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Photo cross-linkable poly(*N*-isopropylacrylamide) copolymers III: micro-fabricated temperature responsive hydrogels☆

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Abstract

Micro-fabricated temperature responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels were produced by photolithographic patterning of photo cross-linkable polymers. These polymers were synthesized by copolymerization of *N*-isopropylacrylamide (NIPAAm) and 2-(dimethyl maleimido)-*N*-ethyl-acrylamide (DMIAAm). The patterning process of polymers with 9.2 mol% DMIAAm and film thickness below 5 μm in the dry state was able to depict a lateral resolution of 4 μm with insignificant shape change. In order to increase the adhesion of the swollen hydrogels, and thus, the resolution of a particular pattern, a special adhesion promoter based on a monochlorosilane anchor group and a chromophore head group was synthesized. If a silicon wafer surface was pretreated with the adhesion promoter, the structures were stable and well adhered even at lower cross-linking densities. The hydrogels are suitable as working substances for micro-actuators because of their thermally induced volume changes. The swelling ratio of the pattern at low temperatures increased with a decreased cross-linking density. As expected from the chemical composition of the gels, the phase transition temperature (T_c) decreased with increasing DMIAAm content. The swelling of microstructures in water in comparison to macroscopic objects occured significantly faster. This behavior was attributed to the small gel dimension but it was even more pronounced because of the sponge-like nanostructure of the hydrogels characterized by high-resolution field emission scanning electron microscopy. Suitable applications of these hydrogels are adjusting limbs in fluid micro-systems such as micro-pumps and micro-valves.

Keywords: Temperature responsive hydrogel; Micro-fabrication; Poly(*N*-isopropylacrylamide)

1. Introduction

Cross-linked poly(*N*-isopropylacrylamide) (PNIPAAm) is a well-known representative of those polymer networks, which show lower critical solution temperature (LCST) behavior. PNIPAAm gels undergo a phase transition in aqueous media at around 32–34 °C [2]. Those hydrogels are promising candidates for the development of micro-actuators because of their thermally induced volume changes [3,4]. At low temperatures the gel is in a highly swollen state containing more than 95 wt% of water. Above the phase transition temperature, the polymer network chains collapse. This property results in a shrunken volume state of a polymer network at elevated temperatures. Networks based on such material can be used for chemo-mechanical systems, i.e. systems transforming chemical into mechanical energy. A drawback of classical hydrogels, typically gels with mm-dimensions, is their slow response behavior to an applied stimulus. Several attempts have been made to decrease the swelling/deswelling times for such gels by changing the chemical and/or the physical gel structure [5–8].

Since the kinetics of swelling and deswelling are proportional to the square of the smallest gel dimension, reduction of the gel size to the μm-scale should be very effective in decreasing the response time [9–11]. For

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☆ Part II: [1].

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applications of such small hydrogels, e.g. in micro-systems, the functional material has to be separated on or in appropriate microstructures. A promising method for the micro-fabrication of hydrogels is photolithography. Patterned hydrogel structures can be obtained starting from monomers and end functionalized oligomers by using a photo polymerization process [12–16]. The adhesion of the gels to the support can be enhanced, if coupling agents are used to attach micro-fabricated hydrogel patterns on silicon dioxide surfaces [14,17,18]. Recently, the photolithographic synthesis of smart hydrogels from photo cross-linkable polymers has been published [19–24].

The cross-linking reaction has been performed typically by photodimerization of hydrophobic chromophores. However, when incorporated in a temperature-sensitive polymer, these substituents produce a strong decrease in the phase transition temperature (T_c). Due to the size and the polar structure of the dimethylmaleimide group, temperature-sensitive polymers and gels with high chromophore contents and T_c values higher than room temperature (RT) are accessible [1,25,28]. Furthermore, it should be possible to use the same cycloreaction to chemically bind the hydrogels onto a surface.

In this report the micro-fabrication of temperature responsive PNIPAAm hydrogels as well as their swelling behavior is described. Suitable applications of these hydrogels are adjusting limbs in fluid micro-systems such as micro-pumps and micro-valves.

2. Experimental section

2.1. Materials

N-Isopropylacrylamide (NIPAAm, Aldrich) was purified by recrystallization from hexane and dried in vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Dioxane, tetrahydrofuran (THF), and diethylether were distilled over potassium hydroxide. All other reagents were of analytical grade.

2.2. Synthesis of 2-(dimethyl maleimido)-N-ethyl-acrylamide (DMIAAm)

The DMIAAm monomer was prepared according to the literature [25].

