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Photo-Cross-Linkable PNIPAAm Copolymers. 1. Synthesis and Characterization of Constrained Temperature-Responsive Hydrogel Layers

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ABSTRACT: Photo-cross-linkable co- and terpolymers of *N*-isopropylacrylamide (NIPAAm), 2-(dimethylmaleimido)-*N*-ethylacrylamide (DMIAAm) as the chromophore, and *N*,*N*-dimethylacrylamide (DMAAm) were prepared by free radical polymerization. Aqueous solutions of the co- and terpolymers showed lower critical solution temperature (LCST) behavior, and the corresponding phase transition temperature (T_c) was detected by differential scanning calorimetry (DSC). T_c decreased with increasing amount of DMIAAm, as low as 24.7 °C for 9.2 mol % DMIAAm, and increased with increasing DMAAm content, as high as 59.5 °C for 52.6 mol % DMAAm. The resulting polymers were shown to be photo-cross-linkable, and the sensitivity of the polymers toward UV light was studied by monitoring the photo-cross-linking reaction with ATR−FTIR. With 2 wt % thioxanthone as the photosensitizer, nearly full conversion could be achieved with 10 min of irradiation even though the photo-cross-linking was performed in the glassy state. Surface plasmon resonance (SPR) spectroscopy and optical microscopy were used to obtain information about the swelling behavior of thin hydrogel films. In the SPR scans the plasmon resonance minimum and the first waveguide mode were fit to Fresnel calculations to determine the refractive index (n) and the layer thickness (d) of the hydrogel. The volume degree of swelling was calculated from the refractive index, and the swelling ratio was calculated from the layer thickness. Changes in the degree of swelling, T_c, and the width of the transition (ΔT_c) were observed by changing the chromophore content and, as a result, the gel cross-linking density. For a hydrogel film with a dry thickness of 200 nm, the collapsed film thickness above T_c was around 220 nm and only weakly dependent on chromophore content. However, at temperatures below T_c, the swollen film thickness was strongly dependent on the chromophore content and ranged from 1200 nm for 2.4 mol % DMIAAm to 800 nm for 9.2 mol % DMIAAm. The reverse is true for the refractive index, which increases as the film thickness decreases. A comparison of volume degree of swelling and swelling ratio was utilized to demonstrate the high anisotropy of swelling in these hydrogel layers that were physisorbed to the substrate and therefore constrained from expanding or contracting laterally. The swollen film expanded 9.5% laterally as compared to the dry film, and this value appeared to be independent of temperature. The swelling perpendicular to the substrate ranged from 6.4% for 9.2 mol % DMIAAm at temperatures above T_c to 630% for 2.4 mol % DMIAAm at temperatures below T_c.

Introduction

Water-soluble polymers and swellable gels with thermosensitivity are of great scientific and technological importance.[1−3] The characteristics of these polymeric materials have been studied extensively as starting materials for applications such as drug delivery and separation systems.[1] The application of these materials in chemomechanical actuators has also been proposed.[2] One of the most intensively studied polymers in this field is poly(*N*-isopropylacrylamide) (PNIPAAm), which exhibits a sharp phase transition in water at 32 °C.[3] It undergoes a temperature-induced collapse from an extended coil to a globular structure, a transition revealed on the macroscopic scale by a sudden decrease in the degree of swelling of PNIPAAm gels. Networks with such behavior are often called “responsive”, “smart”, or “intelligent” hydrogels.

Because swelling/deswelling is a diffusion-controlled process, the macroscopic size of the gel plays an important role. The swelling rate is inversely proportional to the square of the characteristic dimension of the gel.[4] To improve the response time to a usable level, it is therefore necessary to reduce the gel size dramatically. Our ultimate goal is to use these materials in microsystems (e.g., microactuators) in which the gel sizes are reduced to the micrometer range.[5,6]

Photo-cross-linking of thin films of hydrophilic polymers is a convenient pathway to the preparation of network layers with micrometer dimensions. This technique has been utilized in various applications like paint, printing, adhesives, dental materials, and photoresists.[7−9] Recent interest has been expanded to the fields of surface chemistry modifications[10] and biotechnology.[11,12] Most of the photo-cross-linkable polymer systems have been based on poly(vinyl alcohol)[13−16] or polyacrylamide and its derivatives.[11,17] Despite significant development in the photo-cross-linking of hydrophilic polymers, there have been few reports on the preparation of smart hydrogels.[18−20]

