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Photochemical switching of hydrogel film properties[☆]

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Abstract

A copolymer of *N*-isopropyl acrylamide and acrylic acid was modified in a polymer analogous reaction by an acridizinium chromophore capable of reversible photochemical dimerization. The acridizinium chromophore allows a faster and more complete photocrosslinking and a better photoreversibility as compared to stilbene and stilbazolium chromophores. Due to its hydrophilic nature the chromophore only moderately affected cloud points T_c of the copolymer and lower critical solution temperatures (LCST) of photocrosslinked films of the copolymer, even at high chromophore content (3.5% w/w). Such films can be swollen in water to form hydrogels. LCST and T_c depend on the content and on the counterion of the chromophore, on the solvent from which films are prepared, and on the degree of crosslinking. The latter dependence allows the exploitation for isothermal switching of film properties by exposure to light.

Keywords: *N*-isopropyl acrylamide; Copolymer; Acridizinium

1. Introduction

Examples of hydrogels are crosslinked polymers and copolymers based on poly(*N*-isopropyl acrylamide) (PNIPAAm). These gels are known to be sensitive to several external stimuli, such as temperature, pH, and electric fields. In aqueous solution the gels swell at room temperature, while a reversible phase separation (clouding) is observed above a certain temperature, which passes through a minimum as a function of concentration. This minimum (at ca. 33 °C depending on the composition of the crosslinked polymer) is denoted as lower critical solution temperature (LCST). In most of the corresponding non-crosslinked linear polymers an analogous phase separation takes places above a cloud point temperature T_c.

Since its detection [1] there is growing interest in effects due to this phenomenon. The phase separation mechanism has been studied thoroughly [2–18] and numerous attempts to exploit the effect in sensors and actuators are described in the literature [19,20]. Most of the research on sensitive networks has been focused on bulk gels in the shape of disks and rods or on microgels. However, for applications in microsystems, in which the gel size can be reduced to micrometer ranges in order to shorten the gel response time to external stimuli, ways have to be developed to prepare such gels on supports such as silicon-wafers. This can be achieved through the UV-induced crosslinking of thin films of linear macromolecules with photodimerizable chromophores in the side chains. Temperature sensitive thin films of PNIPAAm copolymers with photodimerizable stilbene and stilbazolium (styrylpyridinium) chromophores have recently been investigated [21–23]. These materials are of potential use in microelectronic actuators. Interestingly, the properties of these films showed a dependence on the solvent in which the polymer was dissolved for the preparation of the films [23].

Since the LCST and swelling of hydrogels depend on the degree of crosslinking, it is desirable to develop gels in which this parameter can be varied or switched. Photochemical crosslinking brought about by photodimerization reactions of polymer chain substituents is suitable for this purpose, in particular, when reversible photodimerization reactions are employed. This approach is entirely different from phase separations based on permanent irradiation of chromophores in solutions of non-crosslinked PNIPAAm as described by Irie [20]. However, the introduction of photodimerizable chromophores itself influences LCST (as well as cloud point temperatures, T_c, of the non-crosslinked material), as the balance of hydrophobic and hydrophilic interactions is affected. Because cooling of microsystems

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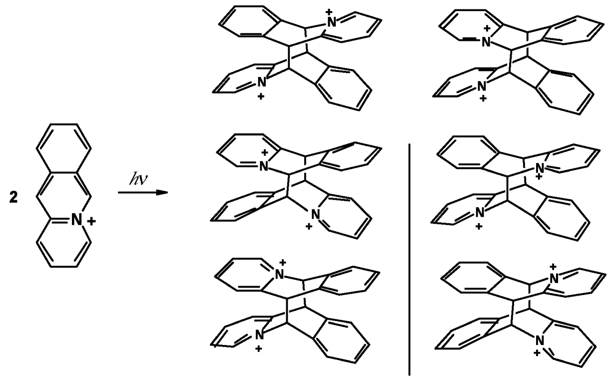

Fig. 1. Photodimerization of acridizinium cations.

may be difficult, it is important that a lowering of the T_c or LCST below room temperature should be avoided. Therefore, suitable photodimerizable substituents should not add substantially to the hydrophobic moieties of the polymer.

