Photolithographic Patterning of Polymer Surfaces Using the Photo-Fries Rearrangement: Selective Postexposure Reactions

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Received February 22, 2007. Revised Manuscript Received April 5, 2007

Photosensitive polymers bearing aryl esters in the side chains undergo the so-called photo-Fries rearrangement upon irradiation with UV light. This photoisomerization reaction leads to the formation of aromatic hydroxyketones in the illuminated areas. In this contribution, we explore the possibilities of postexposure reactions that can be used for a selective functionalization of the polymer. The photogenerated aromatic hydroxyl groups readily react with carboxylic acid chlorides to form new esters. By the choice of the acid chloride, the surface properties can be tuned in a wide range. A further approach is the reaction of the hydroxyl groups with sulfonic acid chlorides as demonstrated for dansyl chloride, a highly fluorescent dye. Furthermore, the hydroxyketones can act as ligands for metal ions. Fe^{3+} was selectively deposited onto the illuminated areas. By a subsequent treatment with ammonium rhodanide, the immobilized ferric ions yield intensely colored thiocyanate complexes. In another derivatization pathway, the carbonyl groups in the photoproduct can be transformed by the reaction with 2,4-dinitrophenylhydrazine to give the corresponding hydrazone. In combination with lithographic techniques, these postexposure reactions lead to patterned functionalized surfaces.

Introduction

Photochemical reactions in polymers that change the chemical reactivity of the irradiated areas are widely used for applications such as patterning of photoresists,[1] immobilization of (bio)molecules on surfaces,[2] electroless plating of plastics,[3] and improving adhesive properties of surfaces.[4,5] Generally, photolithographic techniques provide the possibility to obtain patterns with submicrometer resolution. We have only recently investigated the so-called photo-Fries reaction in polymers with respect to UV-induced changes in refractive index and surface polarity.[6] The photo-Fries rearrangement transforms aryl esters to hydroxyketones as first observed by Anderson and Reese in 1960.[7] Scheme 1 shows the generally accepted mechanism.[8] Upon irradiation with UV light (200−250 nm), photolysis leads to the cleavage of the aromatic ester into the acyl and the phenoxyl radical. This photoreaction proceeds from an exited singlet (S_1) state. The generated radicals can recombine and then yield *o*- or *p*-cyclohexadienone derivatives as the "cage product". Tautomerism gives the corresponding hydroxyketones. Besides the release of free phenols as "escape" product, decarboxylation occurs as competing reaction.[9]

Apart from its use in organic preparative chemistry,[10] the photo-Fries reaction has been applied in polymer chemistry. The photochemistry of poly(phenyl acrylate) and poly(naphthyl acrylates) has been investigated in detail by Guillet et al.[11] Poly(acetoxystyrene) and poly(formyloxy)styrene were investigated as positive resist materials for photolithography.[12] Because of the higher polarity of the hydroxyketones, the polymers become more soluble in alkaline media after UV irradiation. In addition, the photo-Fries reaction leads to a large change in the refractive index ($\Delta n = 0.04-$

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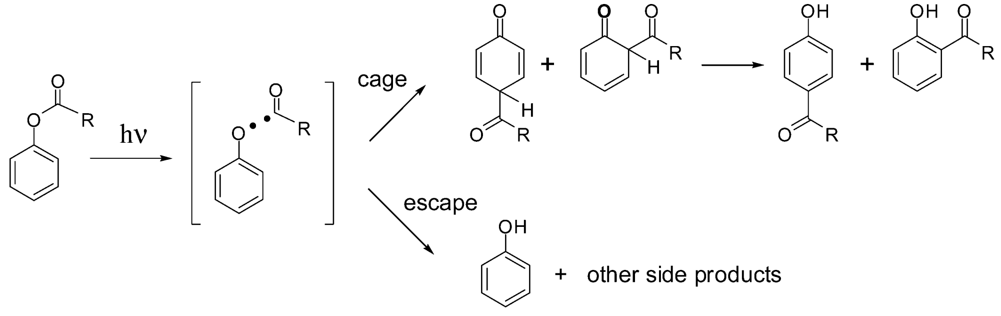
10.1021/cm070506h CCC: $37.00

Scheme 1. Reaction Mechanism of the Photo-Fries Rearrangement



0.05), as has been investigated recently for several polymers bearing photoreactive aryl esters.[6] Because of this large increase in the refractive index, these materials have been considered for applications in holographic data storage.[13]