The cross-linking reaction has been performed by photodimerization of chromophores like cinnamoyl,[16,17] coumaroyl,[11] and stilbene derivatives[12,13,15,21] or by decomposition of phenylazido groups.[18−20] However, these substituents are all hydrophobic, and when incorporated in a temperature-sensitive polymer, they

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produce a strong decrease in the phase transition temperature (T_c).[21,22] With a stilbazolium salt as the chromophore and a chromophore content of 3 wt %, a T_c below room temperature was obtained.[21] It has been known for several years that *N*-substituted dimethylmaleimides undergo [2 + 2] cycloadditions with exposure to light,[23] and polymers with pendant dimethylmaleimide (DMI) groups have been used in a variety of photopolymer applications.[24] Because of the size and the polar structure of the DMI group, temperature-sensitive polymers and gels with high chromophore contents and T_c values higher than room temperature should be accessible.

Experimental Section

Materials. *N*-Isopropylacrylamide (NIPAAm, Aldrich) was purified by recrystallization from hexane and dried in a vacuum. *N*,*N*-Dimethylacrylamide (DMAAm, Fluka) was distilled prior to use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Dioxane, tetrahydrofuran (THF), and diethyl ether were distilled over potassium hydroxide. All other reagents were of analytical grade.

Synthesis of 2-(Dimethylmaleimido)-*N*-ethylacrylamide (DMIAAm). The DMIAAm monomer was prepared according to the literature.[25]

Synthesis of the Copolymer. The PNIPAAm copolymers were obtained by free radical polymerization of NIPAAm, DMAAm, and DMIAAm, initiated with AIBN in dioxane. The total monomer concentration was 0.55 mol/L, and the reaction was carried out at 70 °C under nitrogen for 7 h. The polymer was precipitated in diethyl ether and purified by reprecipitation from THF into diethyl ether (1/3).

Characterization. The ^{1}H NMR spectra were recorded on a Bruker MSL 300 spectrometer (300 MHz). The solvent (acetone-d_6) was used as an internal reference. DSC measurements were carried out with a TA Instruments DSC 2920 to determine the glass transition temperature (T_g) of the polymers (T_g at $\Delta C_p/2$) and the T_c of the polymer solutions. The T_g values were measured with a heating rate of 10 °C/min, and the DSC thermograms of the polymer solutions were recorded at a heating rate of 5 °C/min. The polymer concentration was 50 mg/mL in deionized water, and the onset value of the transition was taken as T_c.[26]

The molecular weight (M_w) and the molecular weight distribution (polydispersity M_w/M_n) of the copolymers were determined by gel-permeation chromatography with a Waters instrument equipped with UV and RI detectors and using Waters' "Ultrastyragel" columns. The samples were measured at 30 °C in chloroform containing 0.1 vol % triethylamine as the mobile phase with a flow rate of 1 mL/min.

Thin polymer films for the irradiation experiments and the optical microscopy swelling experiments were prepared by spin-coating on a ZnSe crystal and a Si wafer, respectively, with a butanone solution containing 20 wt % polymer and 2 wt % thioxanthone with respect to the polymer. The UV irradiation was carried out with a 400 W UV lamp (Dr. Hönle Strahler 400F), which emitted light with a wavelength $\lambda >$ 315 nm. The ATR−FTIR measurements were recorded on a Bruker IFS 88 instrument in the range of 1000−700 cm^{-1}. After offset and baseline correction, the peaks between 755 and 725 cm^{-1} were fit with a Gaussian curve to separate the two absorption bands.

Thin polymer films for the SPR swelling experiments were prepared by spin-coating on an SPR substrate with a cyclohexanone solution containing 5 wt % polymer and 2 wt % thioxanthone with respect to the polymer. The UV irradiation was carried out with a 75 W high-pressure Hg lamp at a wavelength $\lambda >$ 300 nm for at least 60 min. The SPR substrates were LaSFN9 glass slides coated with a 50 nm gold film, which was evaporated with an Edwards 306 autocoater. A more detailed description and schematic of the experimental setup can be found in ref 27. Here, we give only a short overview of the experimental technique.