In this paper, we present experiments using a copolymer of NIPAAm and acrylic acid (AAc) as a prepolymer that was modified by attaching photodimerizable acridizinium chromophores to obtain photopolymers capable of forming crosslinks. We expected the positive charge on the chromophore to compensate for the hydrophobicity of the aromatic chromophore. We, therefore, studied the T_c (in the linear polymers) and LCST (in the crosslinked polymers), respectively, in this material. For comparison, PNIPAAm materials described earlier [23] (containing stilbene and stilbazolium chromophores) were included in these investigations. The chromophore content, the degree of photodimerization (irradiation time), and the anionic counterions of chromophores were varied. Moreover, the reversibility of photocrosslinking, i.e. of the photodimerization, was investigated.

Several studies on the photodimerization of acridizinium ions in homogeneous solution and in surfactant systems have been published [24–27]. Up to six isomeric photodimers are formed [26] (Fig. 1), all of which are suitable to form crosslinks in our polymer systems. The photocrosslinking of polymers bearing acridizinium substituents in their side chains has not yet been reported.

2. Experimental section

2.1. Materials

N-isopropyl acrylamide (NIPAAm) and a 1 M solution of borane in THF were purchased from Aldrich, acrylic acid (AAc) and *syn*-2-pyridinaldoxim were obtained from Fluka and *trans*-4-hydroxystilbene and *p*-(bromomethyl) benzoic acid from Acros. NIPAAm was re-crystallized from *n*-hexane. AAc was purified by distillation under reduced pressure. 2,2′-Azobisisobutyronitrile (AIBN) was purified by re-crystallization from methanol. All other chemicals were used as received. All solvents were purified by the usual methods.

2.2. Synthesis of the chromophore

4-(Hydroxymethyl) benzyl bromide (**1**). Ten grams (46.5 mmol) of *p*-(bromomethyl) benzoic acid was dissolved in 75 ml of dry tetrahydrofuran (THF). The reaction mixture was cooled to 0 °C by means of an ice bath, and dry nitrogen was bubbled through the mixture for 15 min. A 1 M solution of borane in THF (62 ml; 62 mmol) was slowly added during a 60 min period. The ice bath was removed and the reaction mixture rigorously stirred overnight. Then 60 ml of water was carefully added to destroy excess borane. The aqueous phase was saturated with anhydrous potassium carbonate, separated and extracted with two 15 ml portions of diethyl ether. The combined organic phases were dried over magnesium sulfate. The solvents were removed under reduced pressure. A white solid was obtained which was dried in vacuo to yield 8.23 g (88%) of **1**. Mp 67 °C.

^{1}H NMR ($CDCl_3$, 500 MHz) δ (ppm) = 7.39 (d, ^3J = 8.1 Hz, 2 H, Ar-H), 7.33 (d, ^3J = 8.1 Hz, 2 H, Ar-H), 4.68 (s, 2 H, HOCH_2), 4.49 (s, 2 H, CH_2Br) (Fig. 2).

1-(4′-Hydroxymethyl benzyl)-2-aldoximpyrydinium bromide (**2**). Eight grams (39.8 mmol) of **1** and 4.86 g (39.8 mmol) of *syn*-2-pyridinaldoxim were dissolved in 12 ml of dry dimethylformamide (DMF) and stirred for 6 h at 40 °C. Fifty milliliters of ethyl acetate was added to precipitate a light pink solid. The solid was filtered and dried in vacuo to yield 11.92 g (93%) of **2**. Mp 174 °C (ethanol).

^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm) = 13.12 (s, 1 H, NOH), 9.16 (d, ^3J = 6.2 Hz, 1 H, Pyr-H), 8.71 (s, 1 H, HCNOH), 8.62 (t, ^3J = 8.0 Hz, 1 H, Pyr-H), 8.43 (d, ^3J = 8.0 Hz, 1 H, Pyr-H), 8.20 (t, ^3J = 6.2 Hz, 1 H, Pyr-H), 7.49 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 7.23 (d, ^3J = 8.0 Hz, 2 H, Ar-H), 6.07 (s, 2 H, HOCH_2), 4.69 (s, 2 H, ArCH_2).

