition of thin films of NiPAAm using plasma polymerization at low pressure in a one-step process. To overcome disadvantages of low-pressure plasma polymerization, such as high-cost vacuum equipment or the requirement to work using batch processes, the use of atmospheric-pressure plasma processes to deposit thermoresponsive NiPAAm films is highly desirable.

Dielectric barrier discharges (DBDs) are widely used to achieve a functional coating using different film-forming agents. Depending on the process parameters, film composition and surface properties can be tuned widely. Silicon-containing coatings based on silicon organic monomers, polymer-like coatings based on acrylic, and other polymerizable monomers are frequently described.<sup>16–18</sup> From a biomedical point of view, surface functions such as cell adherence or ability to repel proteins can be achieved.<sup>19–23</sup> To date only initial preliminary studies where DBDs at atmospheric pressure are used to deposit plasma polymerized NiPAAm (pp-NiPAAm) can be found in the literature.<sup>24,25</sup> Spridon et al.<sup>24</sup> describe pp-NiPPAAm using a DBD reactor with a plan-to-plan geometry and depositing NiPAAm from the vapor phase. This configuration is similar to the setup we use for our investigations. In contrast, Molina et al.<sup>25</sup> obtained pp-NiPAAm *in situ* by plasma-induced polymerization of an aqueous solution using a DBD at atmospheric pressure. Thermoresponsive behavior of the films was observed in both studies, but there was no mention of the stability of the films after incubation in water. It is well known that the stability of plasma polymerized films deposited in water at atmospheric pressure is crucial, so we focus on that issue in this article. In this work we compare the thermoresponsive behavior and aqueous stability of pure pp-NiPAAm prepared with a DBD at atmospheric pressure with copolymerized films deposited under the same conditions.

## II. EXPERIMENTS

### A. Film Deposition

Film was deposited in a home-built DBD–plasma-assisted chemical vapor deposition reactor, which was described previously.<sup>16</sup> In brief, 2 high-voltage electrodes covered

with 0.2-cm-thick ceramic insulation are fixed over an aluminum plate covered with a polytetrafluorethylene foil, which serves as grounded electrode and substrate carrier. The gas gap between the electrodes is 1 mm.

To achieve uniform deposition on the substrates, the carrier moves back and forth at a velocity of 1 mm/second. All samples were treated for a total of 300 seconds for a given point on the substrate to achieve films sufficiently thick for surface analysis by Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy. Films were deposited using a pulse length of 1 ms and pause lengths between 0 and 20 ms. To remove ambient air from the plasma zone, the reaction vessel was pumped to 100 Pa, whereas the deposition experiments were performed at 95 kPa. Argon was used as process and carrier gas (Ar 5.0; Air Liquide) for all experiments, with total gas flow of 10 L/min STP (standard temperature and pressure). Reactive monomers were introduced into the plasma zone by bubbling a part of the process gas through the monomer(s). Monomer concentration was adjusted by controlling the gas flow through the monomer. The films were deposited on biaxially oriented polypropylene (75  $\mu\text{m}$ ; Goodfellow). NiPAAm (97%) and vinyltrimethoxysilane (VTMOS; 97%) were supplied by Sigma-Aldrich, whereas glycidyl methacrylate (GMA; 98%) was from Polysciences Inc.

## **B. Film Characterization**

### **1. FTIR-ATR Spectroscopy**

Plasma polymerized films were analyzed by FTIR-ATR spectroscopy using a Nicolet iS10 spectrometer (Thermo Fisher Inc.) equipped with a germanium ATR crystal (1 reflection). For each measurement, 64 scans with a spectral resolution of 4  $\text{cm}^{-1}$  were taken. The samples were measured directly after film deposition, and additional measurements were made after soaking the films in water to investigate film stability. The spectra were analyzed with the Omnic software version 8.0. To deconvolute characteristic absorption bands, Origin 8.1G software was used.

