

UV Crosslinking of Fe³⁺-Doped Poly(vinyl alcohol)—Characterization of Optical Properties and Swelling Behavior

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ABSTRACT: The effects of UV irradiation on iron(III)chloride doped poly(vinyl alcohol) (PVA) films, using a high molar mass polymer, have been studied. It has been found that the polymer is oxidized and crosslinked during UV irradiation. UV/VIS spectra reveal an exponential loss of absorption at $\lambda = 360$ nm, and the refractive index of the PVA:FeCl₃ films decreases significantly during UV irradiation ($\Delta n^D = -0.09$). The effects of crosslinking have been studied using the sol-gel technique, which revealed high gel contents due to doping and UV-exposure. Photolithographic patterning of doped PVA films using a medium-pressure mercury-vapor UV source has been carried out, leading to good contrast behavior before and after development in aqueous media. A photobleaching effect was observed, therefore the curing of thicker films is feasible. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Iron(III)chloride doped poly(vinyl alcohol) is a very convenient UV curable organometallic polymer that could be utilized for optical data processing technologies and real time holographic recording. Possible applications are permanent and transient data storage materials and precursors for the fabrication of flexible waveguides.^{1–5} Besides the optical applications this organometallic polymer may be utilized for high-temperature coatings, biosensors, storage electrodes for batteries and capacitors, electrochromics, etc.^{6–10}

The UV initiated crosslinking of FeCl₃ doped PVA of low molar mass has been investigated Kuncser et al. Changes of the optical properties of thin films such as UV-Vis absorption and the refractive index have been described.^{11–14} As PVA and the crosslinking agent FeCl₃ are both physiologically harmless compounds, the preparation of photocurable materials that are as well non-hazardous as environmentally benign is feasible.^{9,15,16}

Two UV initiated crosslinking mechanisms of iron(III)chloride doped PVA are proposed by literature: Manivannan et al. state that crosslinking is caused by charge transfer from Fe³⁺ to the polymer and radical generation [see Figure 1(a)], while Kowalonek et al. claim that chlorine radicals are generated during irradiation of FeCl₃ and react with PVA to give macroradicals, which subsequently recombine [see Figure 1(b)] and form crosslinks.^{3,5,14}

The aim of this present investigation was to prepare an UV curable coating material (PVA:FeCl₃), utilizing a PVA of high molar mass and high degree of saponification, that is suitable for short term UV exposure at high UV irradiation intensity levels. Investigations of changes of the solubility behavior in deionized water were instigated, which would be pivotal for the development process of photolithographic structured resists consisting PVA:FeCl₃.

UV-Vis spectroscopy revealed a loss of absorption at a wavelength of 360 nm upon irradiation, which can be attributed to a change of oxidation state of the Fe³⁺ ions to Fe²⁺.^{5,14,17} Because of UV exposure the swelling behavior of the prepared material is improved, resulting in gel contents up to 70 wt %. Photolithographic patterning of PVA:FeCl₃ films gives excellent contrast behavior and clearly defined structures after immersion of the samples in deionized water.

EXPERIMENTAL

Materials

PVA was provided by the DuPont Chemical Company (Wilmington, USA) and further characterized at the Chair of Chemistry of Polymeric Materials (Leoben, Austria). The average molar mass was determined at the Institute of Chemistry (University of Graz, Austria) by gel-permeation-chromatography using highly purified water as eluent. A value of $M_w = 130,800$ g mol⁻¹ was found. A very high degree of saponification

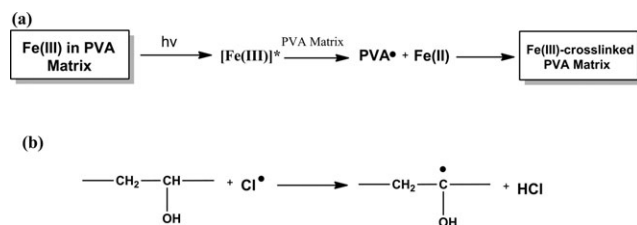


Figure 1. Reaction mechanisms for the crosslinking of PVA/FeCl₃ according to Manivannan³ (a) and Kowalonek¹⁴ (b).

(>99 mol %) was confirmed by ¹H NMR-spectroscopy using D₂O as solvent.

An aqueous PVA solution with a solids content of 10 wt % was prepared by stirring the appropriate amount of deionized water at room temperature, followed by adding of the dry polymer thus creating a slurry. After 10 min of stirring at room temperature, the slurry was heated to a temperature of 85°C. This temperature was kept for at least 60 min until a homogenous solution was obtained.