9-(Hydroxymethyl) acridizinium bromide (**3**). In 80 ml of concentrated hydrobromic acid, 11.2 g (34.8 mmol) of **2** was dissolved. Seven milliliters of acetic acid anhydride

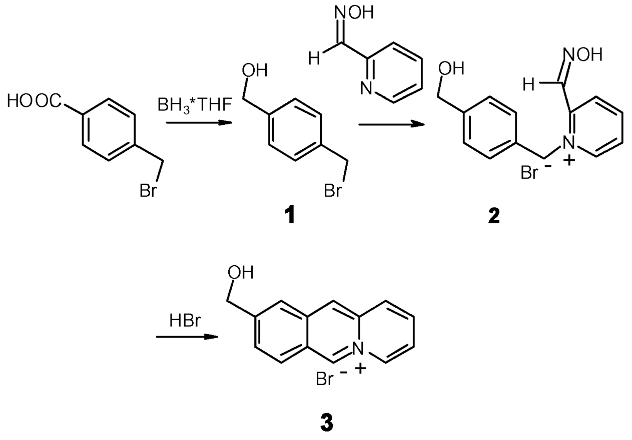

Fig. 2. Synthesis of the acridizinium chromophore.

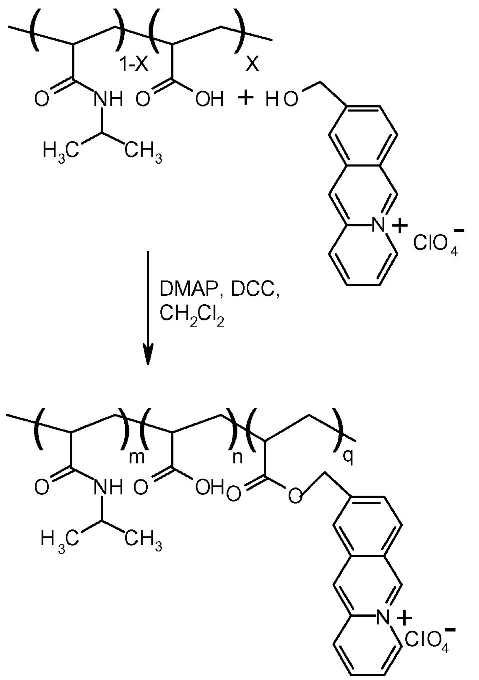

Fig. 3. Synthesis of the photopolymers based on Poly(NIPAAm-*co*-AAc).

was added and the mixture heated for 1 h under reflux. The solution was cooled to room temperature and the solvents were carefully evaporated under reduced pressure. The solid residue was re-crystallized from ethanol and dried in vacuo to give 7.47 g (74%) of dark yellow crystals of **3**. Mp 144 °C.

^{1}H NMR (DMSO-d_6, 500 MHz) δ (ppm) = 10.44 (s, 1 H, H-6), 9.30 (d, $^3J = 7.0$ Hz, 1 H, H-4), 9.22 (s, 1 H, H-11), 8.59 (d, $^3J = 8.9$ Hz, 1 H, H-7), 8.48 (d, $^3J = 8.9$ Hz, 1 H, H-8), 8.44 (s, 1 H, H-10), 8.11 (dd, $^3J = 7.9$ Hz, 1 H, H-2), 8.00 (m, 2 H, H-1 and H-3), 5.40 (s, 2 H, H-12).

The corresponding perchlorate was obtained through the addition of an excess of perchloric acid to the hot solution of **3** in water. The precipitated light yellow solid was filtered and dried in vacuo.

2.3. Synthesis of the prepolymer

The prepolymer (copolymer of *N*-isopropyl acrylamide (NIPAAm) with acrylic acid (AAc)) was synthesized through free radical polymerization in 1,4-dioxane (0.58 M monomer concentration) with AIBN as an initiator (10^{-3} mol/mol monomer) at 70 °C under a nitrogen atmosphere. After 7 h the reaction mixture was poured into diethyl ether. The copolymer was washed with diethyl ether, purified through re-precipitation into diethyl ether from a THF solution and finally dried in vacuum. The molecular weight of 70,000 g/mol of the prepolymer was obtained by GPC with polystyrene standards using THF/*N*-methyl acetamide (0.97 v/0.03 v) as the mobile phase. The polymers are expected to have a random monomer distribution due to their comparable monomer reactivity [12].

2.4. Synthesis of the photopolymers

The photopolymers were prepared by the polymer analogous modification of the prepolymer with the chromophore (Fig. 3).