### **2. Contact Angle Measurements**

Water contact angles were measured with an OCA 20L contact angle measuring instrument from Dataphysics Instruments GmbH. To prevent film delamination, static contact angles were measured with a drop volume of 2  $\mu\text{L}$  of water; 5 seconds after the water drop was deposited on the surface, a picture was taken to analyze the water contact angle.

Measurements at increased temperature were performed on a heated table. The temperature was triggered by an electronic TC/TPC 150 device from Dataphysics. To guarantee that the whole film was heated, water contact angles at elevated temperatures were measured 10 minutes after the desired temperature was achieved.

### 3. X-Ray Photoelectron Spectroscopy

To identify film composition directly on the surface, selected samples also were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI 5500 Multi-Technique spectrometer in high vacuum ( $10^{-9}$  mbar). Measurements were made with an incident angle of  $45^\circ$  using an  $\text{MgK}\alpha$  beam. The data were analyzed using MULTIPAK software version 5.0A.

## III. RESULTS AND DISCUSSION

### A. DBD-based Plasma Polymerization of NiPAAm

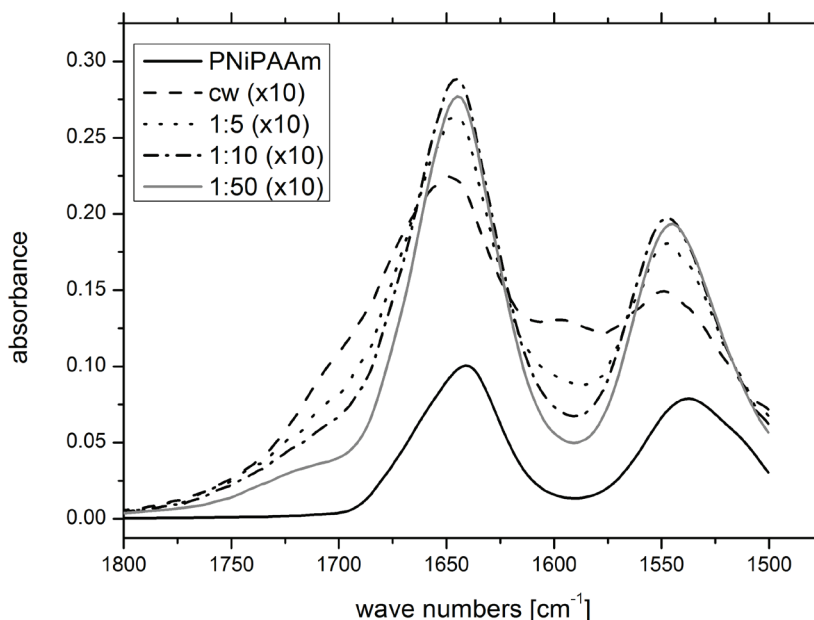
Plasma polymerized films on polypropylene were analyzed with FTIR-ATR spectroscopy. Fig. 1 shows the FTIR-ATR spectra of pp-NiPAAm deposited with different pause lengths at a fixed pulse length of 1 ms, keeping the total treatment duration constant. From the shape of the absorption bands it is obvious that film composition and the retention of the monomer depend on the pause length. Klages and Eichler<sup>17</sup> already described this behavior for other (meth)acrylic monomers.

The absorption bands at  $1645$  and  $1547\text{ cm}^{-1}$  can be attributed to the characteristic amide I and amide II vibrational bands of primary amide groups. At high duty cycles (short pause lengths), additional absorption bands appear in the spectra near  $1600$  and  $1700\text{ cm}^{-1}$ , indicating that new carbonylic moieties have probably been formed in the deposit. It may safely be assumed that thermoresponsive behavior is only achieved at high levels of monomer retention. A comparison with PNiPAAm is shown in Fig. 1. Almost no differences are observed in the spectra when a long pause length (50 ms) is used, confirming that the monomer was deposited with high retention of the monomer structure. Segments of linear PNiPAAm are presumably contained in the film, but cross-linking cannot be fully prevented by depositing film with a DBD.