Iron(III)chloride (FeCl₃; reagent grade, with a purity of 97%) was purchased from Sigma–Aldrich (St. Louis, USA). To avoid aggregation, the powder was dissolved in deionized water at room temperature, resulting in a stock solution with 10 wt % content of FeCl₃. All chemicals were used without any further purification or particular treatment.

Methods

Sample Preparation. Appropriate amounts of both polyvinyl alcohol and iron(III)chloride stock solution were thoroughly stirred at room temperature for a period of 60 min, until a homogenous PVA:FeCl₃ solution (95 : 5 by wt %, with regard to the dry matter) was obtained. This was followed by sonification for 30 min and an equilibrium phase for degassing of ~12 h.

Calcium fluoride (CaF₂) platelets for optical spectroscopy (FTIR, UV/VIS) were coated with PVA:FeCl₃ by the drop coating method and dried under steady air flow at 23°C ± 2°C for a period of 12 h.

PVA:FeCl₃ samples for refractive index measurements, crosslinking studies and photolithographic patterning were prepared by the following method. A defined amount of PVA:FeCl₃ solution was cast onto polypropylene petri dishes, followed by drying at room temperature until constant weight was obtained.

UV Irradiation. For UV light exposure and UV induced crosslinking of the PVA:FeCl₃ samples a FusionUV Light Hammer 6 (Maryland, USA) conveyor-belt irradiation device was applied. It is equipped with a medium-pressure mercury-vapor lamp, which generates UV light of wavelengths ranging from 225 to 450 nm (see Figure 2). The emission spectrum of the light source was recorded using a Sola-Scope spectroradiometer from Solatell (Gloucestershire, UK).

The prepared samples (thin films and coated CaF₂ platelets) were exposed to UV light with an intensity of 55 mW cm⁻² for a duration of 0, 10, 20, 30, 40, and 60 s. After irradiation the effects of UV exposure were studied using optical and spectroscopic methods. Sol–gel analysis of PVA:FeCl₃ films was per-

formed to observe the change of solubility in water caused by irradiation.

FT-IR Spectroscopy. A Perkin-Elmer SpectrumOne Fourier-Transformation Infrared Spectrometer (Waltham, USA) was used to obtain transmission spectra of PVA, PVA:FeCl₃ and irradiated PVA:FeCl₃ samples for the wavenumber range between 2000 and 850 cm⁻¹. Sixteen scans were performed for each sample.

UV-Vis Spectroscopy. UV-Vis absorption spectra were recorded using a Varian Cary 50 spectrophotometer (Santa Clara, USA) to trace changes of the optical absorption of PVA:FeCl₃ films due to UV irradiation. A medium scanning speed was applied at a wavelength range from 250 to 650 nm and the change of the absorption at 360 nm was plotted versus the UV exposure time.

Refractometry. Refractive index changes in PVA:FeCl₃ films due to UV exposure were measured with an Atago NAR1T Abbe refractometer (Tokyo, Japan) using a sodium D-line light source (589 nm). All measurements were performed triplicate.

Swelling Behavior. Irradiated films of PVA:FeCl₃ were cut into 1 × 1 cm² pieces, weighed to obtain the initial sample weight (*w_i*) and immersed in deionized water at 23°C for 48 h to obtain equilibrium swelling. After this period the samples were withdrawn, dipped in chloroform to remove the water from the surface and the weight of the swollen samples (*w_s*) was determined. Drying of the samples was done under steady air flow for ~24 h at 60°C, subsequently the weight of the dried sample (*w_d*) was determined.

The swelling ratio was calculated according to eq. (1)^{15,16}:

$$S(\%) = \frac{w_s - w_d}{w_d} * 100 \quad (1)$$

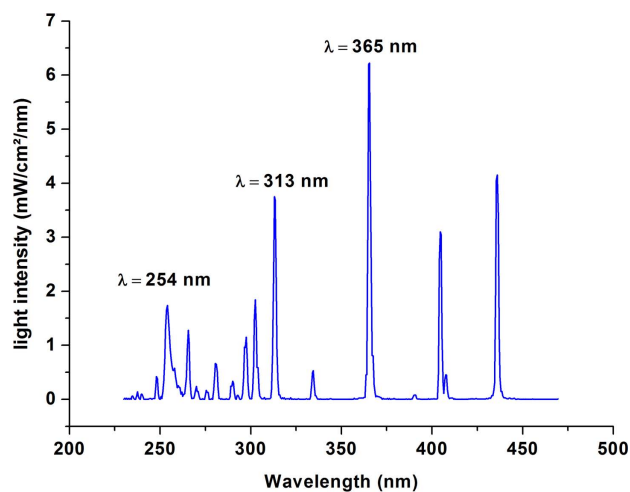


Figure 2. Emission spectrum of the medium-pressure mercury-vapor lamp used for the investigations. The peaks at the wavelengths of 254, 313, and 365 nm are relevant for UV induced crosslinking of PVA:FeCl₃ samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