General procedure. To 10.28 g of the prepolymer containing 4.4 mol% of carboxylic groups, 5.3 g (17.0 mmol) of 9-(hydroxymethyl)acridizinium perchlorate and 0.24 g (1.9 mmol) of dimethylaminopyridine (DMAP) were dissolved in 450 ml of dichloromethane. 5.21 g (25.3 mmol) of dicyclohexyl carbodiimide (DCC) was added and the reaction mixture was stirred for 68 h at room temperature. The solvent was evaporated under reduced pressure. The solid residue was dissolved in 200 ml of DMF. The solution was poured into 600 ml of water, heated to 35 °C and acidified with perchloric acid. The precipitated photopolymer was separated, washed with two 100 ml portions of water and dried in vacuo. The photopolymer was purified by re-precipitation into diethyl ether from THF solution and dried in vacuo to yield 5.44 g of a light brown powder.

We obtained four samples of the photopolymer differing in chromophore content whose properties are summarized in Table 1.

The functionalization of the prepolymer with *N*-methylstilbazolium, (propyloxy)*N*-methylstilbazolium, and stilbene groups, respectively, was described elsewhere [23]. Employing 4-hydroxystilbene, 1-methyl-4-(2-(4-hydroxyphenyl))vinylpyridinium and 1-methyl-4-(2-(4-(3-hydroxy-propoxy)phenyl))vinylpyridinium salts instead of 9-(hydroxymethyl) acridizinium perchlorate. In Table 2 these chromophores were referred to as stilbene, stiblaz, prstilbaz, and acr, respectively (Fig. 4).

2.5. Film preparation and irradiation

Thin films of the photopolymer were obtained by pouring

Table 1
Composition, glass temperatures (T_g), and cloud point temperatures (T_c) of prepolymers and photopolymers

Sample	AAc in feed (in prepolymer) (% w/w)	T_g (°C)	T_c (°C)	Chromophore content (% w/w)	T_g (°C)	T_c (°C)
A	5.9 (4.4)	144	31.4	1.3	142	31.3
B				2.0	140	29.7
C				2.4	139	27.5
D				3.5	138	26.8

Table 2
LCST and T_c for photopolymers differing in chromophore, chromophore content, chromophore counterion, and irradiation state. In parentheses: type of chromophore (Figs. 1 and 4), chromophore content in % w/w, and solvent used for film preparation (if applicable)

		T_c (°C)								
		0 min	2 min	5 min	12 min	20 min	30 min	120 min	300 min	430 min
1	LCST (stilbene, 1.5)	18.6								
2	LCST (stilbene, 2.4)[a]	16.8	15.9				18.6		19.5	
3	LCST (stilbene, 2.7)[a]	16.4								
4	LCST (stilbene, 3.1)	18.1								
5	LCST (stilbazCl, 1.0)	21.4								
6	LCST (stilbazCl, 1.4)	22.7								
7	LCST (stilbazCl, 2.3)	25.8								
8	LCST (stilbazCl, 2.6)	24.9								24.7
9	LCST (stilbazCl, 4.8)	27.8								
10	LCST (stilbazBr, 2.6)	24.8								23.5
11	LCST (stilbazNO_3, 2.6)	25.7								24.8
12	LCST (stilbazClO_4, 2.6)	23.2								24.1
13	LCST (prstilbazCl, 0.3)[a]	26.0								
14	LCST (prstilbazCl, 0.7)[a]	24.2								
15	LCST (prstilbazCl, 1.1)[a]	22.4								
16	LCST (prstilbazCl, 1.5)[a]	18.5								
17	LCST (AcrClO_4, 1.3)	31.3		Sol.				Sol.		
18	LCST (AcrClO_4, 2.0)	29.1		Sol.				Sol.		
19	LCST (AcrClO_4, 2.4)	27.5		Sol.				Sol.		
20	LCST (AcrClO_4, 3.5, H_2O)	26.8		26.1				17.2		
21	LCST (AcrClO_4, 3.5, THF)	26.8	Sol.		23.0	23.1		22.5		
22	LCST (AcrClO_4, 3.5, $CHCl_3$)	26.8		24.2				22.1		
23	LCST (AcrClO_4, 3.5, EtOH)	26.8		24.3				22.1		
24	LCST (AcrClO_4, 3.5, MEK[c])	26.8		24.7				22.6		
25	Prepolymer	30.1[b]								

[a] Data from Ref. [23].

[c] Methylethylketone.