In this contribution, we explore the use of the photogenerated functional groups for selective postmodification reactions of polymer thin layers. The starting point is the recently described photosensitive polymer poly(bicyclo-[2.2.1]-hept-5-ene-2,3-dicarboxylic-acid, diphenyl ester) (poly-**1**), which was obtained by catalytic ring-opening metathesis polymerization (ROMP) using “Grubbs catalyst” $RuCl_2(PCy_3)_2(=CHPh)$ (Cy = cyclohexyl).[6] We have shown that upon irradiation with UV light, the phenyl ester in poly-**1** is almost completely converted into *o*- and *p*-hydroxyketones, phenols, and other products. The generation of aromatic hydroxyl groups at the polymer surface changes the surface polarity. These aromatic hydroxyketones (approximately 21% of the photoproducts) should be excellent precursors for modification reactions that allow the immobilization of a variety of molecules at the polymer surface. We will show that both the aromatic hydroxyl groups and the keto groups can be used for modification reactions. By the use of lithographic techniques, these reactions lead to patterned functionalized surfaces and thin modified polymer layers.

Experimental Section

Materials. All chemicals were purchased from commercial sources and used without further purification. Poly(endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenyl ester) was synthesized as reported previously.[6]

For all modification experiments and spectroscopic measurements, polymer films were prepared on CaF_2 plates by spin-casting from dichloromethane solutions. The film thickness was in the range from 150 to 200 nm according to Fabry−Perot interferometry.

UV Irradiation and Postmodification. UV irradiation experiments were carried out with an unfiltered medium-pressure Hg lamp (Heraeus, 1000 W) in a nitrogen atmosphere. For these experiments, the light intensity (power density) at the sample surface was measured with a spectroradiometer (Solatell, Sola Scope 2000TM, measuring range from 230 to 470 nm). The light intensity was 20 mW cm^{-2} for the spectral range 230−320 nm. Typically, irradiation times were between 20 min (flood illumination) and 35 min (patterned illumination). UV−vis and FTIR spectra were taken prior to and after UV illumination in order to monitor the progress of the photoreaction. Patterned structures were obtained by placing a contact mask (Cr pattern on quartz) directly onto the polymer film prior to illumination.

Warning: UV irradiation causes severe eye and skin burns. Precautions (UV-protective goggles, gloves) must be taken. In the below described postmodification reactions, hazardous chemicals and solvents are used (acid chlorides, dansyl chloride, $FeCl_3$, dinitrophenyl hydrazine, acetonitrile, dichloromethane). All reactions must be undertaken under a fume hood and protective clothing must be used.

Reaction with Carboxylic Acid Chlorides. After UV illumination of a film of poly-**1** on a CaF_2 plate for 20 min, the sample was exposed to vapors of acetyl chloride and dichloromethane (1:1 mixture). After 14 h of exposure, the polymer layer was dried in vacuo for 4 h. Reactions with benzoyl chloride and perfluorobutyryl chloride were carried out in a similar way.

Reaction with Dansylchloride. The irradiated film of poly-**1** was placed in a solution of 50 mg of dansyl chloride in 10 mL of acetonitrile and 100 μL of triethylamine (Et_3N). After 2 h, the sample was extracted with acetonitrile and dried in vacuo for 4 h.

Reaction with 2,4-Dinitrophenylhydrazine. The irradiated film of poly-**1** was placed in a solution of 120 mg of 2,4-dinitrophenylhydrazine hydrochloride in 30 mL of 5% HCl and 10 mL of isopropanol (20 min at 70 °C). After washing with ethanol, the polymer layer was dried in vacuo for 4 h.

Reaction with $FeCl_3$ and NH_4SCN. The irradiated film of poly-**1** was placed in a solution of 1 g of $FeCl_3$ in 10 mL of ethanol for 14 h. After washing with ethanol, the polymer layer was dried in vacuum for 4 h. In a second step, the polymer layer was treated with a 1% solution of NH_4SCN in ethanol for 60 s. The polymer layer was washed with ethanol again and dried in vacuo for 4 h.

FT-IR spectra were recorded with a Perkin-Elmer Spectrum One instrument (spectral range between 4000 and 450 cm^{-1}). All FT-IR spectra were recorded in transmission mode. UV−vis spectra were measured with a Jasco V-530 UV−vis spectrophotometer. All UV−vis spectra were taken in the absorbance mode. Photoluminescence spectra were measured on a Shimadzu RF-5301PC Spectrofluorimeter (detector corrected).

Contact Angle Measurements. The surface tension γ of the sample surfaces was determined by measuring the contact angle with a Drop Shape Analysis System DSA100 (Krüss GmbH, Hamburg, Germany) using water and diiodomethane as test liquids (drop volume of ~20 μL). The contact angles were obtained by means of the sessile drop method and measured within 2 s after deposition of the droplet. The reproducibility was within 2°. On the basis of the Owens−Wendt method,[14] we calculated the surface tension γ as well as the dispersive and polar components (γ^D and γ^P).