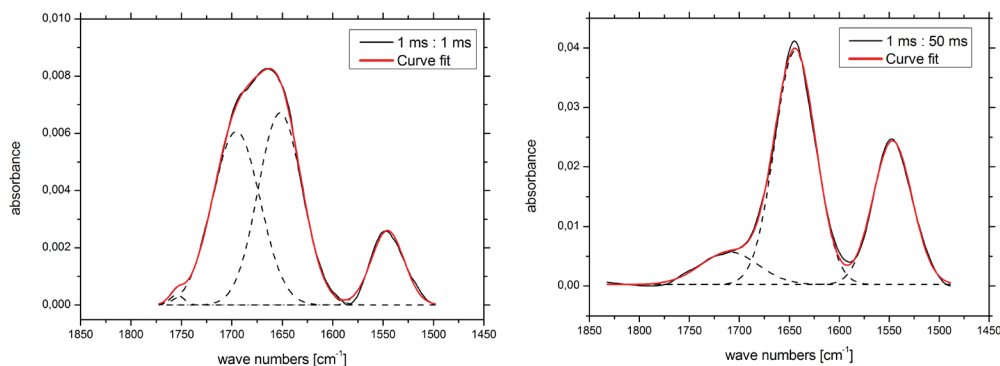
To identify the amount of monomer structure retained, the amide I bands were deconvoluted using Origin 8.1G software (Fig. 2). Only a single  $\text{C}=\text{O}$  absorption band of amide I is expected for a fully retained linear structure, whereas in plasma polymerized films additional  $\text{C}=\text{O}$  bands arise in the FTIR spectrum with decreasing pause length. A measure of monomer retention  $R$  is calculated from the ratio of the area of the amide I band at  $1645\text{ cm}^{-1}$  to the area of the absorption bands of all  $\text{C}=\text{O}$  fragments.

$$R = \frac{A_{\text{C=O amide I}}}{A_{\text{C=O amide I}} + \sum A_{\text{C=O}}}$$

As shown in Fig. 3, less than 5% of the amide groups are maintained in continuous wave mode, whereas by increasing the pause length this figure rapidly increases to  $>80\%$ . At first glance it seems that after increasing the pause length from 20 to 50 ms, the amount of intact amide groups has decreased, but because of the limited accuracy of the determination method, more experiments are required to clarify this question, especially because no longer pause lengths were investigated in this study.

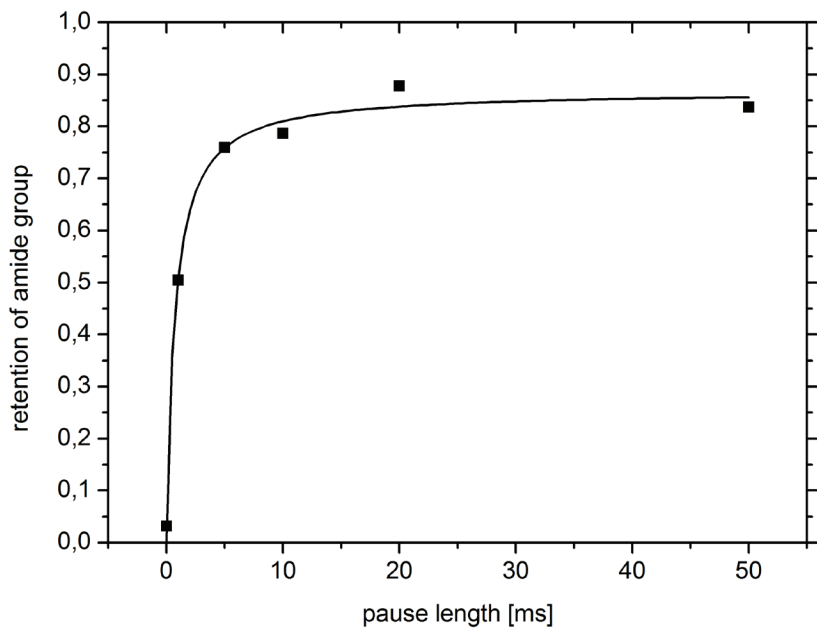


**FIG. 1:** Fourier transform infrared–attenuated total reflection spectra of plasma polymerized *N*-isopropylacrylamide (NiPAAm) deposited with different pulse–pause ratios and with continuous wave (cw) mode. To compare the spectra to poly-NiPAAm (PNiPAAm; solid black line), the intensity of the absorption bands was increased 10 $\times$ .