2.3. Synthesis of 1-[3-(chloro-dimethyl-silanyl)-propyl]-3,4-dimethyl-maleimide (3)

2.3.1. 1-Allyl-dimethyl-maleimide (2)

5.0 g (39.6 mmol) Dimethylmaleic anhydride and 11.3 g (198 mmol) allylamine were dissolved in 50 ml toluene. The mixture was refluxed with a water trap until no water was produced. The solvent and the excess allylamine were evaporated under vacuum. The crude product was purified by column chromatography with silica gel and ethylacetate/hexane 2:1 to yield 6.08 g (93%) of **2**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 5.77 (m, 1H, H-2), 5.13 (m, 2H, H-3), 4.07 (d, $J = 5.5$ Hz, 2H, H-1), 1.95 (s, 6H, CH_3).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 171.7 (s, C=O), 137.2 (s, C-4 and C-5), 132.0 (d, C-2), 117.2 (t, C-3), 40.0 (t, C-1), 8.6 (q, CH_3).

2.3.2. 1-[3-(Chloro-dimethyl-silanyl)-propyl]-3,4-dimethyl-maleimide (3)

In a heated flask 0.5 g (3 mmol) of **2** was dissolved in 5 ml (45 mmol) monochlorodimethyl silane in an argon atmosphere. The solution was cooled to −5 °C and three drops of a 3 wt% solution of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane/platinium (0)-complex in xylol were added. The mixture was stirred for 1 h at −5 °C and subsequently overnight at RT. The solution was evaporated in vacuum to give **3** in quantitative yield.

^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) = 3.46 (t, $J = 4.2$ Hz, 2H, H-1), 1.93 (s, 6H, CH_3), 1.64 (m, 2H, H-2), 0.76 (m, 2H, H-3), 0.37 (s, 6H, Si–CH_3).

^{13}C NMR ($CDCl_3$, 126 MHz): δ (ppm) = 172.2 (s, C=O), 137.0 (s, C-4 and C-5), 40.2 (t, C-1), 22.4 (t, C-2), 16.0 (t, C-3), 8.6 (q, CH_3), 1.4 (q, Si–CH_3).

2.4. Synthesis of the polymer

The PNIPAAm copolymers were obtained by free radical polymerization of NIPAAm and DMIAAm initiated with AIBN at 70 °C in dioxane with a total monomer concentration of 0.55 mol/l under nitrogen for 7 h. The polymer was precipitated in diethylether and purified by reprecipitation from THF into diethylether (1:3).

2.5. Characterization

The ^{1}H NMR spectra were recorded on a BRUKER DRX 500 spectrometer (500 MHz). The solvent was used as an internal reference.

The molecular weights (M_w) of the copolymers were determined by gel permeation chromatography with a JASCO instrument equipped with UV and RI detector using Waters 'Ultrastyragel' columns. The samples were measured at 30 °C in THF containing 0.3 vol% *N*-methyl acetamide as the mobile phase with a flow rate of 1 ml/min.

The adhesion promoter layer was prepared by absorbing **3** from 0.1 vol% solution in dicyclohexyl on silicon wafer activated with Piranha solution (mixture of 70 vol% concentrated sulfuric acid and 30 vol% concentrated hydroperoxide) for 1 h. The substrates were rinsed with chloroform and water and dried in an argon flow.

Film thickness data of the adhesion promoter layer were obtained with a Woollam M44 ellipsometer. The ATR-IR spectra were recorded on a Bruker IFS 66 with MCT detector. XPS characterization was performed with a Physical Electronics PHI 5700 ESCA system.

Thin films on silicon wafers (100) were obtained by spin coating with a 20 wt% solution of the polymer in cyclohexanone. The patterning of the dry polymer films was performed using a common mask aligner (Electronic Vision) with a 350 W mercury lamp producing irradiance at the wafer plane of approx. 8–12 mW/cm^2. The wavelengths of the irradiation effective for the photoreaction investigated were 365, 405, and 436 nm.

The temperature dependent swelling behavior of the hydrogel layers was measured by optical microscopy on a HUND microscope. Spin coated and photo patterned hydrogel films on silicon substrates were swollen in cold water, and then the layer thickness from a 90° side view was observed while successively increasing the bath temperature. Equilibrium swelling was obtained instantly while the water bath was warmed. However, the samples were kept at constant temperature for at least 5 min. The swelling ratio at a certain temperature was determined by the ratio of the layer thickness in the swollen/shrunken state and the thickness in the dry state.

For high-resolution field emission scanning electron microscopy (FESEM), the dry hydrogel as well as the hydrogel rehydrated for a few hours in bidistilled water at RT and at approx. 35 °C were prepared. Samples of these three particular states each supported by a silicon wafer were rapidly frozen by plunging into liquid ethane (cooled to approx. − 196 °C) to avoid ice crystal formation (vitreous ice embedding). After this the frozen samples were transferred in the high vacuum chamber of a freeze-etch device (BAF 300 with turbo molecular pump, Balzers/Principality Liechtenstein). Freeze-drying was performed within 6 h at approx. − 80 °C and at a pressure of about 5×10^{-6} Torr. Subsequently the samples were rotationally coated with 1.5 to 2 nm Pt/C at an elevation angle of 65° to provide a sufficient electrical conductivity at their surface. The film thickness was measured with a quartz crystal film thickness monitor (Balzers QSG 201D, Balzers/Principality Liechtenstein). Secondary electron micrographs were recorded in high vacuum ($p = 5 \times 10^{-7}$ Torr) at RT with an 'in-lens' FESEM (type S-5000; Hitachi Ltd./Japan) at 2 and 5 kV acceleration voltages, respectively. Most of the micrographs were recorded with the first scan to keep the electron dose as low as possible.