Table 1. Physical Properties of the NIPAAm/DMIAAm Photocopolymers

content of DMIAAm [mol %]					T_c [°C]	
feed	polymer	M_w	M_w/M_n	T_g [°C]	soln	hydrogel
1	0.6	33 600	1.87	141.5	30.4	
2	1.7	34 800	2.02	141.5	30.0	28.8
5	4.5	33 700	1.69	142.9	28.0	27.0
10	9.2	29 500	1.51	141.6	24.7	21.6

Surface plasmons are excited using p-polarized light, in this case a He−Ne laser beam with a wavelength of 632.8 nm. The chopped beam is reflected off the gold-coated sample, which is mounted on a $\theta/2\theta$ goniometer in the Kretchmann configuration. The reflected intensity is then monitored by means of a photodiode that is read out by a lock-in amplifier. By varying the angle of incidence, reflectivity vs angle scans can be recorded. The observed minimum corresponds to the excitation of a surface plasmon; i.e., momentum and energy of the laser beam and the surface plasmon excitation are matched. The angle of excitation depends on both the thickness and refractive index of the dielectric on top of the gold film. The same setup can also be used for optical waveguide spectroscopy when the dielectric film is sufficiently thick to act as a planar waveguide. Additional minima are observed, corresponding to the laser beam coupling into a waveguide mode. The resulting scans were fit to Fresnel calculations where the different layers were represented as a simple box model.

The temperature-dependent swelling behavior of the hydrogel layers was also measured by optical microscopy on a HUND microscope. Spin-coated and photo-cross-linked hydrogel films on a Si wafer were swollen in cold water, and then the layer thickness was observed from a 90° side view while successively increasing the bath temperature. The swelling ratio at a certain temperature was determined by the ratio of the layer thickness in the swollen/collapsed state at that temperature and the thickness in the dry state.

Results and Discussion

Temperature-Responsive Polymers. Copolymers of NIPAAm and 2-(dimethylmaleimido)-*N*-ethylacrylamide (DMIAAm) can easily be prepared by free radical polymerization in dioxane using AIBN as the initiator at 70 °C.[26] The physical properties of the NIPAAm/DMIAAm copolymers are listed in Table 1. The composition of the polymers with various comonomer contents could be determined from ^{1}H NMR spectra recorded from polymer solutions in acetone-d_6. The extended Kelen−Tüdös method provides relative reactivity ratio values of $r_{\mathrm{NIPAAm}} = 1.45$ and $r_{\mathrm{DMIAAm}} = 1.33$.[26] Thus, the DMIAAm content in the polymer was somewhat smaller than the feed composition, in the case of low DMIAAm contents. Also, with increasing DMIAAm content the molecular weight of the polymer decreased. However, no cross-linking was observed.

Aqueous solutions of the copolymers showed lower critical solution temperature (LCST) behavior. A suitable method for detecting the phase transition temperature (T_c) in aqueous polymer solutions is differential scanning calorimetry (DSC).[26,28] This method not only provides transition temperatures (onset value in the thermogram) but also supplies information about the heat of transition. The phase transition temperatures of the aqueous solutions of these copolymers decreased with increasing comonomer content and disappeared at DMIAAm contents above approximately 15 mol %.[26] For DMIAAm contents lower than 10 mol % the T_c is higher than room temperature, and thus these polymers are suitable for use as precursor polymers in the preparation of thin patterned hydrogels for microactuators.

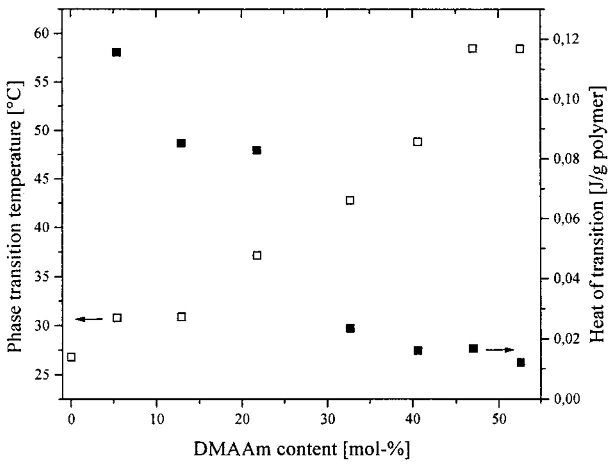
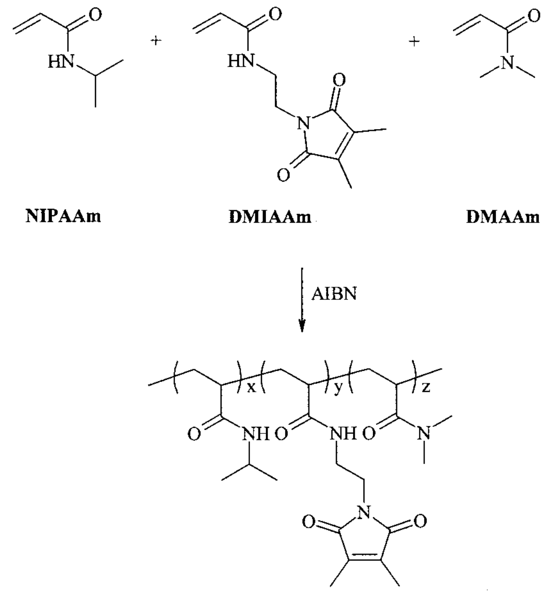