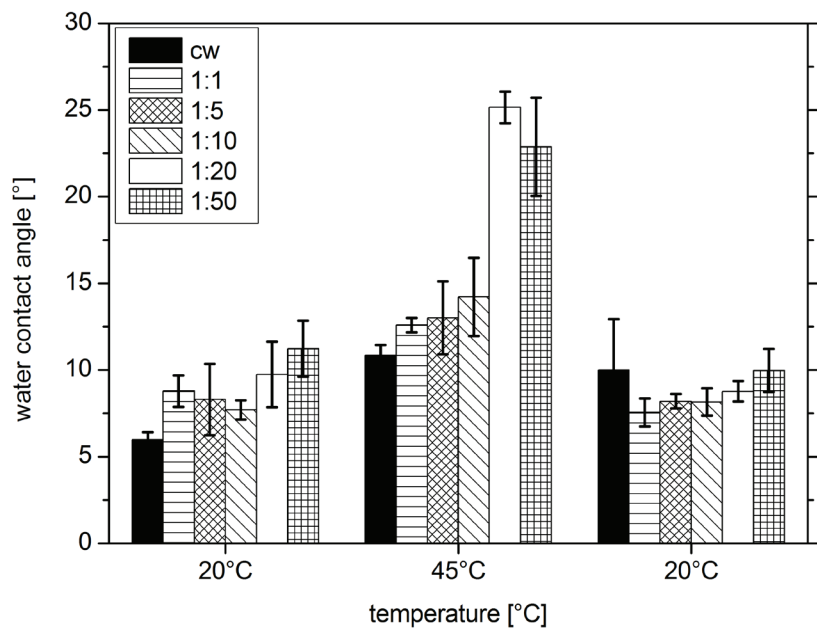


**FIG. 2:** The red line indicates the curve fit after deconvolution of FT-IR spectra of plasma polymerized NiPAAm in the region of amide I at 1645  $\text{cm}^{-1}$  and amide II at 1547  $\text{cm}^{-1}$  using the software Origin 8.G. High conformity with the original spectrum (black line) is reached.

Static contact angles were measured at 20 $^{\circ}\text{C}$  as well as after heating the sample to 45 $^{\circ}\text{C}$  (Fig. 4). At room temperature the samples are quite hydrophilic; the lowest water contact angle was measured for the sample deposited in continuous wave mode.

