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Photocrosslinking of Thin Polymer Films – Materials for Sensors and Actuators

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SUMMARY: Polymers with temperature dependent degrees of swelling, especially polymers which exhibit lower critical solution temperature (LCST) behaviour in aqueous solutions, are of interest for applications in microsystems. For these applications it is necessary to form and pattern thin films in the µm-range. This has been achieved through photocrosslinking of linear prepolymers.
Copolymers based on N-isopropylacrylamide (NIPAAm) were modified with a stilbazolium salt chromophore to yield photocrosslinkable temperature sensitive polymers. The chromophore reacts via a [2+2]-cycloaddition under irradiation, this can be used to crosslink the polymer. The photocrosslinking properties were studied by UV irradiation of thin films and measuring the changes in UV absorption spectra. Through irradiation of thin films through a mask it was possible to obtain patterned networks in the µm-range (20 µm space width and > 50 µm line width). The polymers exhibited LCST behaviour, which was measured using DSC. The resulting patterned networks had temperature dependent swelling properties in aqueous media.

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Introduction

The properties of polymer gels are between those of a liquid and a solid. These properties make them very interesting for intensive studies. Polymer gels can be easily deformed by external stimuli, so that they generate force or execute work on the external environment. If such responses can be translated from the microscopic level (i. e. dimensions of polymer chains) to a macroscopic scale, the conversion of chemical free energy into mechanical work should be realized. As early as 1948 it was found that water-swellable polymer gels can convert chemical energy directly into mechanical work.[1,2] Since then such systems were called "Chemomechanical systems". These first studies were carried out on polyelectrolyte gels changing their state of ionization.[3] Later phase transition behaviour was also found to occur with nonionized gels.[4] The main focus in this direction is the investigation of polymers which exhibit a lower critical solution temperature behaviour (LCST). A famous example of this class is poly(N-isopropylacrylamide) (PNIPAAm), which shows a reversible phase transition coupled with swelling-deswelling upon heating and cooling.[5-9] However, there are other mechanisms e. g. photoinduced transitions.[10,11]

To use these effects in actuators the change of the swelling degree must also occur under pressure. To maximize the executed work the changes in swelling degree and the swelling pressure must be optimized. Therefore, phase transitions in polymer gels are of great interest, because they are often accompanied with a big change in swelling degree and during phase transition with a strong swelling pressure. The most important point is that all this is often caused by a small change of the environmental conditions.

Results and Discussion

Bulkgels (i. e. gel samples in the mm-range) can easily be prepared and modified and the effects of changes in the environmental parameters can be investigated. But the kinetics of swelling and deswelling in these gels are typically governed by diffusion-limited transport of the polymeric components of the network in water, the rate of which is inversely proportional to the square of the smallest dimension of the gel.[6,12] Thus, the response times of the gels are very slow. However, it is possible to decrease the response time, e. g. by changing the synthesis conditions.[13]

Since the kinetics of swelling and deswelling are proportional to the gel dimensions, reduction of the gel size to the µm-scale should be very effective in decreasing the response time.[14] In such cases applications in microsystems are conceivable.[15] In order to investigate these systems networks of sensitive polymers in the µm-range were prepared.

As a result of this work it could be shown that photocrosslinking of linear polymers based on PNIPAAm is a potential way to solve this problem.[16] Photocrosslinking of a linear polymer is advantageous of two reasons: Thin films can be easily prepared and networks can be formed from defined polymers. As a photocrosslinking reaction, a well defined reaction like a [2+2]-cycloaddition should be used to control the crosslinking process. A stilbazolium salt was chosen as the chromophore, because it consists of two structural parts. One is a hydrophobic moiety (stilben backbone), which is necessary for the crosslinking reaction and the other is a hydrophilic domain (pyridinium group with a positive charge), which was selected to compensate for the decrease in the LCST caused by the hydrophobic substituents. The chromophore can be synthezised in three steps from common chemicals.[16]

Several PNIPAAm copolymers with acrylamides bearing carboxylic groups were prepared by free radical polymerization.[17] Acrylic acid can also be used instead of this special monomer. The polymer analogous reaction of these polymers with the chromophore yields PNIPAAm-photopolymers containing different amounts of chromophore.