Figure 1. Phase transition temperature (open squares) and heat of transition (solid squares) of NIPAAm/DMIAAm/DMAAm terpolymers.

Scheme 1. Synthesis of the Photo-Cross-Linkable Polymers



The phase transition temperature of temperature-responsive polymers is strongly influenced by changes in the hydrophilic/hydrophobic nature of the polymer. To increase the T_c of the photo-cross-linkable polymers, terpolymers of NIPAAm, DMIAAm, and a hydrophilic, noncharged monomer, *N*,*N*-dimethylacrylamide (DMAAm), were prepared (Scheme 1). Whereas the DMIAAm feed content was at 5 mol %, the DMIAAm content in the resulting terpolymer was found to be between 2.3 and 2.9 mol %. Molecular weights were in the range of $M_w = 37\,000$ with polydispersities of $M_w/M_n = 1.9$, similar to those of the copolymers.

The phase transition temperatures and the corresponding heats of transition are shown in Figure 1. With increasing content of the hydrophilic DMAAm, T_c increased and the heat of transition decreased. It has been suggested that LCST behavior is caused by a critical hydrophobic/hydrophilic balance of the polymer side groups.[29] At low temperatures, the strong hydrogen bonding between hydrophilic groups and water leads to good solubility of the polymer in water. However, this is also accompanied by the structuring of water around the hydrophobic *N*-isopropyl group, which carries a high entropic penalty. T_c is the temperature above which the entropy term dominates the otherwise exothermic enthalpy of the hydrogen bonds. The free energy change upon mixing becomes positive, with the consequence of phase separation.[3] Hence, the heat of phase transition in an aqueous PNIPAAm solution is primarily related to the destructuring of water around the hydrophobic *N*-isopropyl groups. An increase in hydrophilicity of the polymer leads to a decrease in the amount of destructured water.[30] However, the enthalpy of mixing decreases at the same time as the entropy of mixing decreases greatly, resulting in an increase in T_c. Thus, T_c is influenced by both the amount of comonomer and its hydrophilicity.

Scheme 2. Photo-Cross-Linking Reaction

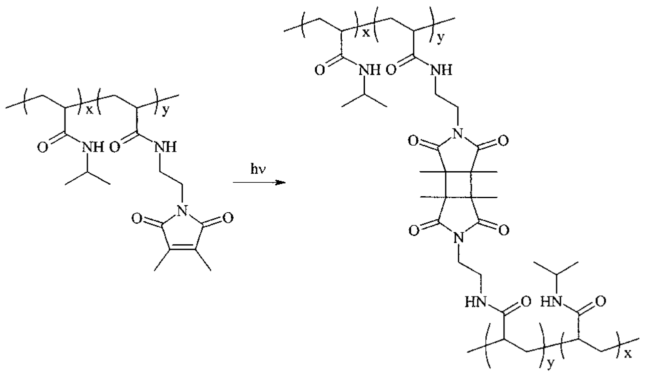


Photo-Cross-Linking. In addition to the weak influence of the DMIAAm monomer on T_c of the photopolymer, the DMI-chromophore was selected for cross-linking because it is known to form stable dimers.[24] As usual for [2 + 2] cyclodimerizations, the reaction is not influenced by oxygen. Therefore, the cross-linking can be performed under laboratory conditions.

The UV absorption of the DMI-chromophore lies in the region of 270−300 nm. Thus, the cyclodimerization requires a light source with an emission maximum in the deep UV. However, under these conditions the polymer backbone may be photochemically cleaved. The cyclodimerization of DMI must therefore be sensitized toward the near UV (360−430 nm). Thioxanthone has proven to be very efficient as a sensitizer for this purpose.[23,24] The conversion of DMI in the presence of thioxanthone was also much faster than conventional photo-cross-linking agents (reacting in a [2 + 2] cycloaddition) like cinnamoyl moieties.