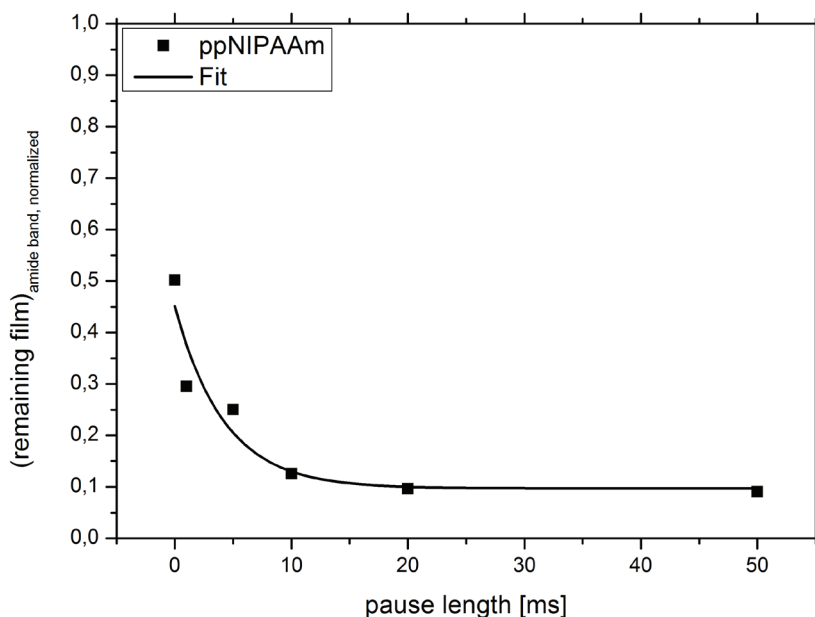


**FIG. 3:** Retention of amide group as determined from the deconvoluted amide I absorption band.



**FIG. 4:** Measurements of the water contact angle for different plasma polymerized *N*-isopropylacrylamide films at 20°C and 45°C. cw, continuous wave.

The highest value was observed for the films deposited at pause length of 50 ms. At increased temperature, the water contact angle of the films deposited at higher pause length increases. After cooling the films to 20°C again, the wettability of the film increases again, meaning that thermoresponsive behavior is observed for films deposited with a highly retained monomer structure. A crucial demand for biomedical applications is stability of the films after incubation in water. Unfortunately, the deposits do not show the desired behavior and even become less stable when treated with plasma with a high pause length, as seen in Fig. 5. Instability of these films in water can be explained by (1) insufficient adhesion of the films to the substrate, which results in the complete delamination of the film, or (2) a low degree of polymerization within the film, resulting in small oligomeric fragments that are washed from the surface after incubation in water. The results shown in Fig. 5 demonstrate that films with low retention of the monomer structure (small pause length) show improved stability in water compared with films with high retention of the monomer structure. Nevertheless, even the former are not fully stable in water. From our point of view stability is achieved by the higher amount of cross-linking observed in these films, but there is still a high number of oligomeric fragments within the film, which are washed out in water. However, adhesion of the film to the substrate seems to be less crucial in this case.

