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UV-Induced Modulation of the Refractive Index and the Surface Properties of Photoreactive Polymers Bearing *N*-Phenylamide Groups

Thomas Griesser,*[†,‡] Jan-Carlos Kuhlmann,[‡] Manuel Wieser,[‡] Wolfgang Kern,[†,‡] and Gregor Trimmel*[‡]

Institute of Chemistry of Polymeric Materials, University of Leoben, Franz Josef Strasse 18, 8700 Leoben, Austria, and Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology, Stremayrgasse 16, 8010 Graz, Austria

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ABSTRACT: Poly(*N*,*N*′-diphenyl-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxamide) was prepared as a functional polymer containing photoreactive arylamide groups. Under 254 nm UV irradiation, the arylamide groups undergo a photo-Fries rearrangement which yields aminosubstituted ketones as the reaction product. In thin films of the polymer, the photoreaction leads to a significant increase of the refractive index n by $\Delta n = +0.10$ which is unusually large for polymeric materials and more than sufficient for optical applications such as waveguiding. Due to the photogeneration of aminoketone groups, the chemical reactivity of the polymer is also enhanced after the irradiation step. This was employed for a selective postexposure modification of polymer films with acid chlorides and fluorescamine. In combination with photolithographic techniques, a structured surface functionalization was demonstrated. By reaction of the amino groups with bicyclo[2.2.1]hept-5-ene-2-carboxylic acid chloride a polymer surface bearing pendant norbornene units was created. Using the ring opening metathesis polymerization technique (ROMP), the immobilized norbornene moieties were successfully employed in a grafting-from polymerization of norbornene monomers. Photoreactive polymers bearing *N*-phenylamide groups are of interest for photolithography, optical applications such as waveguiding and holographic data storage, and for site selective surface functionalization.

Introduction

Photolithographic patterning of polymer films has found numerous applications in optics, microelectronics, biochip- and nanotechnology using the difference in properties generated by UV irradiation. Examples for photoinduced changes are a different solubility making polymers suitable as photoresists[1] and differences in chemical reactivity allowing the site-selective immobilization of (bio)molecules and the electroless deposition of metals[2] at the surface. Other examples are variations in surface energy and adhesion,[3] and changes in the refractive index which can be utilized for data storage and optical elements such as wave guides and distributed feedback (DFB) lasers.[4] As an example, an elastic, mechanically color tuneable DFB laser structures based on refractive index modulation due the photoisomerisation of benzylthiocyanate groups have been realized.[5] Recently, we have reported the photo-Fries reaction in polymers containing aryl ester units which results in a large increase of the refractive index.[6,7] This observation has been confirmed by other researchers.[8] These two photoisomerisations have the additional advantage that the chemical reactivity of the polymer layers is enhanced in the irradiated areas. The isothiocyanate groups readily react with amines[9] and thiols, and the photo-Fries rearrangement reaction of aryl esters generates aromatic hydroxyketones which can be further functionalized by post modification reactions.[10] The photo-Fries rearrangement has first been described by Anderson and Reese in 1960,[11] but is not limited to aryl esters. Corresponding photoreactions have been described for aryl carbonates, carbamates, sulfonates, and sulfamates as well as for anilides, sulfonanilides, and sulfenanilides, as recently reviewed by Miranda and Galindo.[12]

The present paper aims at Fries-type photoreactions in functional polymers bearing pendant *N*-phenylamide units. The first report of the photo-Fries reaction of low-molecular-weight amides was given by Elad describing the photoreaction of different *N*-acyl anilines.[13] Mechanistic studies carried out by Shizuka on acetanilide[14] and Carlson on fully aromatic amides[15] supported the reaction path shown in Scheme 1. After absorption of light, scission of the *N*-acyl bond leads to the formation of a radical pair. The generated radicals can recombine and then yield *o*- or *p*-cyclohexadienones as the "cage product". Tautomerism then gives the corresponding aromatic aminoketones. As side reactions, the release of aniline and other compounds has been observed.[13,14b]

For acetanilide, the quantum yields Φ of the ortho- and para-rearrangement product have been reported in the literature ($\Phi_o = 0.07$ and $\Phi_p = 0.06$, respectively).[14c]A comparison with literature data on phenyl acetate ($\Phi_o = 0.18$ and $\Phi_p = 0.20$, respectively) shows that the photo-Fries rearrangement in anilides proceeds far slower than in the corresponding esters.[16]

The photo-Fries rearrangement of *N*-arylamides in polymers has mainly been investigated in terms of the photodegradation of the material.[17] Poly(*N*-phenyl methacrylamides) showing the photo-Fries reaction have been proposed as photoresists, but the background of this application is based on cross-linking as side reaction.[18]

However, a versatile feature of the photo-Fries rearrangement is the photogeneration of free amino groups. These functionalities can act as anchoring groups for a variety of bio(molecules) and in this context are even more interesting than the hydroxy groups generated by the analogous reaction of aryl esters. A modulation of the refractive index caused by the photoreaction can also be expected for aryl amide based materials.