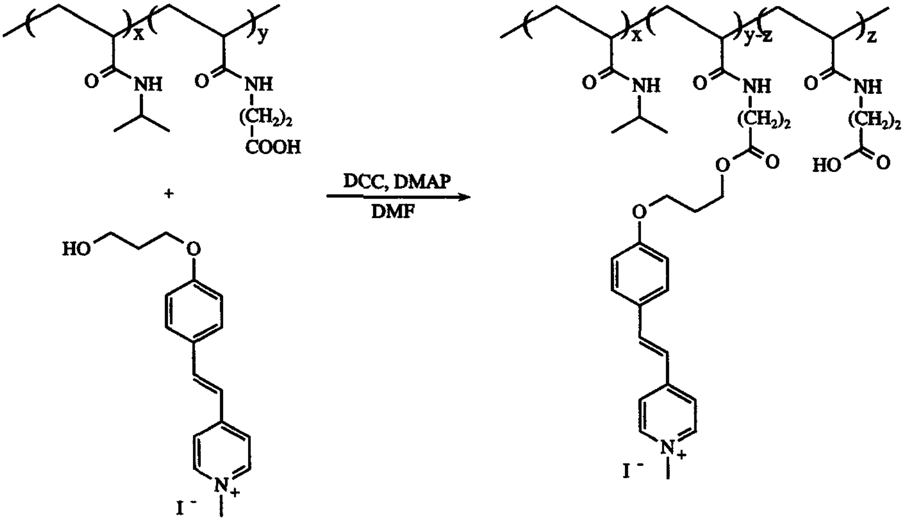

Fig. 1: Preparation of the photocrosslinkable polymers

In Table 1 the characteristics of the photocrosslinkable polymers are shown. The molecular weights are between 40 000 and 60 000 g/mol. By varying the amount of comonomer in the polymer different amounts of the chromophore could be introduced, ranging from a very low content up to a very high content. The cloud point of the prepolymer, measured by DSC, was not influenced by the comonomer content, remaining in the range of homo-PNIPAAm. But after modification the cloud point was strongly effected by the chromophore. Increasing the chromophore content decreased the cloud point of the photopolymer. Finally at very high chromophore contents the LCST behaviour disappeared.

Tab. 1: Characterization of the photopolymers

no.	polymer composition ($x_{comonomer}$)	M_w [g/mol]*	chromophore content	cloud point**	
				prepolymer	photopolymer
I	0.025	59 000	0.2 %	31.3 °C	25.6 °C
II			1.2 %		24.3 °C
III	0.053	57 000	3.2 %	31.9 °C	17.6 °C
IV	0.100	40 000	7.0 %	31.9 °C	14.1 °C
V			12.3 %		-

* with GPC (THF/0.3 % NMAA)

** with DSC (5 wt.-% solution, heating rate 5 °C/min)

As has been mentioned, two chromophore molecules are able to react via a [2+2]-cycloaddition. Coupling the chromophore with a polymer chain followed by irradiation with light of the correct wavelength leads to the formation of networks.

The formation of such junction points can be seen by a decrease of the UV absorption of the chromophore.[18] Thin films were prepared on quarz plates and irradiated with light. The UV absorption was measured after different irradiation times. Fig. 2 shows the decrease of the UV absorption at ca. 380 nm with time. This indicates that a [2+2]-cycloaddition of the stilbazolium moieties occurs, which destroys conjugation in the entire π-electron systems resulting in a decrease in the UV absorption of the stilbazolium unit. By inreasing the irradiation time to longer than 600 min the absorption could be further reduced.