[b] Varies between 28.9 and 31.4 depending on the AAc content.

a 5% w/w solution of the polymer in the chosen solvent onto a quartz plate followed by evaporation of the solvent. The dried films were placed in the center of the photochemical reactor for the irradiation experiment. A UVA-SPOT 400/F (Dr Hoenle GmbH) was used for the photocrosslinking experiments on the quartz plates. The UV lamp had energy of 400 W and a UV irradiance of 30 mW/cm^2. The lamp emitted light with wavelengths >315 nm. To perform the photochemical back reactions, light of 254 nm (±5 nm) wavelength was used, which was selected from the emission of a 100 W mercury lamp by means of an interference filter.

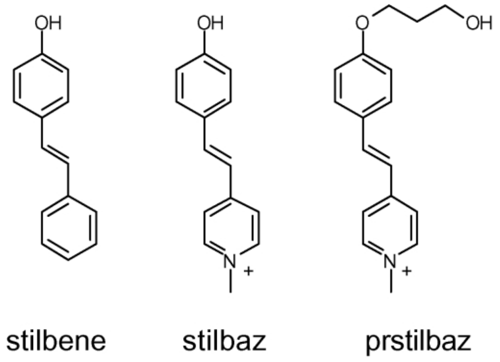

Fig. 4. Structures of chromophores used besides acridizinium ions.

2.6. Apparatus

The composition of the prepolymer was determined by acid–base titration of their aqueous solutions with 0.01 M sodium hydroxide and phenolphthalein as an indicator. The content of the chromophores in the photopolymers was determined by UV measurements on a Perkin–Elmer spectrometer (model Lambda 19). The products were characterized by ^{1}H, ^{13}C NMR- and FTIR-spectroscopy (BRUKER 500 DRX and UNICAM RS 1000).

The glass transition temperatures T_g for all the polymers as well as phase separation temperatures T_c of thermosensitive polymers were obtained by differential scanning calorimetry (TA instruments DSC 2920), an established and widely used method [6,12,13,14,28–30]. A 5% w/w aqueous polymer solution and a heating rate of 10 °C/min were used to determine T_c. The crosslinked photopolymers were immersed in water to swell for 24 h before measuring the LCST. At least two DSC curves were measured for each sample. The onset of the endothermic peak was taken as the transition temperature, which agrees with determinations using optical density measurements [30].

3. Results

3.1. Photocrosslinking

The photochemical crosslinking of the acridizinium photopolymer was achieved by UV irradiation of thin polymer films cast from dilute polymer solutions. As an example the UV spectral changes of an irradiated film cast from THF solutions of the photopolymer sample D (cf. Table 1) are displayed in Fig. 5. The spectral features shown in the figure pertain to the absorption of acridizinium moieties, since the prepolymer does not absorb significantly at wavelengths above 315 nm. A monomolecular degradation of acridizinium chromophores upon irradiation with light of wavelengths >315 nm does not take place [24–27] so that the absorption changes observed monitor photocrosslinking via photodimerization of acridizinium moieties leading to gel formation (Fig. 5). Within 80 min a complete bleaching of the polymers was observed (in the spectral range shown in Fig. 5), indicating an exhaustive conversion of the chromophores. In this respect the acridizinium photopolymers differ from their analogues with stilbene and stilbazolium chromophores [23], which also need longer irradiation times for comparable degrees of photoconversion when irradiated under the same conditions.

The photodimerization of the acridizinium groups requires sufficient mobility in the photopolymer to ensure that an excited and a ground state acridizinium ion can encounter each other within the lifetime of the former. In principle, this prerequisite is disfavored in the glassy state of the polymer. Nevertheless, the glassy state does not prevent the photodimerization of chromophores in our systems: as listed in Table 1 the glass transition temperatures T_g are around 140 °C (as for stilbene and stilbazolium analogues [23]). Thus, photocrosslinking of our samples was carried out in the glassy state. It should, however, be noted that the films, which initially are at room temperature, may be heated during the irradiation to ca. 80 °C due to the thermal radiation of the lamp and due to the partial dissipation of absorbed light energy. This temperature is still below the T_g. Moreover, we have checked that thermal back reactions of all isomeric acridizinium photodimers (see Fig. 1) do not proceed in measurable amounts after heating the dimers to 100 °C for 16 h.