3. Results and discussion

3.1. Copolymer synthesis and characterization

Copolymers of NIPAAm and DMIAAm can easily be prepared by free radical polymerization in dioxane using AIBN as initiator at 70 °C. The molecular weight of the copolymers was about 60,000 g/mol. With increasing DMIAAm content the molecular weight of the polymer decreased [26]. Aqueous solutions of the copolymers showed LCST behavior. The phase transition temperatures of the aqueous solutions of these copolymers decreased with increasing comonomer content and disappeared at DMIAAm contents at or above 15.9 mol%. For DMIAAm contents lower than 10 mol% the T_c is higher than RT and thus, these polymers are suitable substances for use as precursor polymers in the preparation of thin patterned hydrogels for micro-actuators [26].

3.2. Adhesion promoter

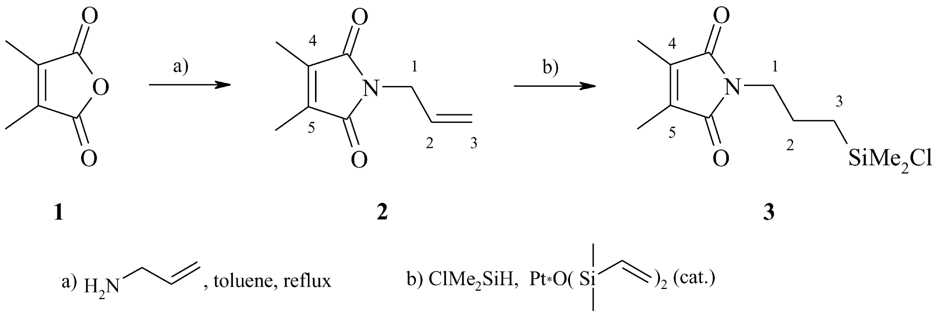
The surface adhesion of swollen hydrogel film pattern revealed as the most serious problem. One reason was the extreme changes of the degree of swelling (feature height changes of up to 10 times that of the dry state) causing a high strain at the hydrogel-substrate interface. Therefore, a special adhesion promoter based on a monochlorosilane anchor group and a chromophore head group has been developed. The synthesis of the adhesion promoter is shown in Scheme 1. The adhesion promoter was applied by absorption from solution on an activated silicon wafer. Due to the chlorodimethylsilane anchor group, which is not capable for polysiloxane gel formation [27], smooth films with a layer thickness of 0.5 nm were obtained. The existence of the adhesion promoter at the surface was proven by ATR-IR spectroscopy and XPS analysis. The ATR-IR spectra of the interface (Figure 1) shows a signal between 2980 and 2870 cm^{-1} arising from the C–H vibration and a signal at 1703 cm^{-1} arising from the C=O vibration of the adhesion promoter. XPS analysis of the surface with a take off angle of 5° showed two different signals for Si and O and three different signals for C. The element signals and the assignments are listed in Table 1.

3.3. Photo patterning

In addition to the weak influence of the DMIAAm monomer on T_c of the photo polymer, the DMI-chromophore was selected for cross-linking because it is known to form stable dimers (Scheme 2). As usual for [2 + 2] cyclodimerizations, the reaction is not influenced by oxygen. Thus, the cross-linking can be performed under

Table 1
XPS analysis of the adhesion promoter coated Si/SiO$_2$ surface (take off angle 5°)

Element	Energy (eV)	Rel. intensity	Assignment
Si 1	102	27	Silyl
Si 2	103.5	73	SiO$_2$
C 1	285	72	CH$_2$
C 2	286	18	CH$_3$
C 3	288	10	C=O
N	400	80	Imide
O 1	531	28	Silyl
O 2	533	72	SiO$_2$



Scheme 1. Synthesis of the adhesion promoter.