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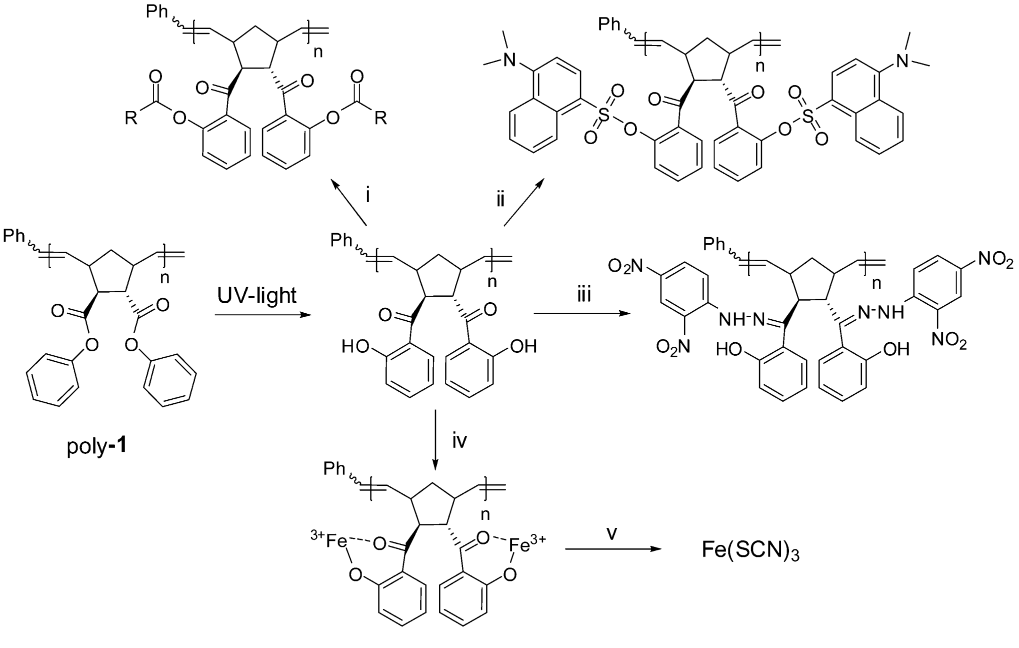
Scheme 2. Photo-Fries Reaction of Poly-1 and Subsequent Postexposure Reactions



(i) Vapors of $RCOCl/CH_2Cl_2$; R = CH_3, C_6H_5, C_3F_7; (ii) dansyl chloride, triethylamine, acetonitrile; (iii) 2,4-dinitrophenylhydrazine, ethanol, HCl (aq); (iv) $FeCl_3$, ethanol; (v) NH_4SCN, ethanol.

Results and Discussion

The synthesis of the photosensitive polymer poly(endo, exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid, diphenyl ester) (poly-**1**) resulted in a polymer with a number averaged molecular weight M_n of 140000 g/mol and a low polydispersity index PDI of 1.13. Poly-**1** shows excellent film-forming properties when spin-cast from CH_2Cl_2 solutions and has a glass-transition temperature T_g = 96.5 °C. For the investigation of the photoisomerization and the postmodification reactions, homogeneous and transparent polymer films were prepared by spin-casting from CH_2Cl_2 solutions.

Upon irradiation with UV light, this polymer undergoes the photo-Fries rearrangement. The chemical reactivity of the illuminated areas is enhanced because of the formation of aromatic *o*- and *p*-hydroxyketones. Scheme 2 provides an overview of the modification reactions that take place only in the illuminated areas and are subject of the present contribution. First, the phenol group can react with carboxylic acid chlorides to form new esters (i). Second, phenols can react with organic sulfonic acid chlorides, e.g., with dansyl chloride (ii). Third, the *o*-hydroxyketone is an excellent ligand and can coordinate metal ions such as Fe^{3+} (iv). This reaction can be made visible by a second postreaction using NH_4SCN (v) that forms an intense red-colored iron complex. Finally, the keto group can be modified by reactions with derivatives of hydrazines to give the corresponding hydrazones (iii).