Thin polymer films on ZnSe crystals were obtained by spin-coating a solution of the respective polymer with thioxanthone as the sensitizer and subsequent vacuum-drying. The substrates were placed under the UV light source, and ATR−FTIR measurements were performed after selected intervals of time. Cross-linking was effected by cycloaddition between double bonds of the DMI moieties, which destroyed the conjugation of the carbonyl moieties and led to the formation of cyclobutane rings (Scheme 2). The changes of the ATR−FTIR absorption spectra for a photo-cross-linkable copolymer (4.5 mol % DMIAAm) are depicted in Figure 2. The decrease of the vibration band at 742 cm^{-1} can be attributed to the conversion of the DMIAAm chromophore.[31] Unfortunately, the selected absorption band overlapped with another absorption band, which belongs to a part of the polymer that did not react under irradiation. To obtain kinetic information from these spectra, a deconvolution process was performed. The

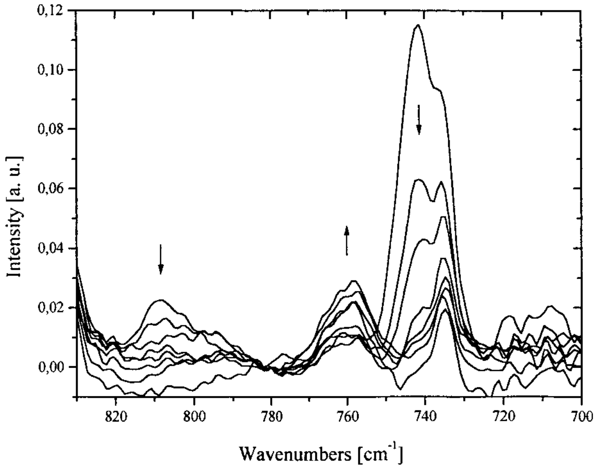


Figure 2. Changes of the ATR–FTIR absorption spectra of a photo-cross-linkable copolymer (4.5 mol % DMIAAm) with increasing irradiation time (0–60 min).

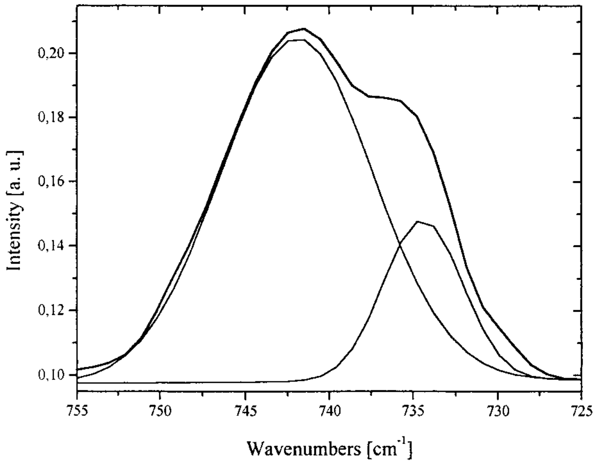


Figure 3. Deconvolution of the absorption band of a photo-cross-linkable copolymer (4.5 mol % DMIAAm) (higher energy band decreased with increased irradiation time; lower energy band remained constant).

double bands between 755 and 725 cm^{-1} were fit with two Gaussian curves (Figure 3). The integral of the absorption band at 734 cm^{-1} remained constant over the entire time of irradiation and confirmed the quality of the fits. With the integral A of the absorption band at 742 cm^{-1} at different times, the degree of cross-linking can be calculated from the following equation:

$$\text{degree of cross-linking} = 1 - A_t/A_0 \qquad (1)$$

The degree of cross-linking was plotted over the irradiation time to obtain kinetic information (Figure 4). The cross-linking reaction reached nearly complete conversion within 10 min of irradiation. The polymers showed a rate of cross-linking that appeared to be independent of the chromophore content. Assuming that the cross-linking reaction was determined by the reaction of two chromophores, cross-linking time constants of 4.6–8.4 s^{-1} were obtained. However, the cross-linking reaction is more complicated than simple second-order kinetics.