laboratory conditions. By using thioxanthone as the photo sensitizer complete conversion of the chromophores could be achieved within a few minutes [28]. Thin films of photo cross-linkable polymers were deposited onto Si/SiO_2 surfaces using spin coating. The film thickness could be set between 1 to 20 μm by varying the concentration of the polymer solution and/or the velocity of rotation. The introduction of an additional commercially available adhesion promoter (hexamethyl disilazane (HMDS)) did not only increase the adhesion, but it also improved the initial wetting behavior of the polymer solution. By the use of the synthesized adhesion promoter **3** the hydrogel pattern was covalently attached to the surface (Scheme 3) during the cross-linking process. The films were irradiated with UV light through common chromium masks for different exposure times (1–16 min). The yield of hydrogel formation increased with increased irradiation time [23]. The patterns used for this investigation were obtained after 16 min exposure time. The photo patterning turned out as a negative process where the hydrogel is formed at exposed areas and left soluble polymer at unexposed areas. Features with 9.2 mol% DMIAAm and a thickness below 5 μm in the dry state could depict a lateral resolution of 4 μm with insignificant shape change (Fig. 2). However, due to the high swelling of the gels with a lower cross-linking density it was hardly possible to depict pattern with a small contact area after the development (Fig. 3(a)). In addition, at high initial film thickness some of the larger pattern lost adhesion, too. This resulted in displaced or even disappeared pattern (Fig. 4(a)) presumably due to the fact that the adhesion forces were too weak to fix the thick physically adsorbed gels on the surface. In contrast to the well-adhered gel pattern, the displaced pattern could swell isotropically. During drying, these patterns were fixed in a stretched form on the surface again. The estimated gel volume of the well adhered and the displaced gel dots were very similar proving a uniform cross-linking process.

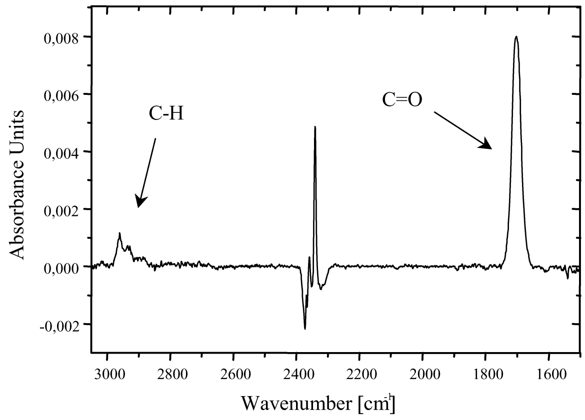


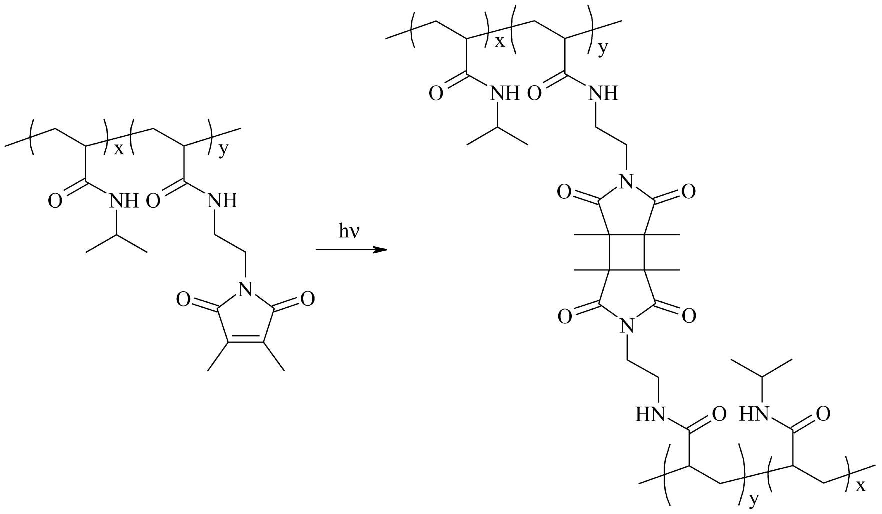
Fig. 1. ATR-FTIR spectrum of the adhesion promoter attached to a silicon wafer.

Hence, the adhesion promoter **3** was used to chemically bond the gels onto the wafer surface by the same reaction used for cross-linking. If the silicon wafer surface was pretreated with the adhesion promoter **3**, the structures were stable and well adhered (Figs. 3(b) and 4(b)).

3.4. Swelling properties

The patterned microdots $(250\ \mu m)^2$ swelled in cold water up to 10 times in height compared to their dry state. The swelling ratio (ratio of film thickness in the swollen state (d) and dry film thickness (d_0)) in dependence on the temperature for different cross-linking densities is shown in Fig. 5. With a decreased cross-linking density the swelling ratio at low temperatures increased. By raising the temperature above T_c all gels collapsed to nearly the same swelling ratio. The resulting data were quantified through fitting with a sigmoidal curve. T_c^{sig} is defined as the inflection point of the sigmoidal curve. For applications, however, the onset values of the swelling curves are of particular interest. In a conceivable actuator application of the gel in a micro-valve, only a part of the swelling curve will effectively be used, because of the restricted space in a flow channel [28]. In those cases the transition temperatures of the gels are better interpreted in terms of the onset values of the swelling curves. T_c^{ons} is defined as the transition of the swelling curve from a completely shrunken state to the swollen state. The phase transition temperatures are listed in Table 2. As expected from the chemical composition of the gels, T_c decreased with increasing DMIAAm content. The obtained T_c^{sig} values were in the range of the transition temperatures of the prepolymers, which is in agreement with recent findings [29].