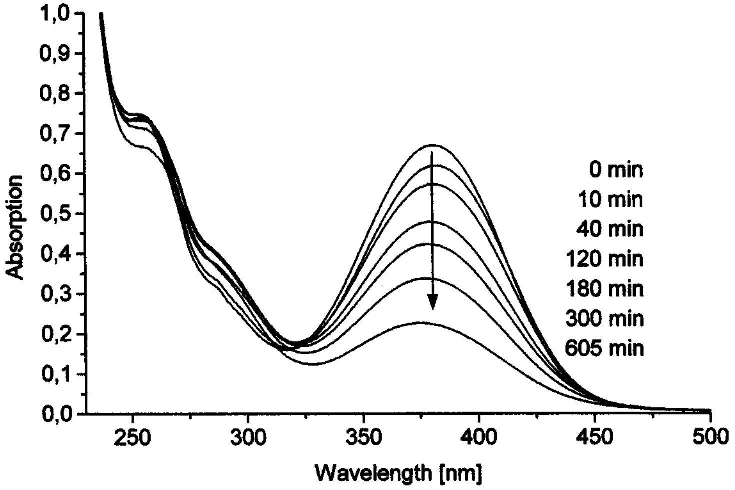

Fig. 2: Changes in the UV spectra of the photopolymer III during irradiation

In Fig. 3 the irradiation kinetics are shown. The crosslinking efficiency increased with the concentration of the chromophore. At very high chromophore contents (sample with 12.3 %) an irradiation time of only 5 min was necessary to form an unsoluble network. The stilbazolium units associate in solution and the degree of association depends on the stilbazolium concentration. After film preparation these associates were fixed in the dry film. A higher amount of associates led to a higher crosslinking efficiency. On the other hand a chromophore content of only 0.2 % was apparently not enough to form a network even with high conversion of the chromophore. Further investigations were focused on polymers with a medium content of chromophore.

One main aim of this work is the preparation of sensitive networks in the µm-range. Therefore, photocrosslinkable sensitive polymers were synthesized in order to use them in a micropatterning process, well-known in the microsystem technology. The preparation steps were as follows:[15] A thin polymer layer was produced by spin coating using polymer solutions. The film thickness in the dry state depends on a variety of parameters such as the concentration of the solution, the rotation speed during the coating process etc. The film thickness can be adjusted to between 0.5 µm and 30 µm. The next step was the photocrosslinking through a photomask. The network can only be formed in the irradiated areas. The final step was the development of the pattern by dissolving the uncrosslinked polymers. In this case water was found to be a suitable solvent.