During the UV irradiation the samples were heated to approximately 80 °C due to the thermal irradiation of the lamp. However, the glass transition temperature of the polymers was in the range of 140 °C. Therefore, the cross-linking reaction still took place with the polymers in the glassy state. For the cross-linking reaction to occur, a chromophore in its excited state must react with another chromophore within the lifetime of the former. Since these chromophores are not predicted to preorganize in the polymer film, like the case of LC-forming molecules, the cross-linking reaction is attributed to the finite motion of the polymer side groups in the glassy state.

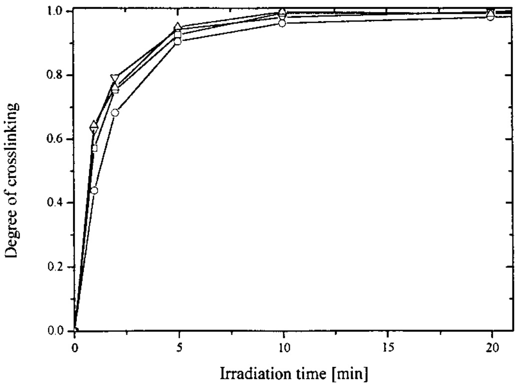


Figure 4. Kinetics of the photo-cross-linking reaction for different copolymers: ▽, 0.6 mol % DMIAAm; □, 1.7 mol % DMIAAm; ○, 4.5 mol % DMIAAm; △, 9.2 mol % DMIAAm.

Swelling. The cross-linking by UV irradiation formed water-swellable films showing LCST behavior, which could be seen from the DSC scans. In general, the peak was broader and the transition temperature was decreased by cross-linking (Table 1). A chromophore content of 0.6% was not sufficient to form a cross-linked hydrogel. This can be easily observed with optical microscopy or SPR by swelling the films in a good solvent, in this case water. The cross-linked materials are swollen by the solvent and remain intact while the un-cross-linked films dissolve. This approach can also be used to measure the fraction of material lost from a film that is not completely cross-linked.

The number of chromophores per polymer chain can be calculated from the composition of the polymers, the molecular weight of the monomers, and the number-average molecular weight of the polymers. For the copolymers with 0.6, 1.7, 4.5, and 9.2 mol % DMIAAm this was found to be approximately 1, 3, 8, and 15 chromophores per polymer chain, respectively. This explains why the copolymer with 0.6 mol % DMIAAm did not form a gel and also why the success of cross-linking for copolymer with 1.7 mol % DMIAAm was dependent on slight changes in the chromophore content and/or molecular weight caused by experimental variations. Because two chromophores are needed to form one cross-link, at least four chromophores per polymer chain are necessary for these photo-cross-linkable polymers to form a gel network. Thus, another copolymer with a feed chromophore content of 2 mol % was synthesized in benzene. The resulting polymer had a chromophore content of 2.4 mol % and a molecular weight M_w = 148 000 (M_w/M_n = 1.32), corresponding to 23 chromophores per polymer chain. T_c was 29.9 °C, and this polymer was used for further investigations.

Surface plasmon resonance (SPR) spectroscopy was utilized in order to obtain information about the swelling behavior of thin hydrogel films. SPR devices are based on the detection of refractive index changes in a thin dielectric layer on top of a noble metal surface and probed by the evanescent field of a laser beam. The reflected intensity of the beam is recorded as a function of incident angle and decreases dramatically as the light

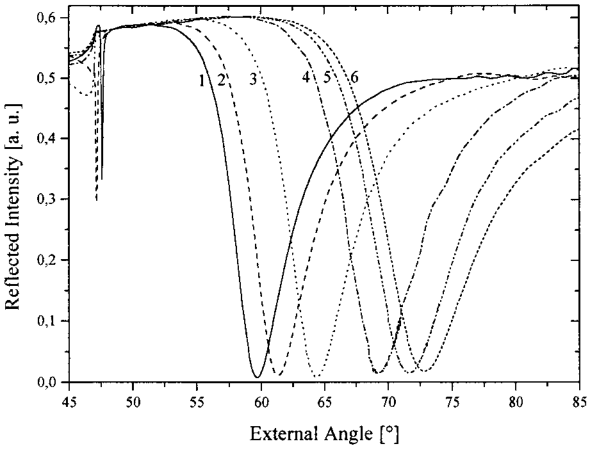


Figure 5. SPR scans of a photo-cross-linked hydrogel layer (4.5 mol % DMIAAm) swollen in water at different temperatures: 1, 14.0 °C; 2, 26.6 °C; 3, 28.6 °C; 4, 30.2 °C; 5, 31.6 °C; 6, 37.9 °C.