In this contribution we present the preparation of a new photoreactive polymer with *N*-phenylamide (anilide) side groups, and demonstrate the versatility of the photo-Fries reaction in

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* Corresponding authors. (T.G.) E-mail: thomas.griesser@unileoben.ac.at. Telephone: ++433842 4022355. (G.T.) E-mail: gregor.trimmel@tugraz.at. Telephone: ++43316-8734958. Fax: + +43316-8738951.

[†] Institute of Chemistry of Polymeric Materials, University of Leoben.

[‡] Institute for Chemistry and Technology of Materials (ICTM), Graz University of Technology.

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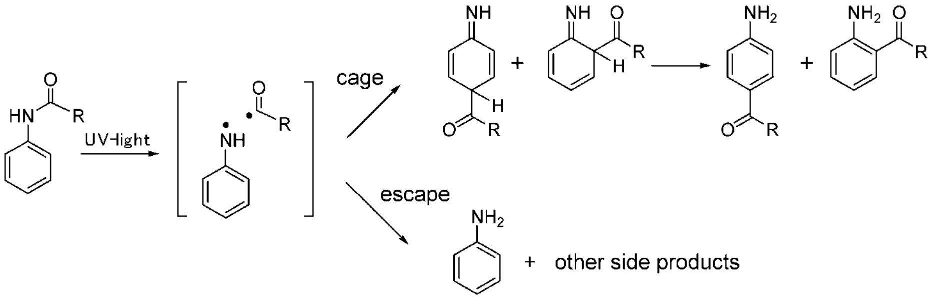
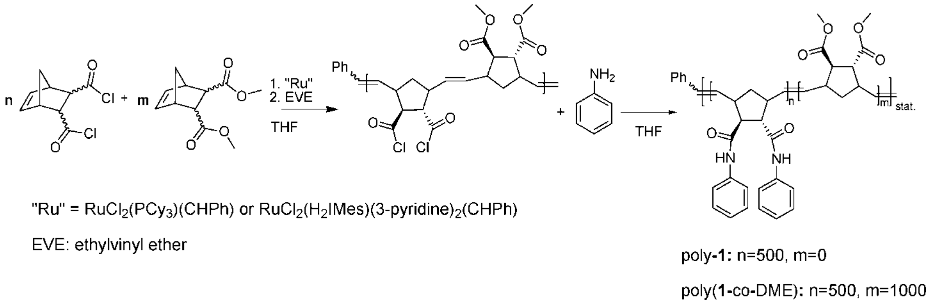
Scheme 1. Mechanism of the Photo-Fries Rearrangement in *N*-Phenylamides



Scheme 2. Synthesis of Poly-1 and Poly(1-*co*-DME)



polymer thin films with respect to refractive index modulation as well as site selective surface functionalization. As polymerization method ring opening metathesis polymerization (ROMP) was chosen which allows the preparation of well defined polymers and copolymers in a convenient fashion.[19]

Experimental Part

All chemicals were purchased from commercial sources and were used without further purification. CH_2Cl_2 was distilled over CaH_2 and degassed with argon. Tetrahydrofuran (THF) was distilled over Na/K and degassed with argon. e*ndo,exo*-Bicyclo[2.2.1]hept-5-en-2-carboxylic acid chloride[20] and $RuCl_2(H_2IMes)(3\text{-pyridine})_2(CHPh)$ (H_2IMes = *N,N*-di(mesityl)-4,5-dihydroimidazolin-2-ylidene)[21] were prepared according to the literature. *endo,exo*-Bicyclo[2.2.1]-hept-2-ene-5,6-dicarboxyclic acid dimethylester (DME) was kindly supplied by Orgentis Chemicals. **Caution!** *For the preparative work, hazardous chemicals and solvents were used. Reactions must be carried out in a fume hood and protective clothes and goggles must be used!*