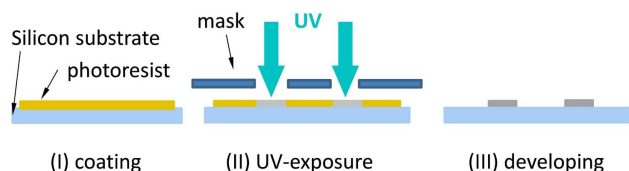


Figure 3. (a) coated substrate (bearing a PVA:FeCl₃ film); (b) UV exposure through a mask pattern, the nonilluminated areas remain soluble in appropriate solvents; (c) development by immersion in a solvent (in this case deionized water). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The gel content was defined according to eq. (2)¹⁵:

$$Gel(\text{wt}\%) = \frac{w_d}{w_i} * 100 \quad (2)$$

All measurements were performed triplicate.

Photolithographic Patterning. Photolithographic patterning of PVA:FeCl₃ was carried out using two methods. The first was placing a silicodioxide/chromium mask with 100 μm features directly onto a 1 × 1 cm² film samples, followed by illumination for 20 s with an intensity of 55 mW cm⁻².

The second method was to use a Suss MJB 4 Mask-Aligner (Suss, Garching, Germany), which is equipped with a medium-pressure mercury-vapor lamp and optical filters to provide UV light with wavelengths ranging from 270 to 350 nm and an intensity of 25 mW cm⁻². Samples were irradiated for 120 s in soft-contact printing mode, applying a patterned silicodioxide/chromium mask and constant power lamp-operating mode. The exposed areas of the PVA:FeCl₃-films are crosslinked, thus reducing the solubility in water. The principle of the photolithographic patterning process is depicted in Figure 3.

After patterning the structured samples were investigated with an Olympus BX51 optical microscope (phase contrast). Developing of patterned samples was done by immersion in deionized water for 30 min, followed by drying at 40°C under steady air flow. The structures were observed again with the microscope and the effects of developing on the structures were compared.

RESULTS AND DISCUSSION

FT-IR Spectroscopy

Figure 4 shows the FT-IR spectra of films of pure PVA and PVA:FeCl₃ before and after UV illumination. The spectra display several bands characteristic of stretching and bending vibrations of —OH—, —CO—, and C—H units.

All three FT-IR spectra show an absorption peak at 1660 cm⁻¹ that corresponds to hydrogen bonding resulting from residual water or between the polymer chains. The band observed at 1430 cm⁻¹ corresponds to the —CH— deformation vibration of the polymer backbone and the strong absorption band at 1090 cm⁻¹ can be assigned to the C—O valence vibration.^{18,19} Both for in the neat PVA and the PVA:FeCl₃ film a weak signal at 1705 cm⁻¹ is discernible, which increases in intensity after UV exposure. This leads to the conclusion that main chain keto groups are formed in the polyvinyl alcohol film as a result of UV exposure. At the same time, the photoreactive species Fe³⁺ is reduced to Fe²⁺ as has already been reported by Changkakoti, Kowalonek, and David.^{5,14,17}

UV-Vis-Spectroscopy

Whilst PVA does not show UV absorbance above 250 nm, as a result of doping with FeCl₃ the absorption is strongly increased for the wavelength range 250–500 nm, which is caused by Fe³⁺ cations, see Figure 5.^{3,12}