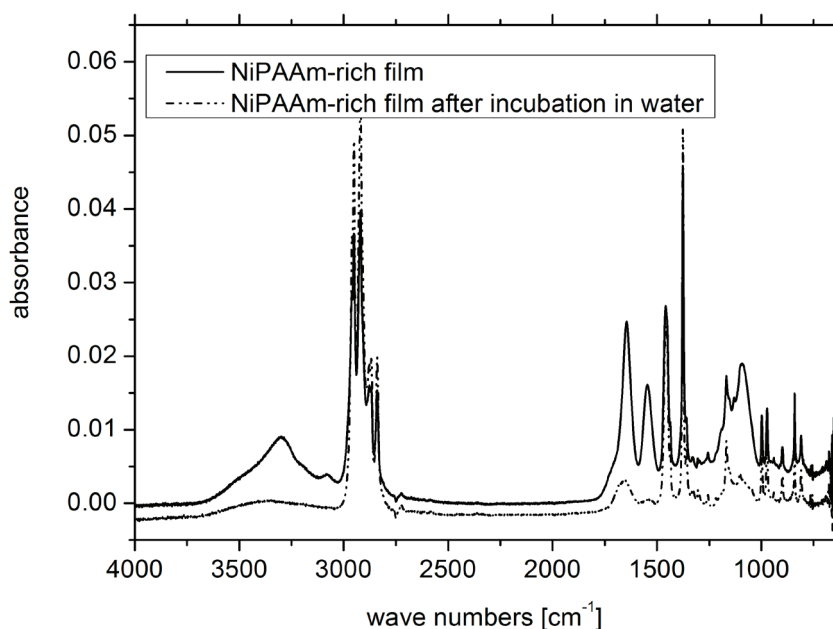


**FIG. 5:** Water stability of pure plasma polymerized *N*-isopropylacrylamide (pp-NiPAAm) films.

## B. Plasma Copolymerization

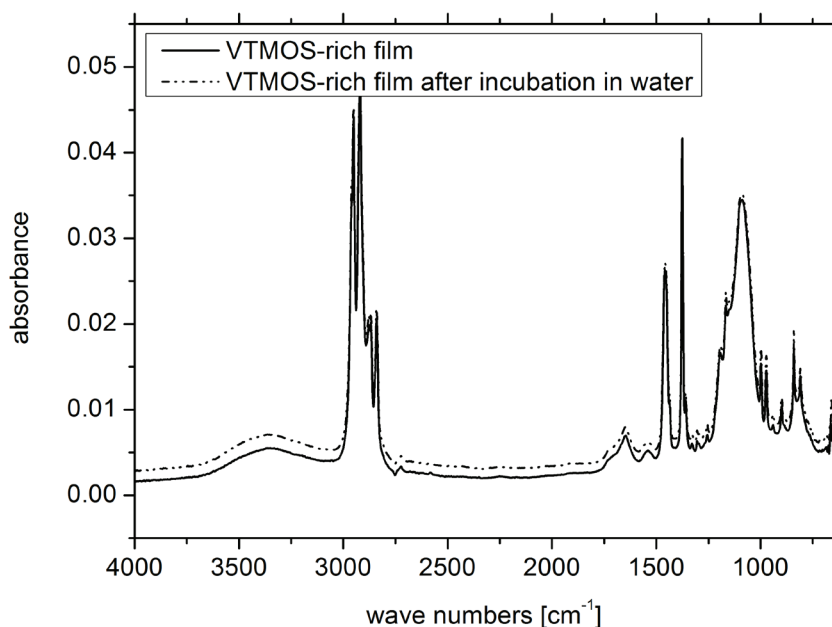
In the literature plasma copolymerization is described to improve stability in water. Thomas et al.<sup>26</sup> used VTMOs to improve the stability of maleic anhydride plasma polymers deposited in water by a DBD. To stabilize deposits of pp-NiPAAm, VTMOs as well as GMA were used in this study. In the case of copolymerization with VTMOs, it is expected that hydrolysis of the methoxy groups of the siloxane and silanol condensation leads to a network cross-linked via Si–O–Si linkages. For this, the concentration of VTMOs within the films should be as low as possible to retain thermoresponsive behavior. The higher amount of cross-linking should stabilize the films because of the reduction of oligomeric fragments. The FTIR-ATR spectra shown in Figs. 6 and 7 detected characteristic absorption bands of both film-forming agents, depending on the concentration of each monomer. The strong absorption band at  $\sim 1070\text{ cm}^{-1}$  can be attributed to Si–O-related vibrational bands from VTMOs, whereas the absorption band at 1645 and  $1547\text{ cm}^{-1}$  belong to NiPAAm, as described earlier.

The stability of these films in water depends strongly on film composition. At high concentrations of NiPAAm (Fig. 6) the deposits are not stable in water, whereas at a higher concentration of VTMOs the films become stable (Fig. 7). Unfortunately, in both cases thermoresponsive behavior is no longer observed. This observation leads us to the conclusion that even small amounts of siloxanes greatly reduce the flexibility of



**FIG. 6:** Stability of *N*-isopropylacrylamide (NiPAAm)-rich films in water (plasma polymerized NiPAAm-co-plasma polymerized vinyltrimethoxysilane).