Reactions with Carboxylic Acid Chlorides. Polymer poly-**1** itself absorbs UV light up to a wavelength $\lambda \approx 280$ nm, as shown in Figure 1. UV absorption in this range is typical of the phenyl chromophore with its $\pi-\pi^*$ transitions. The ester C=O group itself absorbs weakly around 190 nm ($\pi-\pi^*$) and with extremely low absorbance around 270 nm ($n-\pi^*$), whereas the C=C double bonds absorb around 200 nm ($\pi-\pi^*$ transition). After flood UV illumination under a nitrogen atmosphere, one can observe a significant increase in UV absorption. For the irradiated sample of poly-**1**, two weak absorbance maxima localized at $\lambda = 260$ nm and $\lambda = 330$ nm are detectable. These changes indicate the formation of aromatic hydroxyketone units. These absorptions are assigned to the $\pi-\pi^*$ and $n-\pi^*$ orbital transitions, respectively. After illumination, the polymer film was exposed to vapors of a mixture of acetyl chloride and CH_2Cl_2. The latter reagent causes some swelling of the polymer film, so that acetyl chloride can react through the whole layer. This postmodification reaction leads to a general decrease in the UV−vis absorption, as can be seen in Figure 1. However, the absorbance remains still higher than for the original polymer film prior to illumination.

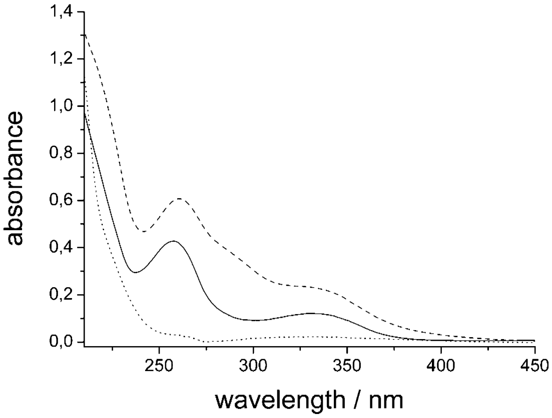


Figure 1. UV spectra of a film of poly-**1** on CaF_2 prior to illumination (dotted line), after illumination with UV light (energy density E = 24 J cm^{-2}, measured in the range $\lambda = 230-320$ nm) (dashed line) and after reaction with acetyl chloride (solid line).

Polychromatic irradiation causes significant changes in the chemical structure of the polymer, which can be easily followed by FTIR spectroscopy. Figure 2 shows detailed FTIR spectra of poly-**1** before (a) and after (b) illumination

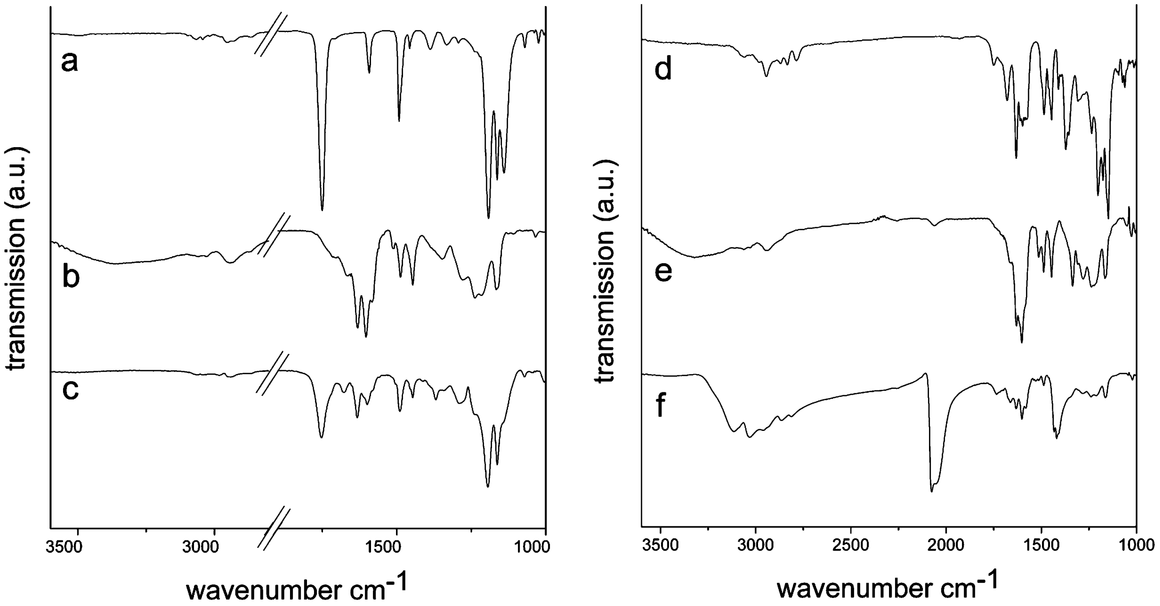


Figure 2. FT-IR-spectra of poly-**1** (a) before and (b) after illumination with UV-light, followed by posttreatment with (c) acetyl chloride, (d) dansyl chloride, (e) 2,4-dinitrophenylhydrazine, and (f) $FeCl_3$ and NH_4SCN.