The swelling of microstructures in water occurred

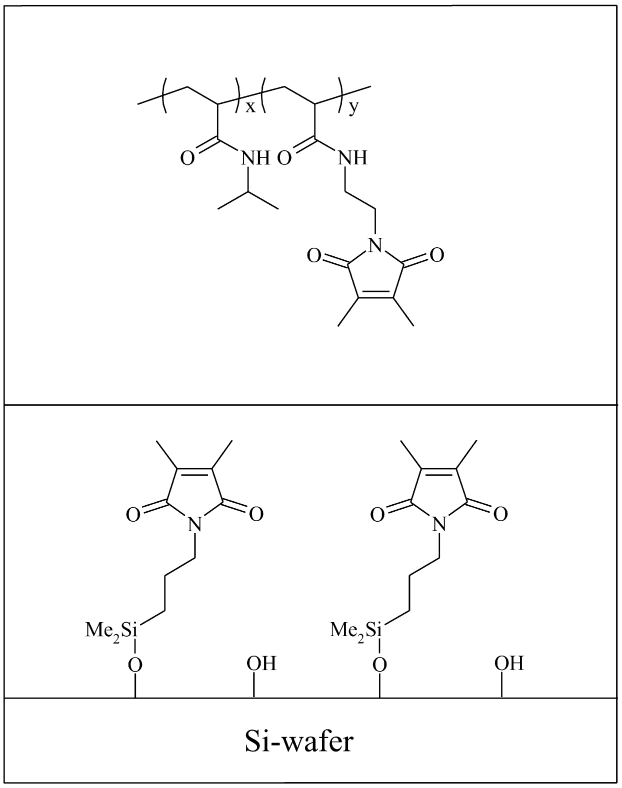


Scheme 2. Cross-linking reaction of the photo polymers.

Table 2
Phase transition temperatures of micro-fabricated hydrogels and their prepolymer solution

Chromophore content (mol%)	T_c^{sig} (°C)	T_c^{ons} (°C)	T_c^{soln} (°C)[a]
2.6	26.7	31.7	30.0
4.5	25.5	30.2	28.0
9.2	17.8	23.9	24.7

[a] Determined by DSC [25].



Scheme 3. Schematic picture of the gel attachment to the silicon wafer.

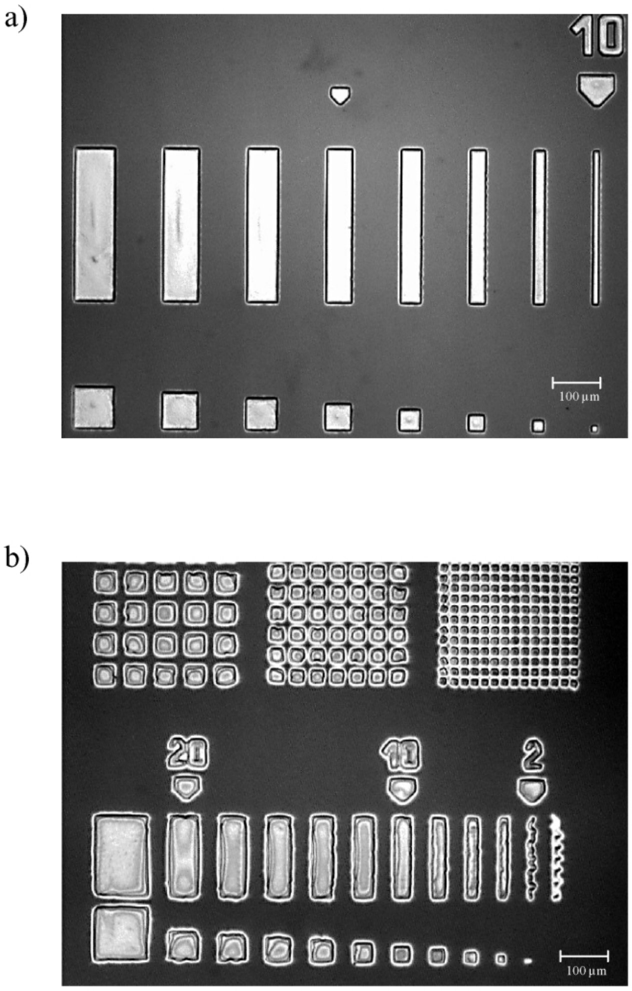


Fig. 2. Optical micrographs of micro-patterned hydrogels (9.2 mol% DMIAAm) on a HMDS pretreated Si wafer having (a) 10–80 µm pattern and (b) 1–30 µm pattern, respectively.