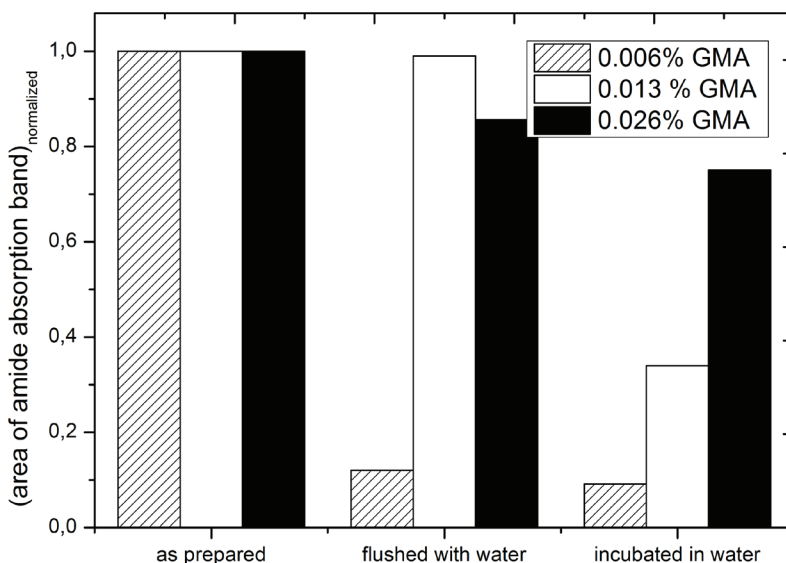


**FIG. 7:** Stability of vinyltrimethoxysilane (VTMOs)-rich films in water (plasma polymerized *N*-isopropylacrylamide-co-plasma polymerized VTMOs).

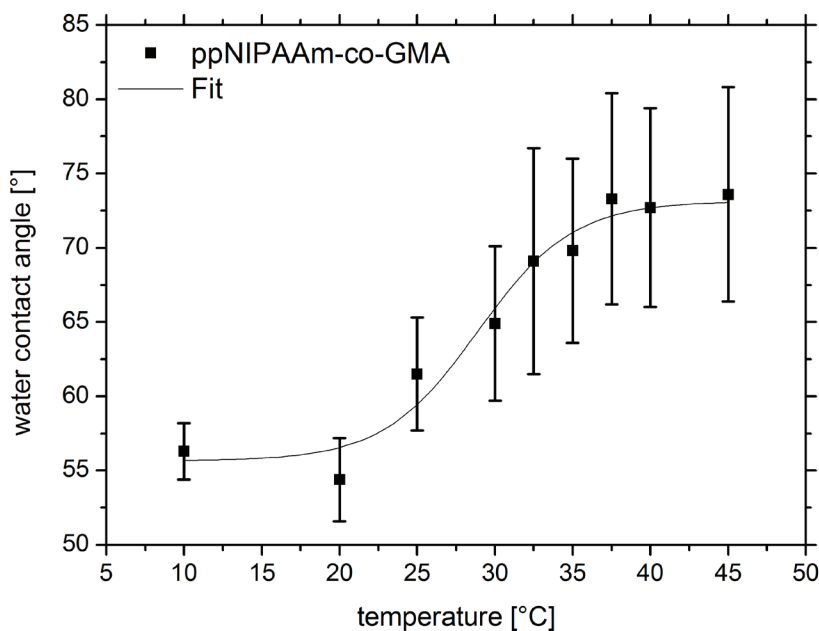
these films, so that this monomer is not suitable for copolymerization to obtain a stimuli-responsive surface.

GMA is another monomer tested for copolymerization because it has a more hydrophobic character than NiPAAm and water stability should be improved by copolymerization. Plasma copolymerization with GMA results in the formation of statistical copolymers of plasma polymerized GMA and pp-NiPAAm, with a low amount of cross-linking. Once again, we observed that film stability in an aqueous environment was dependent on the amount of the second film-forming agent within the film: At 0.026 vol% GMA in the gas phase, up to 80% of the deposit remained on the substrate (Fig. 8) after storage in water. Higher concentrations of GMA were not tested to avoid obtaining too large an amount of the methacrylic compound within the film, which may reduce the thermoresponsive properties.

Compared to the pure NiPAAm films, copolymers of NiPAAm and GMA show significantly larger water contact angles at room temperature. The thermoresponsive behavior of pp-NiPAAm-co-GMA<sub>0.026</sub> is presented in Fig. 9. Here, the temperature was elevated step-wise from 20 to 45°C before the sample was cooled to 10°C. It can be seen that the water contact angle increases by about 18°. Moreover, the effect is reversible after cooling the sample. In contrast to examples in the literature, no sharp increase in the water contact angle is observed. Lugo-Medina et al.<sup>27</sup> also described this phenomenon. They explained the continuous increase in water contact angle with cross-linking within



**FIG. 8:** Stability of plasma polymerized *N*-isopropylacrylamide-co-glycidyl methacrylate (GMA) film with different amounts of GMA in the process gas.