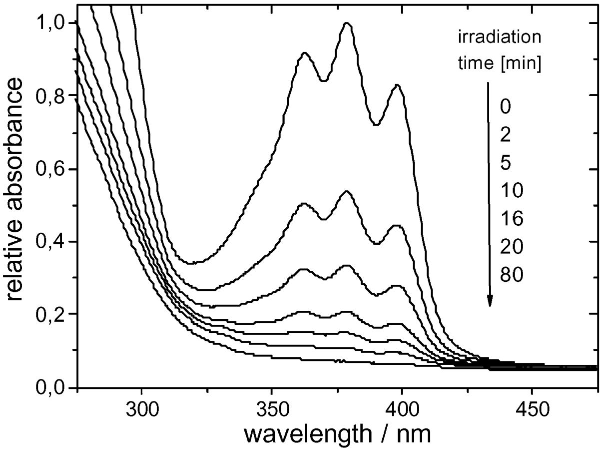

Fig. 5. Relative UV absorption changes during photoinduced crosslinking of a film prepared from photopolymer sample D (Table 1).

With the molecular weight of 7×10^4 g/mol for the prepolymer one can calculate an average number of photochemically formed links per chain for the absorbance change upon irradiation, i.e. for a chromophore content of 3.5% w/w (molecular weight: 297 g/mol for the perchlorate) we may have 8.3 chromophores per chain capable of forming a corresponding number of crosslinks after complete dimerization. These crosslinks, however, need not be all intermolecular.

3.2. Reverse photoreaction

Attempts to reverse the photochemical crosslinking reaction of acridizinium photopolymers by irradiation with short wavelength light are shown for two sample films in Fig. 6. The film with a chromophore content of 3.5% w/w was irradiated with light >300 nm (dimerization only) until a relative absorption of 0.25 was reached, corresponding to 75% conversion of chromophores or 6 links per chain. Then splitting of the dimers was started using 254 nm light and progressed until a relative absorption of 0.45, which is near the photostationary equilibrium as the curve indicates leveling off. Then the irradiation wavelength was changed to >300 nm again to reset the system to a relative absorption of 0.25 and reverted once more with 254 nm light. A fair reversibility can be stated for the two irradiation cycles. The

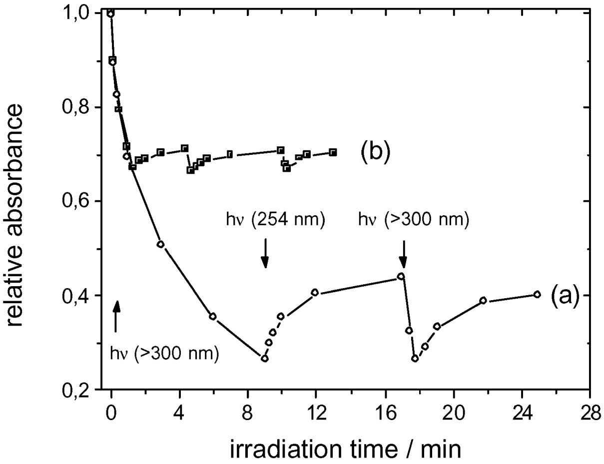

Fig. 6. Absorption changes in an acridizinium photopolymer film upon irradiation with $\lambda > 300$ nm and re-irradiation with $\lambda = 254$ nm. (a) Chromophore content 3.5% w/w and (b) chromophore content 2.4% w/w; counterion ClO_4^-.

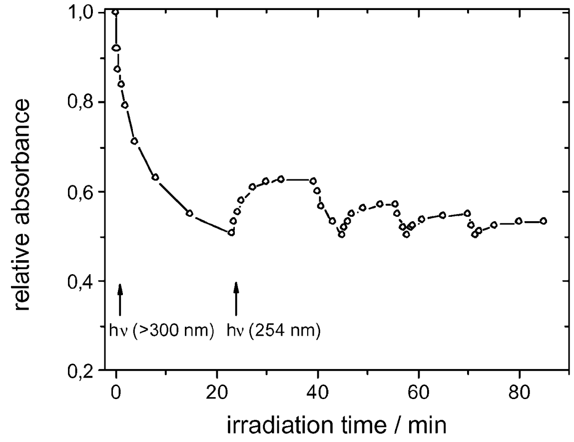

Fig. 7. Absorption changes in a stilbene photopolymer film upon irradiation with $\lambda > 300$ nm and re-irradiation with $\lambda = 254$ nm, chromophore content 2.4% w/w.

same is due to the sample containing less chromophore (2.4% w/w). Here the initial irradiation was stopped at a relative absorption of 0.66 (2 links per chain). Thereafter the system was cycled between this value and 0.71.