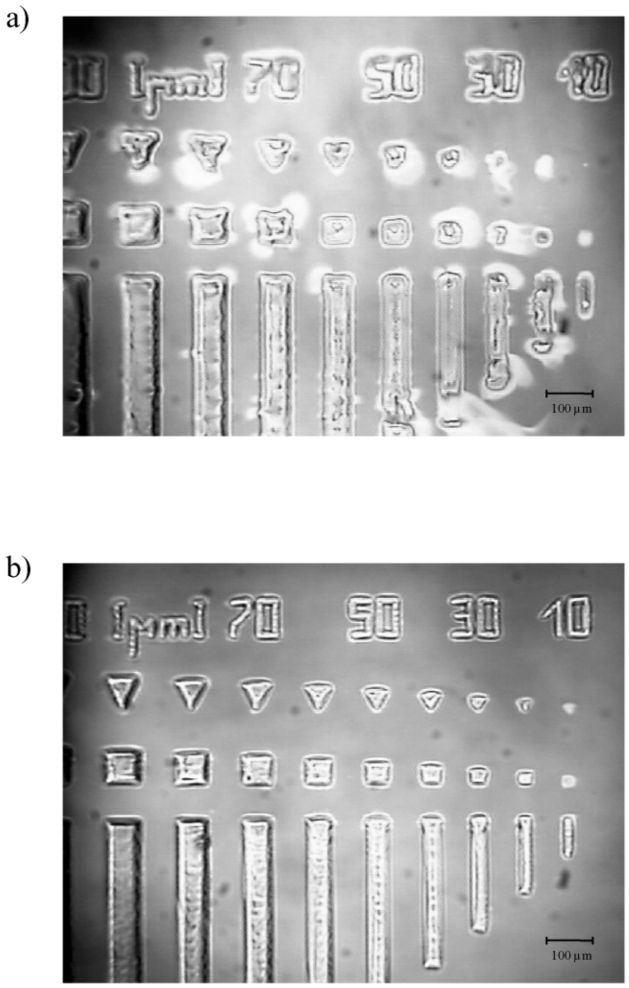


Fig. 3. Optical micrographs of micro-patterned hydrogels (4.5 mol% DMIAAm, thin films). (a) HMDS pretreated Si wafer with a structure height of 650 nm; (b) DMMI pretreated silicon wafer with a structure height of 770 nm.

significantly faster in comparison to macroscopic objects. Measurements yielded times of swelling in the one-second range (2–8 s) for swelling from the dry state. However, swelling transitions from hydrated states (swollen to shrunken state and vice versa) should occur faster. The temperature-induced swelling/deswelling of thin PNIPAAm hydrogel layers occurred too fast to obtain reliable data by optical microscopy. The swelling/deswelling followed immediately the temperature gradient applied to the water bath. Hence, the swelling/deswelling kinetics was dominated by the heat capacity of water as the swelling solvent. In consequence, the kinetics of thermally induced phase transitions of the presented system in water is indeed very fast.

3.5. Field emission scanning electron microscopy (FESEM)

Silicon wafers covered with dry or rehydrated hydrogels were investigated by FESEM [30]. Water was chosen as the solvent to ensure that no crystallization took place within