^1H NMR and ^{13}C NMR spectra were recorded with a Varian INOVA 500 MHz spectrometer operating at 499.803 and 125.687 MHz, respectively and were referenced to $Si(CH_3)_4$. A relaxation delay of 10 s and 45° pulse were used for acquisition of the ^1H NMR spectra. Solvent residual peaks were used for referencing the NMR spectra to the corresponding values given in the literature.[22]

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). Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer "Pyris Diamond" under a nitrogen flow of 20 mL/min and a heating rate of 10 °C/min. Glass transition temperatures (T_g) from the second heating run were read as the midpoint of change in heat capacity. Refractive indices (n_D^{20}) of liquids were measured with an Abbe refractometer (Krüss, Germany). Ellipsometric measurements were

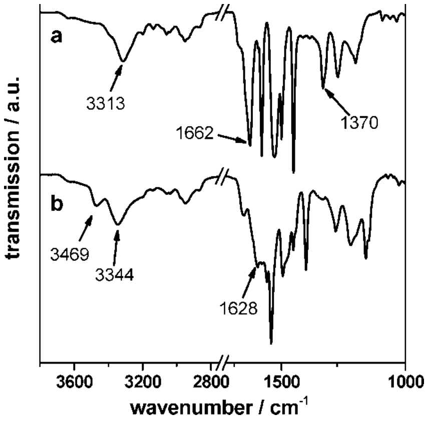


Figure 1. FTIR spectra of a film of poly-**1** before (a) and after (b) illumination with UV-light of 254 nm (radiant energy per unit area = 9.7 J cm^{-2}).

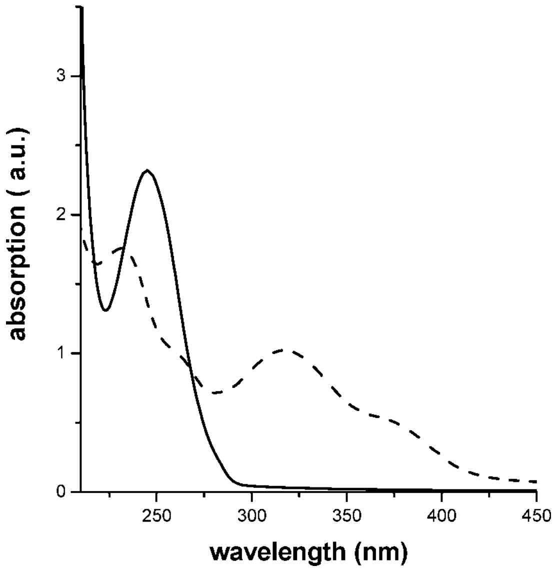


Figure 2. UV–vis spectra of poly-**1** prior to (solid line) and after illumination (dashed line). λ = 254 nm; radiant energy per unit area = 9.7 J cm^{-2}.

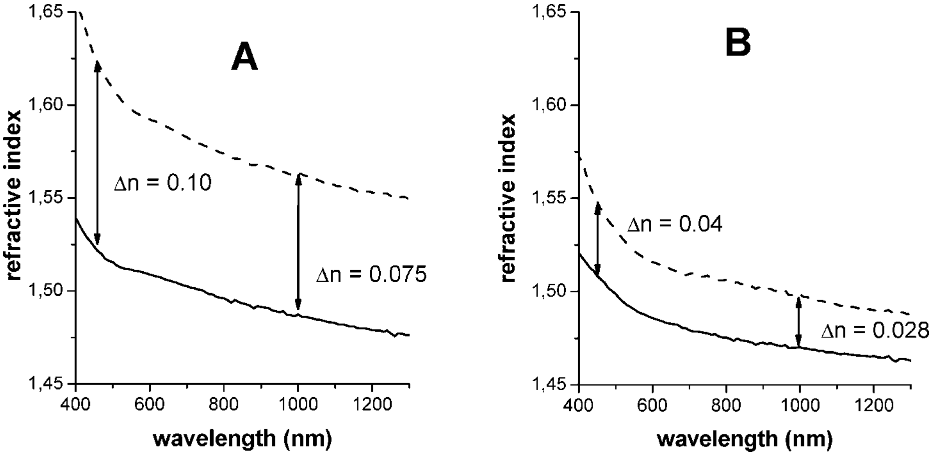


Figure 3. (A) Cauchy fit of the dispersion of the refractive index of poly-**1** before (solid line) and after illumination (dashed line), radiant energy per unit area = 16.2 J cm^{-2}. (B) Cauchy fit of the dispersion of the refractive index of poly-(**1**-*co*-DME) before (solid line) and after illumination (dashed line), radiant energy per unit area = 9.7 J cm^{-2}.