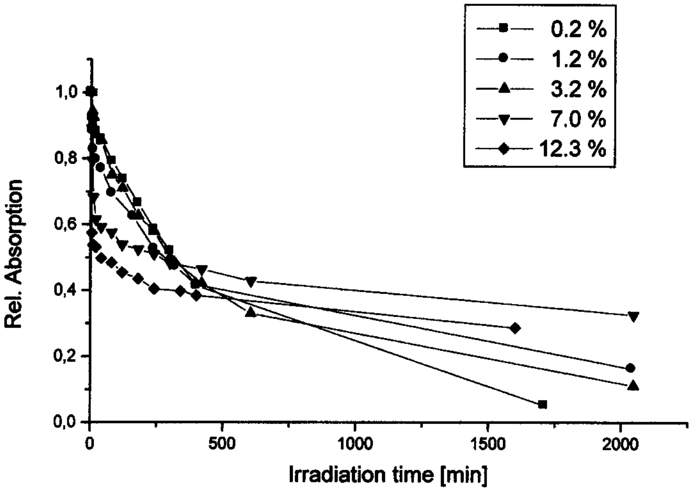

Fig. 3: Irradiation kinetics of the photopolymers

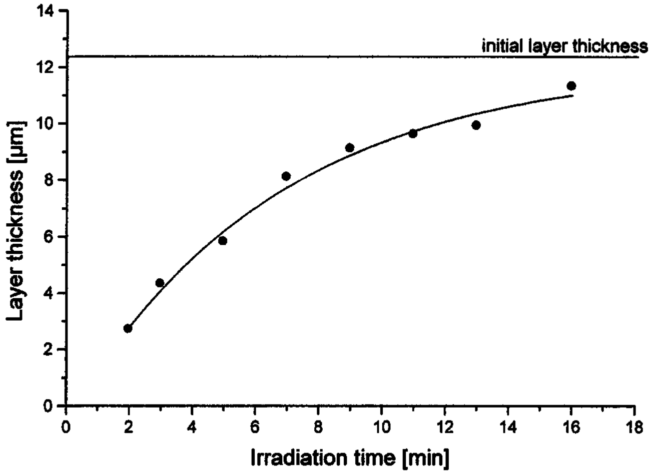

Fig. 4: Growth of layer thickness during irradiation

Another important influence on the layer thickness of the pattern was the irradiation time. In Fig. 4 it could be seen that an increasing irradiation time increased the layer thickness. During irradiation more junction points were formed and more polymer was fixed, resulting in an increase in the film thickness. The film thickness exponentially approached the value of the initial film thickness. With an increase of the irradiation time not only the amount of fixed polymer increased but also the crosslinking density. The crosslinking density plays an important role in the resolution properties of the patterning process. A loosely crosslinked network can swell during the development to very high degrees of swelling. This resulted in a high stress on the adhesion of the network to the wafer, which normally caused the network to lose contact with the wafer. The result can be seen in Fig. 5a (after 3 min irradiation time). An increase in irradiation time increased the crosslinking density and less defects in the pattern were formed. After 7 min and 11 min, respectively, the patterns are well formed for such highly swellable polymer layers.

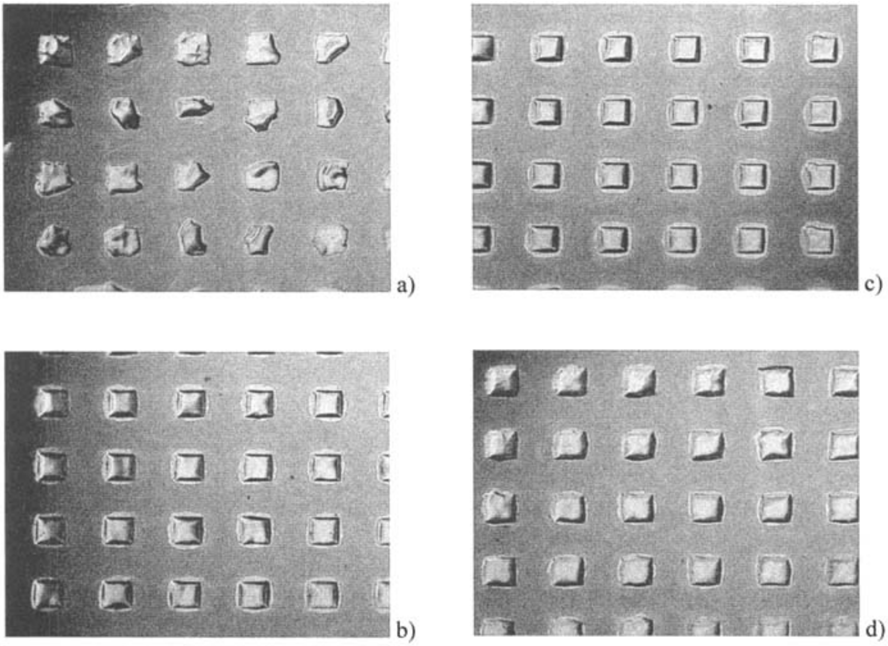

Fig. 5: Pattern of PNIPAAm-Gels after different irradiation times (3 min, 5 min, 7 min and 11 min, respectively)

To test the resolution properties of the patterning process a lot of patterns were created. One example is shown in Fig. 6. The complete wheel structure (Fig. 6a) was well depicted. The view of the outer part of this structure (Fig. 6c) shows that this structure consists of long fine polymer stripes. The view of the inner part of the structure (Fig. 6b) shows that the width of the stripes is decreased. As a result the contact area of the network on the wafer is decreased. The polymer lost contact during development and some worm like structures were obtained.