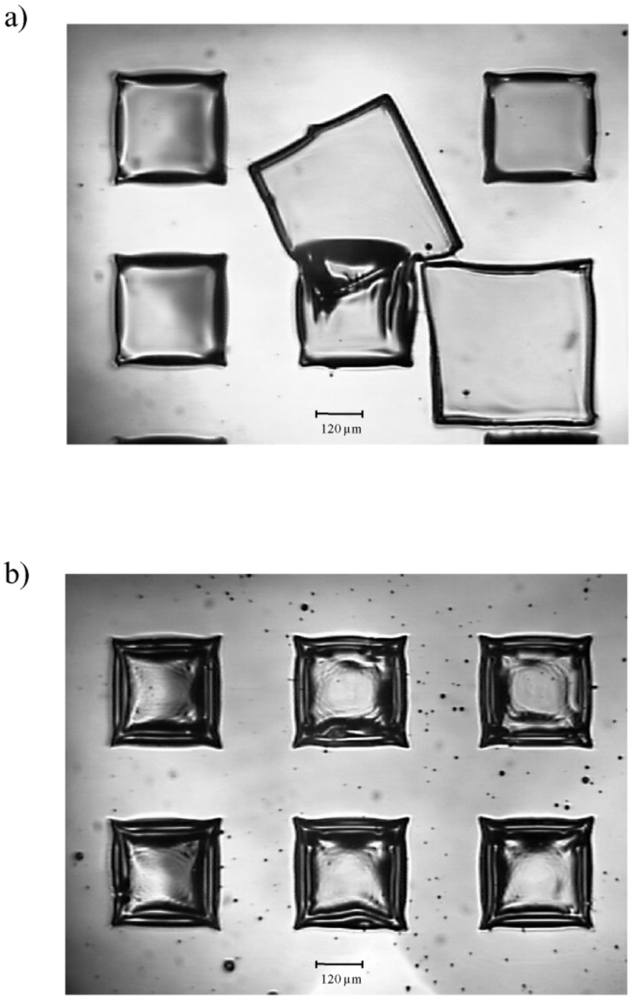


Fig. 4. Optical micrographs of micro-patterned hydrogels (4.5 mol% DMIAAm, thick films). (a) HMDS pretreated silicon wafer with a structure height of 4.6–13.8 µm; (b) DMMI pretreated silicon wafer with a structure height of 12.9 µm.

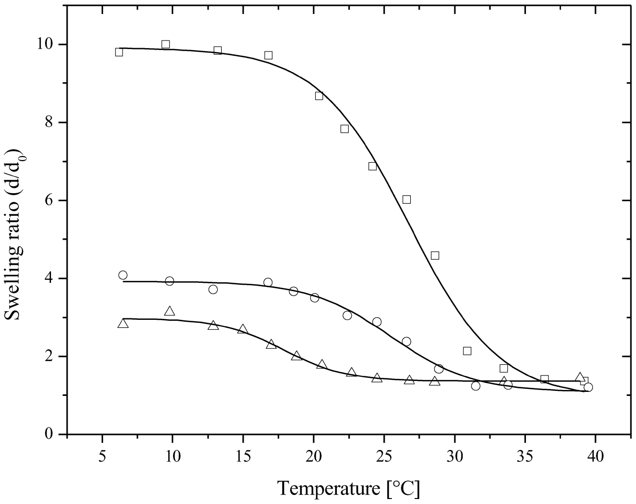


Fig. 5. Swelling ratio of micro-patterned hydrogel layer with different DMIAAm contents (□, 2.6 mol%; ○, 4.5 mol%; △, 9.2 mol%) (solid lines: sigmoidal fits).