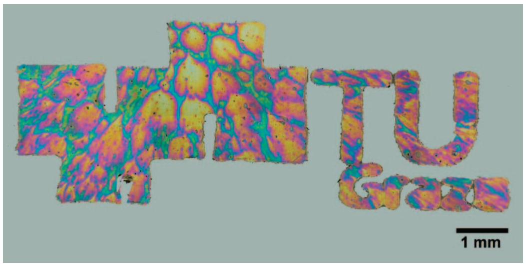


Figure 4. Optical micrograph of a film of poly-**1** after photopatterning (254 nm) and subsequent development with THF.

performed with a Woollam VASE spectroscopic ellipsometer (Xenon short arc lamp, wavelength range 240 nm-1100 nm, spectral bandwidth 4 nm). The implemented software uses the Levenberg–Marquardt fit algorithm. From ellipsometric data both the film thickness and the dispersion of the refractive index (Cauchy fit) were obtained.

GPC. The weight and number average molecular weights (M_w and M_n) as well as the polydispersity index (PDI) were determined by gel permeation chromatography with THF as solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 × 300 mm STV 5 μm grade size (106 Å, 104 Å, and 103 Å), combined refractive index–viscosity detector from Viscotec, Viscotec 200. Polystyrene standards purchased from Polymer Standard Service were used for calibration.

Syntheses. *Poly((±)endo,exo-N,N′-diphenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxamide) (Poly-1).* To a solution of (±)*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid chloride (300 mg; 1.37 mmol) in 10 mL of THF was added a solution of $RuCl_2(PCy_3)_2(CHPh)$ (2.25 mg; 2.7 μmol, Cy = cyclohexyl) dissolved in 2 mL of THF. The reaction mixture was stirred at room temperature for 48 h, and then the reaction was stopped by addition of 150 μL of ethyl-vinylether. To the polymer solution aniline (510 mg; 5.48 mmol) was added and after 24 h the polymer was precipitated by dropping the solution into 50 mL of 5% aqueous HCl. The obtained polymer was redissolved in THF and was precipitated in 50 mL of 5% aqueous HCl again. The precipitate was dried in vacuum and 0.443 g (96%) of poly-**1** was obtained as a white solid. GPC (*THF*): M_n = 130 000 g/mol (M_n theor.: 166 300 g/mol); PDI = 2.15; T_g = 206 °C.

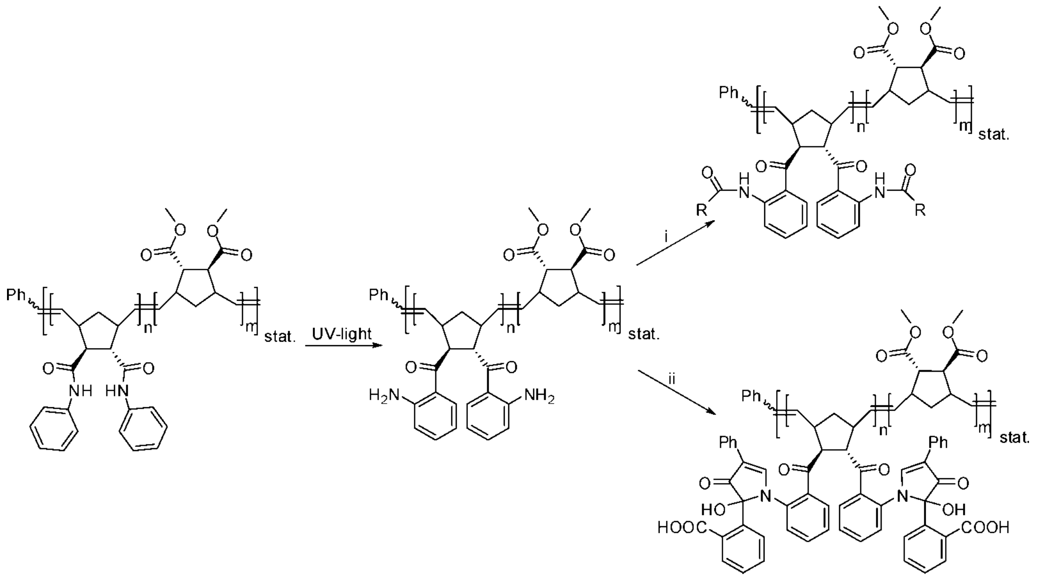
^{1}H NMR (δ, 500 MHz, 20 °C, DMSO): 10.02–9.67 (2H, NH); 7.70–6.80 (10 H, Ph); 5.70–4.90 (2H, CH=CH); 4.09–0.65 (6H, nb-CH, CH_2) ppm. $^{13}C\{^1H\}$ NMR (δ, 125 MHz, 20 °C, DMSO): 171.9; 170.7 (C=O); 138.9 (C1); 131.4 (CH=CH); 128.4 (C3,5); 123.0 (C4); 119.1 (C2,6); 53.8 (CH_3,$Cp^{1,5}$); 46.7 ($Cp^{2,4}$); 39.4 (C3) ppm. FT-IR (CaF_2, cm^{-1}): 3628, 3394, 3313, 3199, 3138, 3060, 2952, 2870, 1945, 1727, 1662, 1618, 1599, 1535, 1499, 1442, 1397, 1368, 1338, 1309, 1247, 1177, 1078, 1051, 1029, 970, 899.