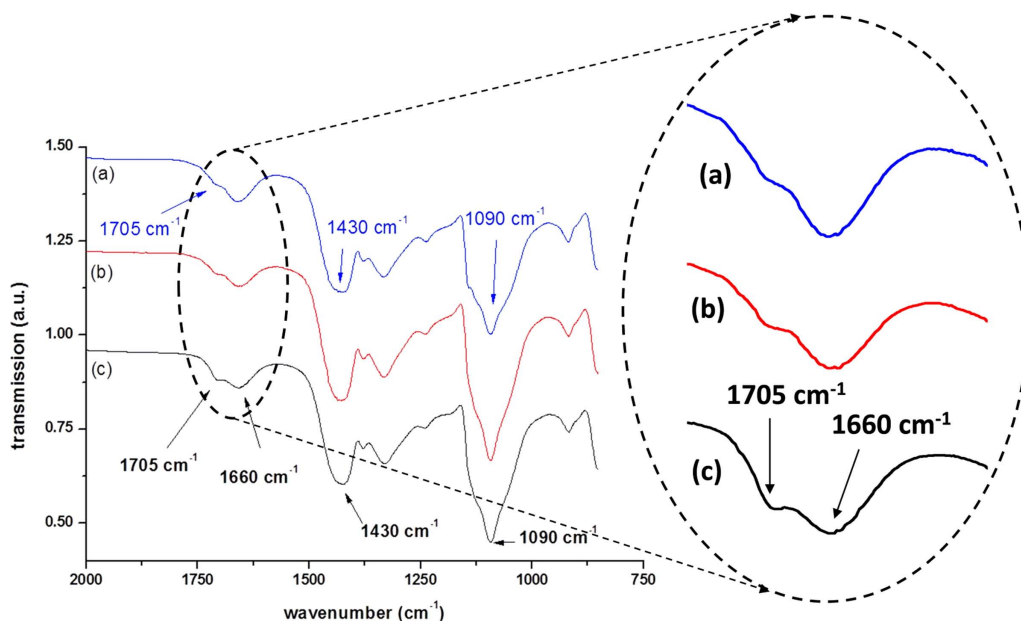


Figure 4. FT-IR spectra of pure PVA (a) and PVA:FeCl₃ before (b) and after UV illumination (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

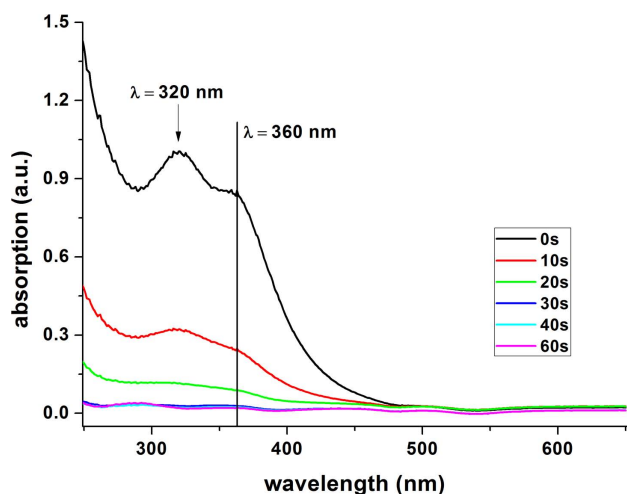


Figure 5. Absorbance spectra of PVA:FeCl₃ (films on CaF₂ platelets) after different UV exposure times with a medium-pressure mercury-vapor lamp with an integrated power density of 55 mW cm⁻². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Three absorbance maxima at 360, 320, and 250 nm are observed, which match well with the emission lines of the applied medium-pressure mercury-vapor lamp used for cross-linking (compare Figure 2 with Figure 5). As a result of UV irradiation, the absorbance of PVA:FeCl₃ strongly decreases as shown in Figure 5. To visualize the effects of UV exposure of PVA:FeCl₃ on the absorption behavior, the decrease of the peak intensity at 360 nm is plotted versus the irradiation time, see Figure 6. The absorbance reaches zero value after 30 s of exposure.

The decrease of absorbance at 360 nm is almost exponential and corresponds to the change of the oxidation state of Fe³⁺ to Fe²⁺.^{1,2} Additionally, the transmission in the visible range changes significantly and a change of color from yellow to colorless is observed, as reported by Mannivannan et al.³ Contrary

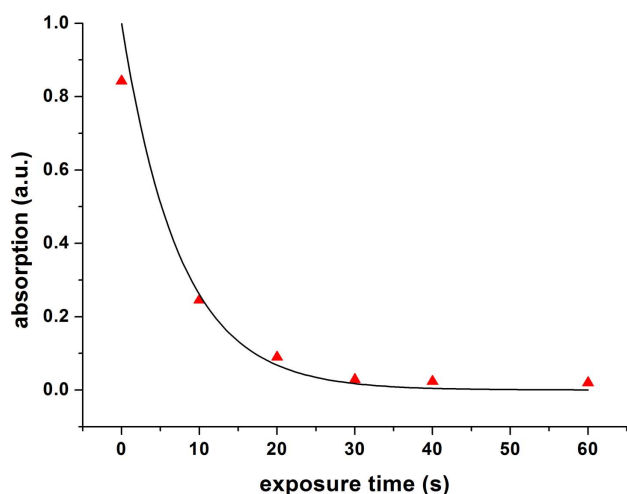


Figure 6. Change of the absorbance of PVA:FeCl₃ (film on a CaF₂ platelet) at 360 nm versus the UV exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