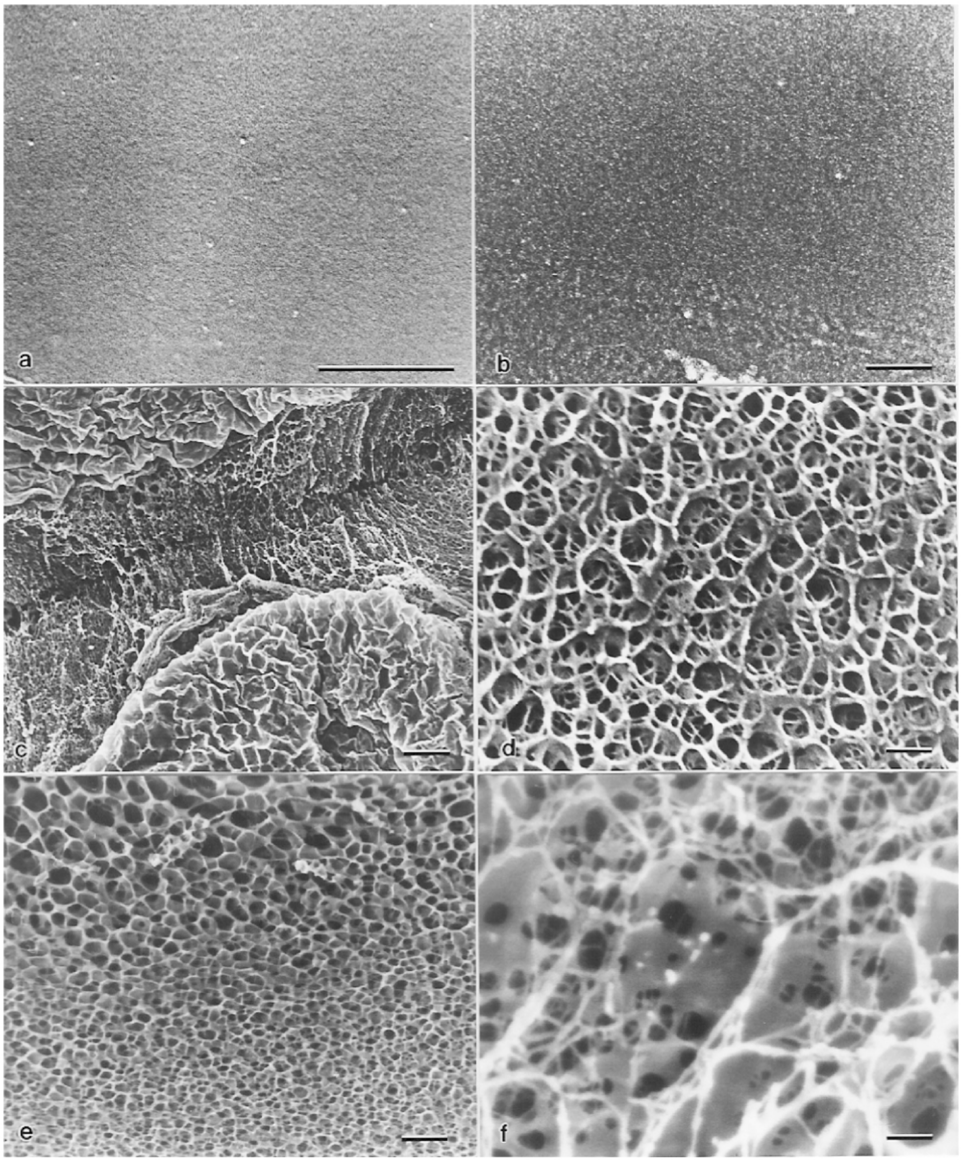


Fig. 6. FESEM micrographs of a micro-patterned hydrogel (4.5 mol% DMIAAm). The micrographs show the hydrogel in the dry state, swollen in water below T_c (approx. 22 °C), and shrunken in water above T_c (approx. 35 °C) at different magnifications. The bars correspond to 500 nm (a, c, and e) and 100 nm (b, d, and f), respectively.

the gels. The gel structure can clearly be observed at low electron energy. Typical micrographs are shown in Fig. 6. The preparation process of the micro-fabricated hydrogel by spin coating and development in a thermodynamically good solvent for the soluble prepolymers yielded a hydrogel with an extremely smooth surface in the dry state (Figs. 6(a) and (b)). The swollen state of the hydrogel both at RT and at 35 °C is characterized by three-dimensional sponge-like features, which consist of many small cavities that absorb solvent in a network of connected fibers of the polymer rich phase. At RT the cavities have typically a mean size of 50–500 nm, and the fibers have a minimum diameter of approx. 10 nm (Fig. 6(c) and (d)). The actual size of the cavities strongly depends on their location within the 250 μm-micro-dots. Their mean size is in the lower part of the size-range for locations in the central area of the microdots and in upper part of the size-range for locations at the rim of the microdot. Caused by swelling on one hand and geometric constraints on the other hand it seems understandable that at various locations different tensile forces may occur. After heating to 35 °C the gel collapsed. The micrographs show that the gel is still porous with three-dimensional sponge-like features. The mean size of the cavities decreased and their overall appearance was more irregular (Fig. 6(e) and (f)). This may be caused by deswelling and existing geometric constraints similar to the effect mentioned above.

The sponge-like structure is very likely the reason why the swelling/deswelling times of these gels were much faster than predicted by the theory [11,31]. The relaxation time of swelling τ can be estimated from the following relationship

[11]:

$$\tau \propto \frac{r^2}{D_{\mathrm{coop}}} \quad (1)$$

where r is the smallest gel dimension in the swollen state and D_{coop} is the cooperative diffusion coefficient of the network in the swelling solvent (D_{coop} for PNIPAAm/water $3 \times 10^{-7}\ \mathrm{cm^2/s}$ [10]). The real time response of the gel depends on the gel geometry and is always larger than τ. Analyzing various gel geometries showed that the gel response was mainly determined by the smallest gel dimension. Thus, the influence of the gel geometry can be neglected for our estimation. For a 50 μm thick, swollen hydrogel pattern, τ was calculated to be 83 s. Taking this τ-value into account, swelling of the hydrogel layer should occur within 4 min [9]. In contrast, the complete swelling/deswelling of the investigated photo patterned hydrogels occurred within a few seconds or even faster. This behavior can now evidently be explained by the sponge-like structure of these hydrogels having characteristic dimensions of three orders of magnitude smaller than the gel pattern. The transition for 50 nm-sized gels should occur within 0.3 ms.

4. Conclusion

The photolithographic patterning of PNIPAAm photo polymers is a suitable way to prepare micro-fabricated thermo-responsive hydrogels. The patterning results obtained on a HMDS pretreated Si-wafer were sufficient for the proposed applications. Pattern with lateral dimensions down to 4 μm at reasonable film thickness of this highly swellable material could be obtained. For advanced applications, the resolution properties and the adhesion of the gels were increased by the use of a specially designed adhesion promoter. The swelling properties of the resulting pattern could be adjusted either by the chromophore content of the photo polymer or by the irradiation time.

The investigated gels showed response times faster than 2 s. This was much faster than expected taking into account the sizes of the pattern only. It has been shown that this behavior is attributed to the sponge-like nanostructure of the hydrogels having characteristic dimensions of three orders of magnitude smaller than the gel pattern. Based on these polymers, tailor-made and cheap micro-valves and micro-pumps can be developed and applied as yet unrivalled in different fields of micro-technology.

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