Poly((±)endo,exo-N,N′-diphenylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxamide-co-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (Poly(1-co-DME)). To a solution of (±)*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid chloride (343 mg; 1.56 mmol) and (±)*endo,exo*-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (DME; 658 mg; 3.12 mmol) in 60 mL of THF a solution of $RuCl_2(H_2IMes)(3\text{-pyridine})_2(CHPh)$ (2.3 mg; 3.1 μmol) dissolved in 2 mL in THF was added. The reaction mixture was stirred at room temperature for 48 h and the reaction was subsequently stopped by adding 150 μL of ethyl vinyl ether. To the polymer solution was added aniline (726 mg; 7.8 mmol), and after 24 h the polymer was precipitated by dropping the solution into 50 mL of 5% aqueous HCl. The obtained polymer was resolved in THF and was precipitated in 50 mL of 5% HCl solution again. The precipitate was dried in vacuum to give 0.819 g (69%) of poly(**1**-*co*-DME). GPC (THF): M_n = 390 000 g/mol (M_n theor.: 375 000 g/mol); PDI = 2.56; T_g = 161 °C. ^{1}H NMR (δ, 500 MHz, 20 °C, DMSO): 10.06–9.70 (2H, NH); 7.70–6.87 (10H, Ph); 5.70–4.90 (4H, CH=CH); 3.67–0.75 (18 H, CO–O–CH_3, nb-CH, CH_2) ppm. $^{13}C\{^1H\}$ NMR (δ, 125 MHz, 20 °C, DMSO): 173.4; 172.3 (C=O); 139.1 (C1); 133.5 (CH=CH); 128.4 (C3,5); 127.9 (C4); 119.1 (C2,6); 51.5 (CH_3,Cp1,5 (mono 1)); 47.9 (Cp2,4); 39.3 (C3) ppm. FT-IR (CaF_2, cm^{-1}): 3621, 3337, 3201, 3140, 3061, 3001, 2953, 2869, 1732, 1683, 1666, 1618, 1560, 1539, 1500, 1441, 1383, 1359, 1309, 1248, 1199, 1173, 1121, 1079, 1053, 1044, 1027, 973.

UV Irradiation. Flood UV illumination was carried out in inert atmosphere (argon) by using an ozone free mercury low pressure UV lamp (Heraeus Noblelight; 254 nm) with a power density of 1.35 mW cm^{-2}. Patterned structures were obtained by placing a contact mask (Cr pattern on quartz) directly onto the organic layer prior to illumination. *Caution! UV irradiation causes severe eye and skin burns. Precautions (UV protective goggles, gloves) must be taken!*