**FIG. 9:** Thermoresponsive behavior of plasma polymerized *N*-isopropylacrylamide-co-glycidyl methacrylate<sub>0.026</sub> (pp-NiPAAm-co-GMA<sub>0.026</sub>).

the films. Since cross-linking is not fully prevented for plasma polymerized deposits, this explanation also seems to be valid for our investigations.

After storage in water the films no longer switch their wettability at elevated temperatures. FTIR-ATR spectra show that the film thickness decreased to ~80% compared to the freshly prepared film, but no differences in film composition were observed using this technique. To detect any constitutional changes, the elemental composition on the surface before and after storage in water was analyzed using XPS. The elemental compositions of both samples are summarized in Table 1. It can be seen that the amount of nitrogen decreases after storing the samples in water. Because nitrogen is only present in NiPAAm, it is obvious that NiPAAm is washed out of the film. Assuming that the films are deposited with high retention of the monomer structure, the ratio of NiPAAm to GMA in the copolymer can be calculated from the elemental composition determined by XPS.

The molar ratio of NiPAAm to GMA,  $n:m$ , in the polymer film with composition  $-(\text{NiPAAm})_n-(\text{GMA})_m-$  is calculated as follows:

$$x_{i,XPS} = n \sum_i x_{i,\text{NiPAAm}} + m \sum_i x_{i,\text{GMA}} \quad (1)$$

$$n + m = 1 \quad (2)$$

where  $n$  and  $m$  are the molar fractions of the corresponding monomers in the copolymer,  $x_{i,XPS}$  are the results of elemental analysis of the heavy elements  $i$  (carbon, nitrogen, and oxygen) by XPS, and  $x_{i,\text{NiPAAm}}$  and  $x_{i,\text{GMA}}$  are the atomic fractions of these elements in the monomers. Therefore, the fraction of NiPAAm as calculated from the nitrogen content in the freshly prepared film is 0.22, whereas after storage in water it decreases to 0.15.

The thermoresponsive behavior can probably only be ascribed to pp-NiPPAAm oligomeric fragments on the surface, which are not covalently bound to the underlying layers. Future investigations should test experiments that prevent the formation of such unbound oligomeric fragments and thus improve the stability of thermoresponsive behavior even after soaking in water. All in all, these films show behavior similar to that of pure pp-NiPAAm, even though film stability is improved. Future investigations should focus on the stability of these films in water because this is a crucial issue for potential applications.

**TABLE 1.** Elemental Composition of Plasma Polymerized *N*-Isopropylacrylamide-co-Glycidyl Methacrylate 0.026 Determined by X-Ray Photoelectron Spectroscopy Analysis

Sample	Carbon (%)	Oxygen (%)	Nitrogen (%)
As prepared	70.96	26.26	2.78
Stored in water	71.41	26.72	1.87

The number of monomer units of NiPAAm and GMA on the surface was assessed based on the amount of nitrogen in the film.

## IV. CONCLUSIONS

This study demonstrated that plasma polymer films from NiPAAm can be deposited by a DBD at atmospheric pressure. Deposits, where the monomer structure is largely retained, show an increase in water contact angle at elevated temperatures. Unfortunately, water stability decreases with a lower amount of cross-linking. The films can be stabilized by copolymerization with suitable monomers. Cross-linking or the formation of networks must be avoided, since no thermoresponsive behavior is observed when VTMOs is used as second monomer.

Copolymers of NiPAAm and GMA show better stability in water, and thermoresponsive behavior is observed as well. But after incubating the films in water, an increase in contact angle is no longer observed. Oligomers of pp-NiPAAm or pp-NiPAAm-co-GMA probably are responsible for the thermoresponsive behavior, but these fragments are washed out of the films since no covalent bonds are present between them and the rest of the film. In summary,

Thermoresponsive films can be deposited by pulsed plasma polymerization using a DBD. In tests done to date, the effect does not remain when the samples are stored in water.

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