Table 1. Contact Angle (*θ*) and Surface Tension Data (γ = surface tension; γ^D = dispersive component; γ^P = polar component; surface polarity = 100 (γ^P/γ)) for Poly-1 before and after Illumination and after Posttreatment with Acetyl Chloride[a]

poly-**1**	θ H_2O[b] (deg)	θ CH_2I_2[b] (deg)	γ (mJ m^{-2})	γ^D (mJ m^{-2})	γ^P (mJ m^{-2})	surface polarity (%)
before illumination	89	33.6	43.5	42.7	0.8	1.9
after illumination	81.3	47.2	39.7	35.8	3.8	9.7
+ acetyl chloride	99.5	47.3	35.9	35.8	0.12	0.33
+ perfluorobutyryl chloride	92.7	64.5	28.3	26.0	2.3	8.2

[a] Power density $P = 20$ mW cm^{-2}. [b] Contact angle (sessile drop).

with UV light. In the spectrum of the nonirradiated film, the signals at 1750 cm^{-1} (C=O stretch) and at 1191 cm^{-1} (asymmetric C−O−C stretch) are typical of ester units R_1−(C=O)−OR_2, with R_1 being an aliphatic unit and R_2 being a phenyl ring.[15] After UV irradiation, the vibrational bands of the phenyl ester group at 1750 and 1191 cm^{-1} have almost quantitatively disappeared. Instead, a new broad band evolving at 3380 cm^{-1} stems from the O−H stretching vibration of hydroxyl groups, and the new signal at 1631 cm^{-1} can be attributed to the carbonyl stretching vibration of an *o*-hydroxyketone. Both signals prove the formation of the expected photo-Fries product (i.e., the *o*-hydroxyketone). In addition to this, a weak signal appears at 1670 cm^{-1}. Considering the position of the C=O group in 4-hydroxyacetophenone (1675 cm^{-1}), this signal indicates the formation of *p*-hydroxyketone groups.

The following postmodification reaction with acetyl chloride can be observed by FT-IR spectroscopy as well, see Figure 2c. After exposure to vapors of acetyl chloride, the formation of a carboxylic acid ester leads to the reappearance of ester signals at 1752 cm^{-1} (C=O stretch) and 1194 cm^{-1} (asymmetric C−O−C stretch). The band at 1369 cm^{-1} can be attributed to the C−H deformation vibrations in the methyl group of the acetate. At the same time, the disappearance of the hydroxyl signal at 3380 cm^{-1} indicates the conversion of the aromatic alcohol.

This procedure can be generalized to other organic carboxylic acid chlorides. We have undertaken experiments with perfluorobutyryl chloride and with benzoyl chloride. The reaction can be carried out in a manner similar to that described above by exposing the illuminated film to vapors of the carboxylic acid chloride and CH_2Cl_2 but also by immersing the exposed films directly into the carboxylic acid chloride if the vapor pressure is too low. However, a drawback of using carboxylic acid chlorides with a higher boiling point is that the residual acid chloride is difficult to remove from the polymer layer.

By the choice of the acid chloride, the surface properties can be tuned in a wide range. Table 1 summarizes the results from contact-angle measurements before and after illumination of poly-**1** as well as after the postmodification reaction with acetyl chloride and with perfluorobutyryl chloride, respectively. The data on the surface tension γ and its dispersive (γ^D) and polar components (γ^P), as calculated by the Owens−Wendt method, are also presented.

The contact angle θ of water is high on the nonirradiated polymer surface ($\theta = 89°$), whereas the contact angle of diiodomethane is low ($\theta = 33.6°$). These values indicate the hydrophobic character of this polymer. After UV irradiation (20 min), the polymer became more hydrophilic, as the contact angle of water decreased to $\theta = 81.3°$ and the contact angle of diiodomethane increased to $\theta = 47.2°$. This behavior is consistent with the formation of phenolic OH groups at the surface. After treatment with acetyl chloride, the contact angle of water increases to 99.5° again; however, the contact

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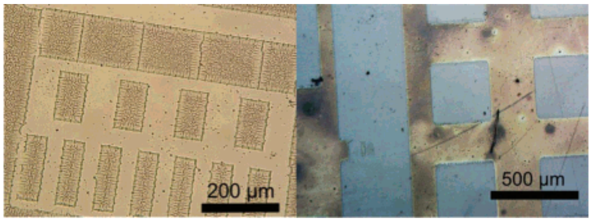

Figure 3. Optical micrograph of a thin film of poly-**1** after structured illumination followed by posttreatment with vapors of acetyl chloride/dichloromethane (left). Alternative posttreatment: immersion in neat benzoyl chloride (right).

angle of diiodomethane remains constant. These findings are in agreement with the conversion of the hydroxyl groups to ester units. Using perfluorobutyryl chloride instead, the contact angle of water increased from 81.3 to 92.7°. This value is lower than after treatment with acetyl chloride. A possible explanation is that the perfluorobutyryl chloride cannot react quantitatively with all OH groups because of the incompatibility of the fluoro-compound with the polymer surface. However, the contact angle of diiodomethane increases from 47.2 to 64.5°, which indicates an oleophobicity of the modified surface as expected for a modification with fluorocarbon groups.