Analogous experiments using stilbene and stilbazolium photopolymers are shown in Figs. 7 and 8. It can be seen that the amplitudes of photoreversion are higher, in particular, in the stilbazolium case. This clearly indicates that photostationary equilibria lie more towards the monomer as compared to the acridizinium case.

3.3. T_c and LCST variation

Table 2 shows the LCST data of crosslinked films together with the T_c data of the non-crosslinked materials. Inspection of the table reveals that (i) LCST and T_c are in the range of room temperature for the ionic acridizinium and stilbazolium photopolymers, in contrast to the non-ionic hydrophobic stilbene photopolymer, (ii) in most cases, the LCST is somewhat lower than the T_c with the exceptions of samples 2 and 12, (iii) there are influences on the LCST of the counterions of ionic chromophores and of the solvent used for the film preparation.

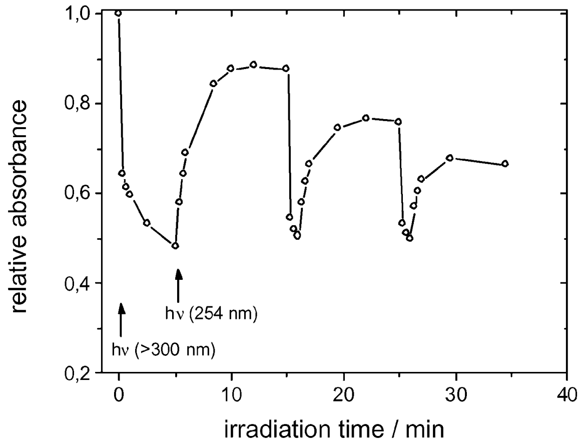

Fig. 8. Absorption changes in a stilbazolium photopolymer film upon irradiation with $\lambda > 300$ nm and re-irradiation with $\lambda = 254$ nm, chromophore content 2.6% w/w; counterion NO_3^-.

3.4. Film properties

Despite the relative absorption changes of more than 50% the irradiated films containing up to 2.4% chromophore remained soluble in water (samples 17–19). The same was due for the film made from THF solutions of the 3.5% chromophore containing photopolymer after 2 min of irradiation (50% absorption change, 4 links per chain, sample 21). The formation of a solid network capable of swelling in water obviously requires a certain number of intermolecular crosslinks, which depends on the solvent.

The phase separation temperature, for networks denoted as the LCST, of the hydrogels was also affected by the degree of crosslinking (Table 2).

4. Discussion

4.1. Photochemical crosslinking and reversibility

Most of the previous research has been focused on the UV-induced crosslinking of photosensitive polymers with the pendant chromophores undergoing two competing photoreactions: photodimerization and *cis–trans* isomerization. The latter gives rise to considerable problems in the analysis of the crosslinking process [31]. It is known that the acridizinium ion undergoes reversible photodimerization reactions upon irradiation with a low tendency for side reactions: it dimerizes through a [4 + 4]-cycloaddition, and the dimers split into their monomers on photolysis at lower wavelengths or on thermolysis at elevated temperatures. Thus, by choosing this chromophore to synthesize hydrophilic, temperature-responsive, photosensitive polymers we achieved a higher photoreactivity (i.e. a faster and more complete crosslinking) as compared to the polymers containing styrylpyridinium salts or stilbenes as photocrosslinkable moieties [23]. The fact that the photoreaction obviously proceeds in the glassy state adds to the importance of these distinctions. A preorientation of acridizinium moieties close to each other upon film formation (due to aromatic interactions, the charge being neutralized by nearby counterions) might reduce the need of motion in the glass state. Also, a local heating of the immediate surrounding of reacting chromophores due to vibrational relaxation of excited states can add to the mobility. On the other hand, since samples containing up to 2.4% w/w of the chromophore do not form insoluble films (although 3–5 crosslinks per chain are possible), we have to consider either that intramolecular crosslinking takes place or that the photodimers link linear chains mainly in the cases of low chromophore content.