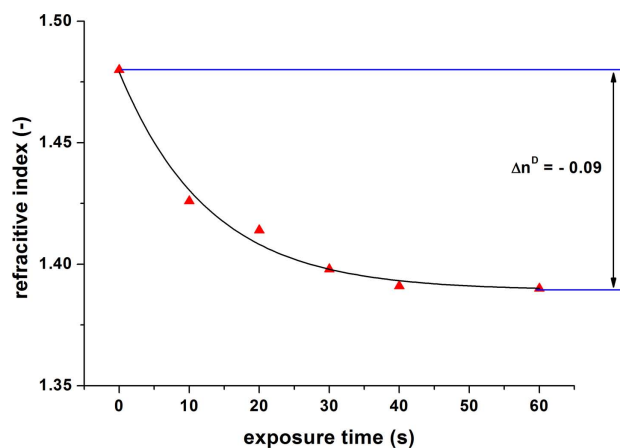


Figure 7. The refractive index n^D (at $\lambda = 589$ nm) of PVA:FeCl₃ films versus the UV exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to published results, no increase of the absorption at wavelengths higher than 450 nm was detected.^{2,3,11,12} Filoti et al. suggest that this increase may be caused by the formation of scattering centers such as crystals, which do not arise for short term exposed samples (see Figure 5).¹³

Because of the photobleaching effect, the UV curing of thicker PVA:FeCl₃ films is feasible as the radiation can penetrate deeper in the illuminated and bleached areas of the photoreactive film.

Refractometry

Refractive index measurements using an Abbe refractometer reveal that the refractive index of PVA:FeCl₃ at 589 nm rapidly decreases under irradiation. After 40 s of UV irradiation with an intensity of 55 mW cm⁻² the refractive index reaches a constant value. The refractive index n^D (at $\lambda = 589$ nm) is reduced by $\Delta n^D = -0.09$ (see Figure 7), similar values of this loss are reported for the refractive index at $\lambda = 632.8$ nm.^{2,4,5,11}

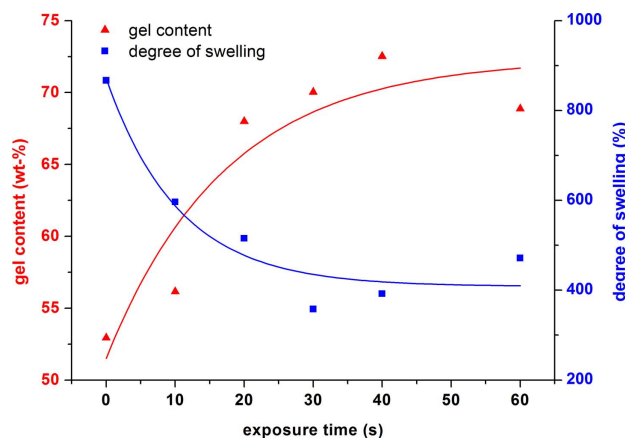


Figure 8. Degree of swelling and gel content of PVA:FeCl₃ films in dependence of the UV exposure time (integrated power density = 55 mW cm⁻²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