A more quantitative picture is provided by the changes in surface tension and its components, which are also listed in Table 1. Upon irradiation, the overall surface tension γ is lowered, mainly because the dispersive component γ^D decreased significantly from 42.7 to 35.8 mJ m^{-2}, whereas the polar component γ^P increased slightly from 0.8 to 3.8 mJ m^{-2}. As a result, the surface polarity ($100(\gamma^P/\gamma)$) increases from 1.9 to 9.7%. After posttreatment with acetyl chloride, the overall surface tension decreased slightly because of the almost total absence of the polar component ($\gamma^P = 0.12$) and the surface polarity is very low (0.3%). In contrast to this, the treatment with perfluorobutyryl chloride leads to a surface with a very low surface tension ($\gamma = 28.3$ mJ m^{-2}). However, because of the reasons discussed above, the polar component is higher than for the surface treated with acetyl chloride but lower than for the surface directly after UV illumination. The dispersive component of the surface tension of the fluoro-modified film is the lowest of all samples ($\gamma^D = 26.0$ mJ m^{-2}).

In combination with lithographic methods, these postexposure reactions can be applied for the production of patterned polymer films and surfaces. For this purpose, a contact mask was placed onto the polymer film prior to illumination. After UV exposure, the polymer layer was still optically transparent and no structural features were discernible by optical microscopy. The postmodification step with carboxylic acid chlorides leads to the evolution of structural features, see Figure 3. The features can be detected by optical microscopy because the postmodification reaction is accompanied by an increase in film thickness. This leads to different optical pathlengths and interference colors in nonilluminated and modified areas of the polymer film. Without any optimization, a resolution of several micrometers was achieved.

Postmodification Reaction with Dansyl Chloride. Another approach for the immobilization of molecules on the irradiated areas of the surface is the reaction of hydroxyl groups with sulfonic acid chlorides. To demonstrate this, we used dansyl chloride, a fluorescent dye. After UV illumination of a film of poly-**1**, the sample was developed with a solution of dansyl chloride and triethylamine in acetonitrile. The aromatic hydroxyl groups react readily with the sulfonic acid chloride to give the corresponding sulfonic acid ester. Figure 2d displays the FTIR spectrum of an irradiated film of poly-**1** after treatment with dansyl chloride. The changes in the spectrum are in accordance with the proposed reaction. The depletion of the broad hydroxyl stretching vibration at 3380 cm^{-1} is accompanied with the appearance of new bands at 1372 and 1202 cm^{-1}, which can be attributed to the asymmetric and symmetric SO_2 stretching vibrations. An additional band at 1148 cm^{-1} is typical of the C−N stretching vibration in $R-N(CH_3)_2$ groups and is assigned to the corresponding unit in the dansyl chromophore.

A comparison of the UV−vis spectra of the illuminated film of poly-**1** prior to and after the development step is given in Figure 4a. After the reaction with dansyl chloride, the film absorbs light up to $\lambda \approx 420$ nm exhibiting two maxima at $\lambda = 256$ and 339 nm.

The modified film displays photoluminescence with the maximum of fluorescence emission at $\lambda_{em} = 530$ nm and the maximum of excitation at $\lambda_{excit} = 364$ nm. These values are comparable to those reported for dansyl moieties immobilized on OH-modified polystyrene resins ($\lambda_{em} = 506-528$ nm; $\lambda_{excit} = 336-390$ nm).[16]