The cleavage of the photodimers investigated here affords light of wavelengths around 250 nm. Unfortunately, in this wavelength region, the monomers also absorb. A complete reversion of the photodimerization, therefore, is impossible, since both—back and forth reaction—take place upon irradiation at this wavelength. Instead a photostationary equilibrium is reached which depends on quantum yields of back and forth reaction and on the absorption coefficients of monomer and dimer at the irradiation wavelength. It is, therefore, not surprising that the re-formation of the monomer upon irradiation at 254 nm is comparatively poor (Fig. 6), since the monomer absorption exceeds the dimer absorption throughout the spectrum (cf. Fig. 5). This is different in stilbazolium and stilbene chromophores, in which at 254 nm the dimers exhibit higher absorption than the chromophore monomers [23].

In the latter photopolymers, however, the reversibility is considerably worse in the second and third irradiation cycles (Figs. 6 and 7). Obviously chromophore consuming side reactions occur. One of these very probably is the formation of phenanthrene structures, formed from *cis*-isomers in the presence of oxygen or compounds with isolated double bonds [32]. Other side reactions may arise from light absorption of the PNIPAAm material, which strongly absorbs at 254 nm. Radical fragments produced thereby may irreversibly react with the chromophores. This, however, apparently does not happen to acridizinium chromophores to any measurable extent. On the other hand, in stilbene and stilbazolium photopolymers, the amplitudes of the photoreversion cycles are much higher than in the acridizinium photopolymer clearly indicating that photostationary equilibria at 254 nm are more on the monomer side.

4.2. T_c and LCST variation

In previous papers [21–23], we reported that the chromophore has an important influence on the phase separation temperature T_c of the photopolymers. In the acridizinium photopolymers a decrease of T_c with an increase of the chromophore content was also observed. The difference $\Delta T_c = -2.7$ °C (vs. prepolymer) for the photopolymer with 3.5% w/w chromophore, however, is small compared to $\Delta T_c = -11.0$ °C as observed in the stilbazolium photopolymers with a chromophore content of 1.5% w/w (sample 16 in Table 2). Thus, in the acridizinium photopolymers, the conception is widely fulfilled that the positive charge on the chromophore compensates for the hydrophobicity of the aromatic moiety. The generally low T_c values for the stilbene photopolymers are in keeping with this conception.

In stilbazolium and acridizinium photopolymers, the LCST decreases with the degree of crosslinking (with the exception of sample 5, stilbazolium perchlorate). The effect may be rationalized, if the preferred conformation of the diacridizinium crosslinks is assumed to be head-to-tail [26]. Then the dipole moment of the chromophore bearing side groups is diminished by crosslinking. Due to the decreased dipole moment, the hydrophilicity of the polymer is decreased as well, resulting in lower LCST values upon crosslinking. The effect is more pronounced in acridizinium than in stilbazolium photopolymers. Combining the findings that (i) LCST varies with the degree of photocrosslinking and (ii) the latter is reversible within certain limits, we may conclude that the LCST can be switched isothermally simply by exposure of the sample to light of an appropriate wavelength.

Table 2 further reveals that the kind of counterion present in the stilbazolium photopolymers affects the T_c and LCST (samples 8, 10–12). Both decrease in the order nitrate $<$ chloride $<$ bromide $<$ perchlorate, i.e. the order does not follow the Hoffmeister series, since nitrate disagrees. The order agrees, however, with the increase of the acidity of the corresponding acids. This is counterintuitive, since one expects the highest compensation of hydrophobicity in the case of the most dissociating anion. Obviously other influences on T_c prevail (at least in some of the examples), e.g. the stronger association of badly dissociating anions to the cation implies a better shielding of the charge and thus allows for different sites of the chromophores and their dimers in the polymer bulk. Also, specific influences related to ‘salting out effects’ may be considered [33].

Finally there is the influence of the solvent used in the preparation of films of the acridizinium photopolymers (samples 20–24). As the differences in the LCST of films cast from organic solutions are small as compared to the films prepared from aqueous solutions, general solvent properties may cause the effects. Since only water can be considered a ‘good’ solvent for the non-crosslinked photopolymer, we may expect more globular structures to be present in the organic solvents. Thus, films prepared from the latter ones may give rise to more intra(macro)molecular crosslinking and an overall less dense film is formed thereby exhibiting higher LCST [23].

5. Conclusions

Acridizinium photopolymers allow a high chromophore content and T_c above room temperature. This property is indispensable for applications to microsystems that cannot be thermostatted [20–22]. It is expected that swelling and deswelling of the crosslinked films can be isothermally induced via photochemical switching of the LCST.

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