couples into the plasmon mode of the metal or the waveguide modes of the dielectric. The evanescent tail of the plasmon decays exponentially into the dielectric and is therefore very surface sensitive. For a known film thickness, this can be used to measure the refractive index of the dielectric film. Conversely, assuming a constant refractive index, this method can also be used for the determination of film thickness. However, for a film thickness greater than 0.5 μm it can be assumed that changes in the SPR minimum are caused only by changes in the refractive index. When the dielectric film is sufficiently thick to act as a planar waveguide (approximately 1 μm for the materials in this study), the SPR setup can also be used for optical waveguide spectroscopy. For these thicker films, the position of the plasmon minimum is sensitive only to the refractive index while the position of the waveguide modes depends on both film thickness and refractive index. Therefore, refractive index and film thickness can be determined independently. The method is nondestructive, does not require labeling, is suited for solid−air or solid−liquid interfaces including nontransparent media (as run in reflection mode), and allows for the real-time analysis of changes in the probed zone.

Figure 5 shows different SPR scans from a thin hydrogel layer (4.5 mol % DMIAAm). The scans show two important features: the SPR minimum (between 58° and 76°) and the first waveguide mode (between 47° and 48°). The resulting scans were fit to Fresnel calculations to determine the refractive index n and the layer thickness d of the hydrogel. The film thicknesses were all on the order of 1 μm in the swollen state, and therefore as discussed above, both d and n could be calculated without further assumptions. Because of the large changes in the SPR scans, the temperature-dependent change of the refractive index of water (-1.0×10^{-4} K^{-1}) is negligible.[32]

The temperature-dependent change in the refractive index n is shown in Figure 6. The resulting data were quantified through fitting with a sigmoidal curve, using the parameter n (swollen), n (collapsed), transition temperature T_c, and transition width ΔT_c (Table 2). The refractive index for the sample with 4.5 mol % DMIAAm changed from n (swollen) = 1.365 at low temperatures to n (collapsed) = 1.456 at higher temperatures, which is in good agreement with values measured on bulk hydrogels.[33]

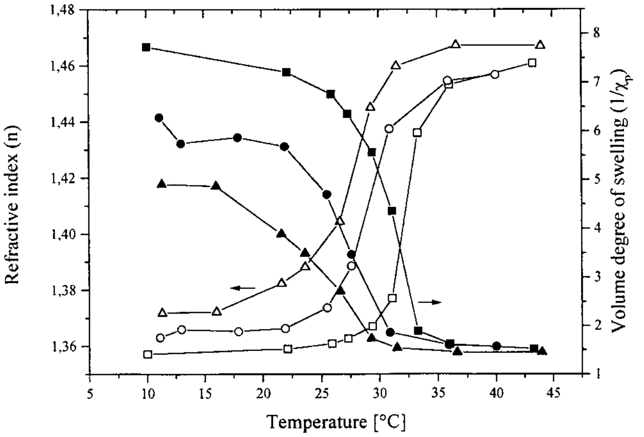


Figure 6. Refractive index (n) (open symbols) and volume degree of swelling ($1/\chi_p$) (solid symbols) of photo-cross-linked hydrogel layers: □, 2.4 mol % DMIAAm; ○, 4.5 mol % DMIAAm; △, 9.2 mol % DMIAAm.

Table 2. Summary of the SPR Results

content of DMIAAm [mol %]	dry film thickness [nm]	n(swollen)	n(collapsed)	T_c [°C]	ΔT_c [°C]
2.4[a]	201	1.361	1.459	32.4	0.9
4.5	184	1.365	1.456	29.1	1.4
9.2	211	1.374	1.468	27.6	1.8

[a] Polymer synthesized in benzene.

The obtained transition temperatures decreased with increasing DMIAAm content, which is in agreement with the DSC results. However, the T_c values from SPR measurements are slightly higher. This is most likely due to the difference in how T_c is defined by the two techniques. The sigmoidal fit defines T_c as the midpoint of the transition while DSC defines T_c as the onset of the transition. Also, DSC is a dynamic technique while the SPR measurements were performed in the equilibrium state. Therefore, it is expected that DSC will give slightly lower values for T_c. The transition width (ΔT_c) increased with increasing cross-linking density. This behavior is predicted by the Flory−Rehner theory and can also be found in bulk gels.