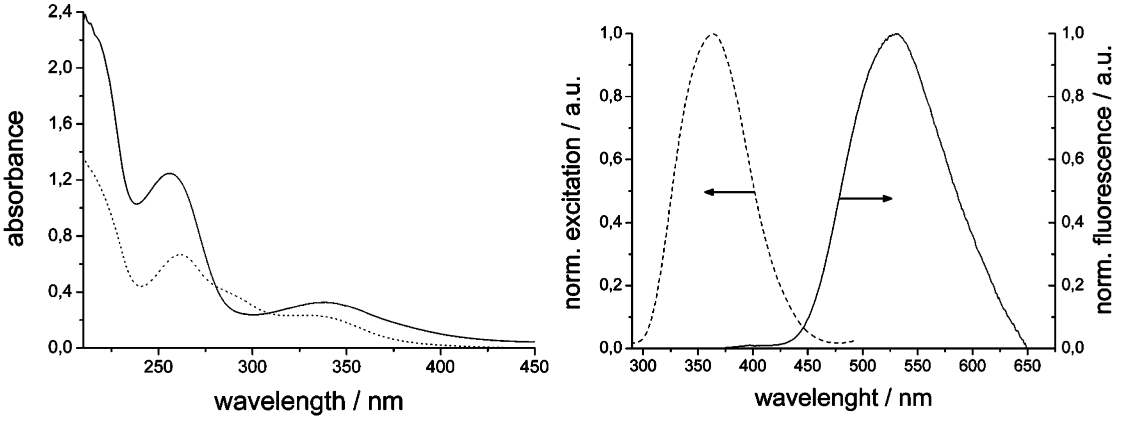

Figure 4. (a) Comparison of the UV−vis spectra of a irradiated film of poly-**1** on CaF_2 before (dotted line) and after posttreatment with dansyl chloride (solid line). (b) Photoluminescence excitation (dashed line) and emission spectra (solid line) of a film of poly-**1** after reaction with dansyl chloride.

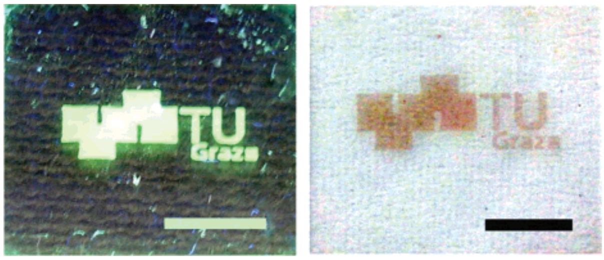

Figure 5. (a) Image of a film of poly-**1** after patterned UV irradiation and subsequent modification with dansyl chloride (the sample was illuminated with $\lambda = 302$ nm while taking the photograph). (b) Image of a film of poly-**1** after structured illumination followed by posttreatment with iron(III)chloride and subsequently with NH_4SCN.

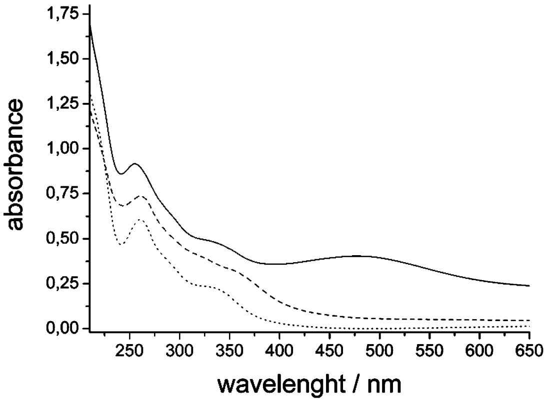

Figure 6. UV−vis spectra of a film of poly-**1** on CaF_2 after illumination (dotted line), after reaction with $FeCl_3$ (dashed line), and after subsequent reaction with NH_4SCN (solid line).

In combination with lithographic techniques, this postmodification reaction can be used to prepare fluorescence patterns on polymer films. A possible application is the production of dye spots for analytical applications. The result of a patterned modification, using a simple contact mask during the illumination step, is shown in Figure 5a. The sample was illuminated by UV light ($\lambda = 302$ nm) while taking the photograph.

Postmodification with $FeCl_3$. The photogenerated *o*-hydroxyketones in poly-**1** can coordinate metal ions. A known test reaction for the presence of ferric ions is the reaction with phenol to give an iron−phenol complex.[17] However, the hydroxyketone can also coordinate the ferric ions as chelating ligand, similar to iron(III) acetylacetonate. The irradiated film of poly-**1** was immersed in a solution of $FeCl_3$ in ethanol for several hours, resulting in a slightly yellowish film. The UV−vis spectrum in Figure 6 taken after the reaction with $FeCl_3$ shows that the absorbance is now shifted to higher wavelengths (up to $\lambda \approx 450$ nm).

The immobilization of Fe^{+3} ions was further proven by reaction with NH_4SCN in a solution of ethanol, which led to the formation of a deeply red-colored iron(III) thiocyanate complex. The UV−vis spectrum of poly-**1** (after reaction with Fe^{+3} and subsequently with NH_4SCN) displayed an additional increase in absorbance and an additional broad absorbance band peaking at $\lambda = 477$ nm, as seen in Figure 6. This value is in accordance with data reported for ferric thiocyanate complexes ($\lambda_{max} = 450-480$ nm, depending on the concentration of SCN^-).[18] The FT-IR spectrum (Figure 2f) shows the typical strong bands of such a complex at 2075 cm^{-1}, which are assigned to the asymmetric N═C═S stretching vibration of inorganic thiocyanates.[15]