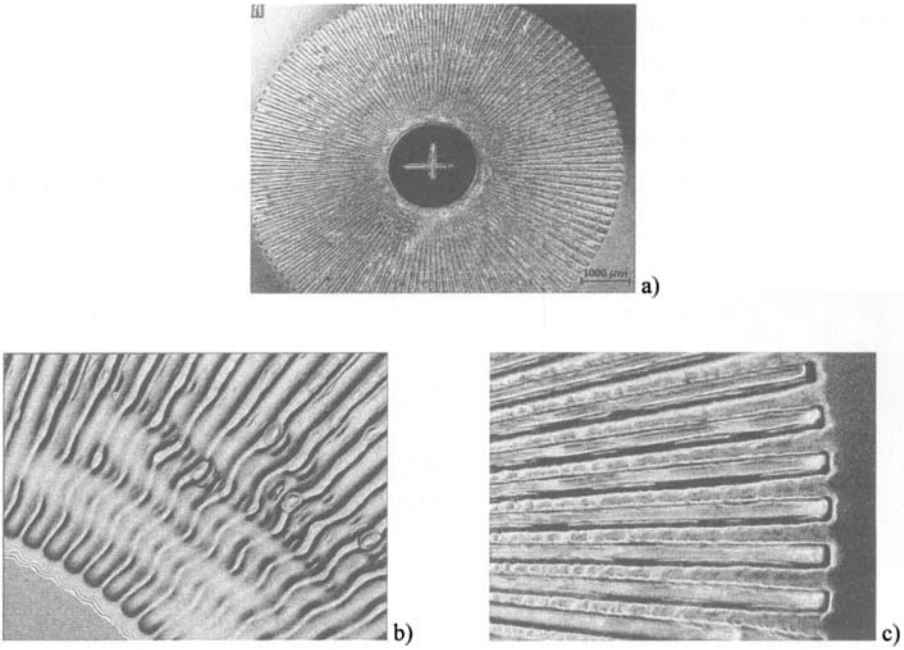

Fig. 6: Resolution properties of the patterning process

It was possible to demonstrate the temperature sensitivity of the networks. In order to do this the square patterns were immersed in water and the gel thickness could be measured by viewing the side of the pattern with a microscope. Fig. 7 shows the temperature dependent degree of swelling. At low temperatures the gel was in the swollen state. Different degrees of swelling resulted from different irradiation times and thus from different degrees of crosslinking. The gel began to shrink when the temperature was raised to above the LCST (and this is approximately the same as in the uncrosslinked state). At temperatures above 25 °C the gel was in the shrunken state independent of the degree of crosslinking. The properties of PNIPAAm bulkgels could be transfered into thin layers. The gels reached the equilibrium degree of swelling within a few seconds.

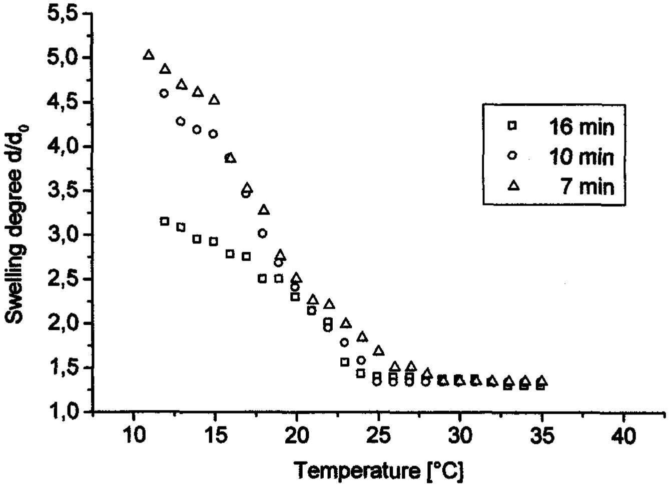

Fig. 7: Change in degree of swelling of thin crosslinked PNIPAAm-layers

Conclusion

Though the combination of temperature sensitive polymers and photodimerizable chromophores it is possible to obtain temperature sensitive networks in the µm-range. The reduction of the gel dimensions also decreases the response time of the gels down to seconds and these networks should be useful for actuators and sensors in microsystems.

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