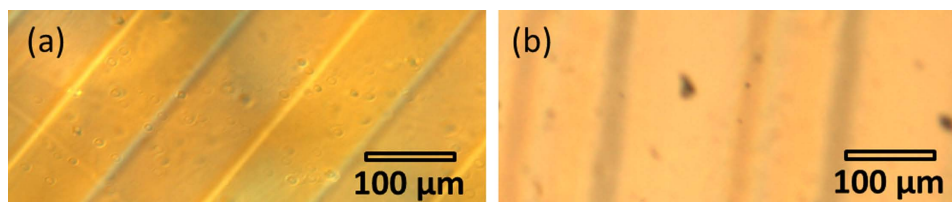


Figure 9. Photolithographic patterning of PVA:FeCl₃ using a mask with 100 μm features in direct contact with the film during UV-exposure. The optical micrographs show (a) PVA:FeCl₃ film after 20 s of illumination with 55 mW cm⁻² and (b) the same film after immersion in deionized water and subsequent drying. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To explain these results, the refractive indices of 10 wt % aqueous solutions of FeCl₃ and FeCl₂ were recorded and compared. For the FeCl₃ solution n^D was found to be 1.355, whilst the refractive index of the FeCl₂ solution amounted to $n^D = 1.338$. Therefore it is concluded that the refractive index change of PVA:FeCl₃ as a result of UV irradiation is caused by the change of the oxidation state of the iron ions.^{5,20} As the wavelength for measuring the refractive index ($\lambda = 589$ nm) is outside the optical absorbance of Fe⁺³, anomalous dispersion can be ruled out in this case. It should be noted that crosslinking of polymers usually results in a slight increase of the refractive index. In the case of PVA:FeCl₃ this effect is overruled by the effects of changing from Fe⁺³ to Fe⁺².^{2,4,5,11}

The strong reduction in refractive index can be utilized to create flexible polymer waveguides, which has been investigated by Trepanier et al. in the early 1990s on low molar mass PVA.⁴ The photobleaching effect provides the possibility to generate waveguides in comparably thick films of PVA.

Swelling Behavior

As pristine PVA is water-soluble, the degree of swelling and the gel content cannot be evaluated for the neat polymer. After doping of the PVA with 5 wt % of FeCl₃, a gel content of 53 wt % is found, while the degree of swelling is ~900%. Upon UV exposure the insoluble fraction of PVA increases exponentially and reaches 73 wt % after 40 s of irradiation time, followed by a slight decrease to 68 wt % after prolonged irradiation, see Figure 8. This may be caused by chain scission of PVA due to oxidation via a radical reaction mechanism.

The degree of swelling is reduced 3.9 to 4.7 times smaller values after UV irradiation. The relatively high scattering of the data may have been caused by residual water on the surface of the swollen sample films which causes errors in the gravimetric measurements.

Photolithographic Patterning

The photolithographic patterning resulted in a change of color upon UV-exposure, which has already been characterized by UV-Vis spectroscopy.

The illumination of PVA:FeCl₃ films through a quartz/chromium mask with 100 μm features shows excellent pattern contrast, see Figure 9. After immersion of the illuminated samples in deionized water for 30 min (followed by drying under steady air flow at 30°C) the structures still show good contrast behavior.

The illumination of PVA:FeCl₃ films with the Süß MJB 4 mask aligner in the soft-contact mode resulted in even better contrast compared to the first method of patterning. This may be the result of a longer irradiation time using lower intensities and improved contact of the patterning mask with the PVA:FeCl₃ substrate. The contrast which is discernible with optical microscopy (phase contrast mode) after irradiation results from the large change in refractive index. After development with deionized water, topographical features contribute to the index contrast pattern.

CONCLUSIONS

The UV exposure of PVA:FeCl₃ leads to oxidation and crosslinking of the polymer, which is accompanied by a photobleaching effect due to a reduction of Fe³⁺ to Fe²⁺. This leads to improved swelling behavior and gives the feasibility to cure thicker samples. Photolithography gives excellent contrast behavior of patterned films after development with deionized water. As the refractive index was changed significantly, the prepared material would be suitable for the preparation of polymer waveguides.

Therefore PVA:FeCl₃ can be considered for the use as water-soluble and water-developable photoresist for rapid curing applications using high UV irradiation intensities. A great advantage compared to common resists is that no organic solvent, neither for the coating of substrates nor for the developing step, is required. Another improvement is the utilization of a biocompatible polymer and a nonorganic and environmentally benign photoinitiator, which does not give hazardous and volatile cleavage products upon irradiation.

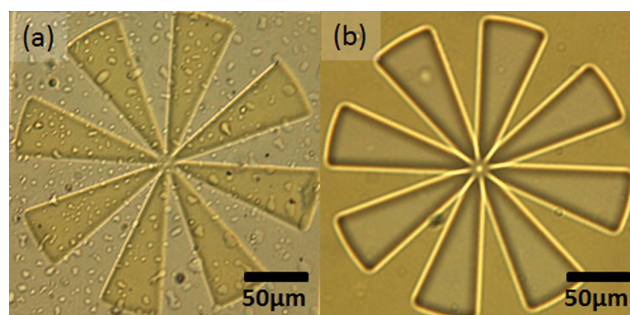


Figure 10. Optical micrographs of PVA:FeCl₃ films after patterning with a mask aligner. (a) PVA:FeCl₃ film after 120 s of illumination; (b) the same film after immersion in deionized water and drying. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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