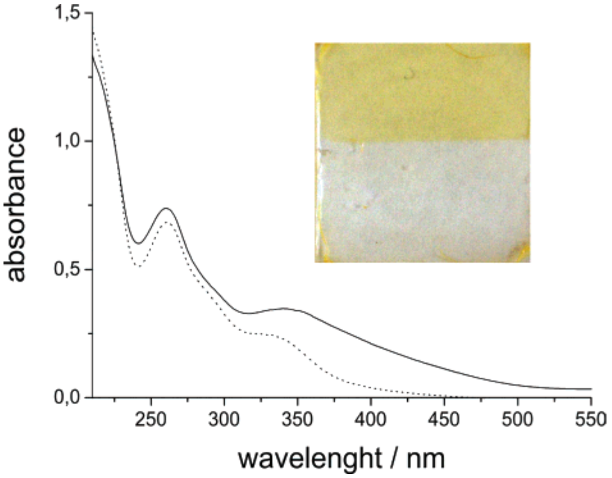

Figure 7. UV spectra of a film of poly-**1** on CaF_2 after illumination (dotted line) and after subsequent posttreatment with 2,4-dinitrophenyl hydrazine (solid line). Insert: image of a film of poly-**1** after structured illumination (one-half of the film was shielded from light) followed by posttreatment with 2,4-dinitrophenylhydrazine (sample size 1.5 cm × 1.5 cm).

Figure 5b shows the colored features obtained by patterned illumination of poly-**1** followed by the $FeCl_3/NH_4SCN$ postmodification reaction.

Postmodification Reaction with 2,4-Dinitrophenylhydrazine. An interesting approach for selective functionalization of the illuminated areas is the reaction of the carbonyl group of the hydroxyketone with hydrazine compounds to give the corresponding hydrazones. For this purpose, a UV irradiated film of poly-**1** was treated with a solution of 2,4-dinitrophenylhydrazine hydrochloride in a mixture of diluted aqueous HCl and isopropanol.

As a result of this treatment, the color of the polymer film changed to yellow. Figure 7 displays the photograph of a polymer film that was illuminated and then treated with 2,4-dinitrophenylhydrazine. A UV−vis spectrum taken after this reaction shows a general increase in absorbance and a shift of absorbance to higher wavelengths when compared to an illuminated film of poly-**1**, see Figure 7. Two absorbance maxima are observed at $\lambda = 260$ nm and $\lambda = 340$ nm. The UV−vis absorbance now extends to $\lambda > 500$ nm, which indicates the immobilization of 2,4-dinitrophenylhydrazine.

Figure 2e displays the FTIR spectrum of a film of poly-**1** after reaction with 2,4-dinitrophenylhydrazine. New bands which evolve at 1485 and 1336 cm^{-1} can be assigned to the symmetric and asymmetric NO_2 stretching vibration, typical of aromatic nitro compounds.

Conclusion

In this contribution, we have explored the photo-Fries rearrangement in combination with postexposure modification reactions for the patterning and functionalization of

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polymer films. The photo-Fries reaction generates reactive hydroxyketone groups due to a shift of the acyl group. The hydroxyketone groups enhance the surface polarity of the polymer, and in addition, they can be employed for a selective modification of the irradiated areas of the polymer. We have shown different types of posttreatment reactions that can be easily combined with lithographic processes to obtain structured functional polymer films. The aromatic OH groups react with carboxylic acid chlorides to give esters groups. The choice of the acid chloride then determines the polarity of the surface. In another approach, organic sulfonic acid chlorides have been used, as demonstrated with the fluorescent compound dansyl chloride. Using lithographic techniques, fluorescence patterns with bright luminescence were obtained. In addition, it is possible to immobilize metal ions in the irradiated zones of the polymer surface. This was evidenced for Fe^{3+} ions. For visualization and contrast enhancement, the surface was subsequently treated with ammonium rhodanide to give a red-colored complex. Finally, the reaction of the photogenerated carbonyl groups with 2,4-dinitrophenylhydrazine yields the corresponding hydrazones.

Photoreactive aryl ester units can be conveniently integrated in polymer architectures. Therefore, the photo-Fries reaction represents a versatile tool for tuning the surface properties, optical patterning, and polymer functionalization.

Acknowledgment. Financial support by the Austrian Science Fund (FWF) in the framework of a national research network (NFN Interface controlled and functionalized organic films—Project: S9702−N08 “*Design and application of tunable surfaces based upon photoreactive molecules*”) is gratefully acknowledged.

Supporting Information Available: Additional spectroscopic data for postmodification reaction with carboxylic acid chlorides and $FeCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

CM070506H