The refractive index of the PNIPAAm hydrogel can be correlated to the polymer fraction χ_p by a known linear relationship.[34] From these data the volume degree of swelling (reciprocal polymer fraction, $1/\chi_p$) can be calculated. The resulting curves are also shown in Figure 6. With a decreased cross-linking density the volume degree of swelling at low temperatures increased. By raising the temperature above T_c, all gels collapsed to nearly the same volume degree of swelling.

Analysis of the SPR measurements on these hydrogel films also provided information on the film thickness. For a hydrogel film with a dry thickness of 200 nm, the collapsed film thickness above T_c was around 220 nm and only weakly dependent on chromophore content. However, at temperatures below T_c, the swollen film thickness was strongly dependent on the chromophore content and ranged from 1200 nm for 2.4 mol % DMIAAm to 800 nm for 9.2 mol % DMIAAm. The reverse is true for the refractive index, which increases as the film thickness decreases, and this is consistent with the data in Figure 6. From these data the swelling ratio, calculated as the ratio of film thickness in the swollen/collapsed state and in the dry state, could be determined (Figure 7). For thick hydrogel films (ap-

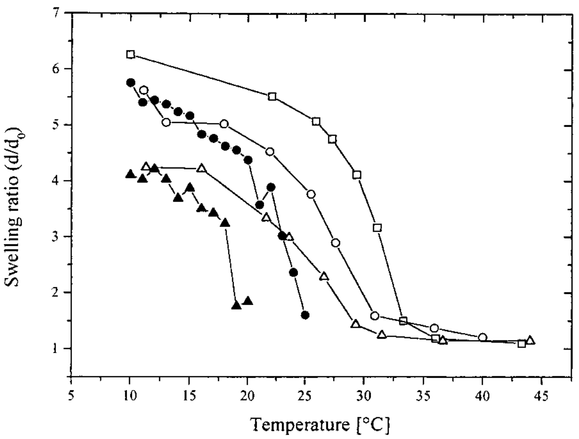


Figure 7. Swelling ratio (d/d_0) of photo-cross-linked hydrogel layers measured by SPR (open symbols) and optical microscopy (solid symbols): □, 2.4 mol % DMIAAm; ○, 4.5 mol % DMIAAm; △, 9.2 mol % DMIAAm.

proximately 10 μm dry film thickness) the swelling ratio could also be obtained by optical microscopy (Figure 7). However, this method was only suitable for hydrogel layers in the swollen state. When the temperature was increased above the transition temperature, the hydrogel collapsed and the contrast between substrate and hydrogel vanished. In the swollen state both methods yielded comparable swelling ratios. However, the transition temperatures of the thicker films were consistently lower than those of the thinner films but remained in the range of T_c obtained from DSC. This behavior is likely due to the confinement of the thin gel layer on a fixed substrate and is the subject of further investigations.

The thin hydrogel layers in this study were physisorbed to the gold substrate. In contrast to gels under free swelling conditions, this restricts the ability of the thin layers to expand and contract laterally, effectively confining the transition to one direction perpendicular to the substrate. The ratio of volume degree of swelling and swelling ratio should give an estimate of the degree of anisotropy of the swelling. For a perfectly anisotropic swelling perpendicular to the surface, this ratio equals one. Here, this ratio was found to be approximately 1.2 and independent of the temperature. In other words, on average only 9.5% of the swelling occurred laterally as compared to the dry state. In contrast, the swelling perpendicular to the surface was up to 630% for the lowest cross-linking density (Figure 7). The anisotropy of swelling was even more pronounced in the swollen state. Since the ratio of the volume degree of swelling and the swelling ratio scales with the square of the swelling ratio, the former should be an order of magnitude higher in the swollen state than in the collapsed state. These findings illustrate that hydrogel layers are highly constrained by being physisorbed to a substrate but are still able to swell laterally to some extent.

Conclusions

By the use of DMIAAm as the chromophore, photo-cross-linkable copolymers based on NIPAAm could easily be synthesized by free radical polymerization. Phase transition temperatures of the soluble copolymers between 24.7 and 58.5 °C were obtained by changing the amount of DMIAAm or DMAAm. These polymers could be efficiently converted into gel networks by UV irradiation in the presence of thioxanthone as the photosensitizer. Investigation of the swelling properties of thick films showed that T_c was only slightly influenced by the cross-linking reaction. However, by decreasing the film thickness T_c shifted toward higher temperatures, which was attributed to the confinement effect of the substrate. This effect also caused a highly anisotropic gel swelling. Lateral swelling amounted to only a few percent of the swelling perpendicular to the surface.

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