Postmodification reaction with acetyl chloride: after UV illumination of a film of poly-**1**-*co*-DME on a CaF_2 plate for 120 min (9.7 J cm^{-2}), the sample was immersed in a solution of acetyl chloride (0.5 g; 6.4 mmol) in 4 mL of acetonitrile. After 2 h the sample was dried *in vacuo* for 4 h. Reaction with fluorescamine: the irradiated film (120 min, 9.7 J cm^{-2}) of poly-(**1**-*co*-DME) was placed in a 5 mM solution of fluorescamine in a 1:4 mixture (v/v) of acetone/cyclohexane. After 2 h the sample was washed with acetone/cyclohexane and dried *in vacuo* for 4 h. Grafting of poly(DME) from the poly-(**1**-*co*-DME) surface: the illuminated poly(**1**-*co*-DME) film was exposed to a 0.11 M solution of (±)*endo,exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid chloride in CH_2Cl_2 for 2 h. After washing with CH_2Cl_2, the film was immersed in a solution of $RuCl_2(H_2IMes)(3\text{-bromopyridine})_2(CHPh)$ (25 mmol

Scheme 3. Photo-Fries Reaction in Poly(1-*co*-DME) and Surface Modification Reactions with (i) Acetyl Chloride (in Dichloromethane) and (ii) Fluorescamine (in Acetone/Cyclohexane)



L^{-1} in CH_2Cl_2) for 30 min. After a second washing step the polymer film was immersed in a solution of DME (3 mol L^{-1} in CH_2Cl_2) for 60 min and subsequently rinsed with CH_2Cl_2 and dried in a vacuum.

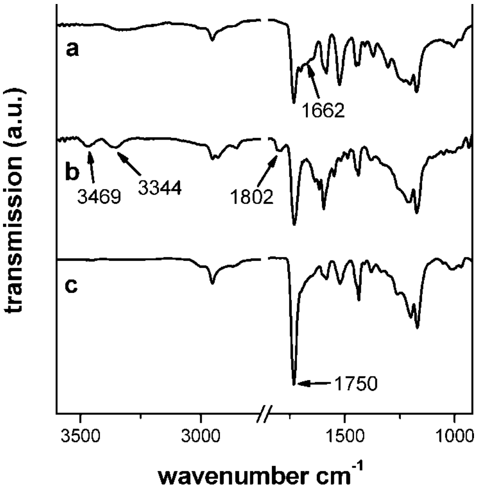


Figure 5. FTIR spectra of poly(**1**-*co*-DME) after postmodification reaction with (a) acetic acid chloride, (b) fluorescamine, and (c) grafting of poly-DME.

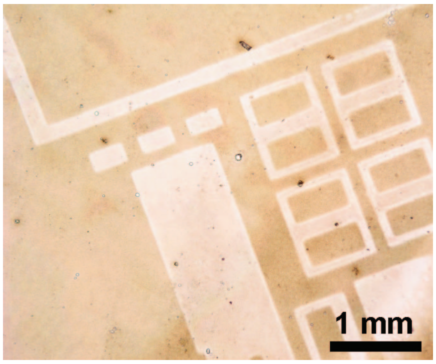


Figure 6. Optical micrograph of a film of poly(**1**-*co*-DME) after patterned UV irradiation and subsequent modification with acetyl chloride.

Results and Discussion

Synthesis of Polymers Poly-1 and Poly(1-*co*-DME). The targeted polymer structures of poly-**1** and poly(**1**-*co*-DME) are not directly accessible by ring opening metathesis polymerization (ROMP) using the ruthenium based Grubbs initiators due to strong interactions of the amide functionality with the ruthenium center. All attempts of polymerization using the Grubbs initiators – $RuCl_2(PC_{y3})_2(CHPh)$, $RuCl_2(H_2IMes)(PCy_3)$-$(CHPh)$ and $RuCl_2(H_2IMes)(3\text{-pyridine})_2(CHPh)$ - failed. Therefore, we chose an indirect route toward the desired polymers by first polymerizing the carboxylic acid chloride derivative, *endo,exo*bicyclo[2.2.1]hept-5-en-2,3-dicarboxylic acid dichloride, following the approach of Moore et al.[23] and a subsequent polymer-analogous reaction to give the amide as schematically shown in Scheme 2. For the first step, either the classical Grubbs initiator $RuCl_2(PCy_3)_2CHPh$ (Cy = cyclohexyl) or the highly reactive initiator $RuCl_2(H_2IMes)(3\text{-pyridine})_2(CHPh)$ (H_2IMes = *N*,*N*-di(mesityl)-4,5-dihydroimidazolin-2-ylidene) are suitable for ROMP. After the addition of ethylvinylether as termination reagent, the polymers were converted into the corresponding anilides by adding an excess of aniline to the reaction solution without isolating the intermediate polymer. The concentration

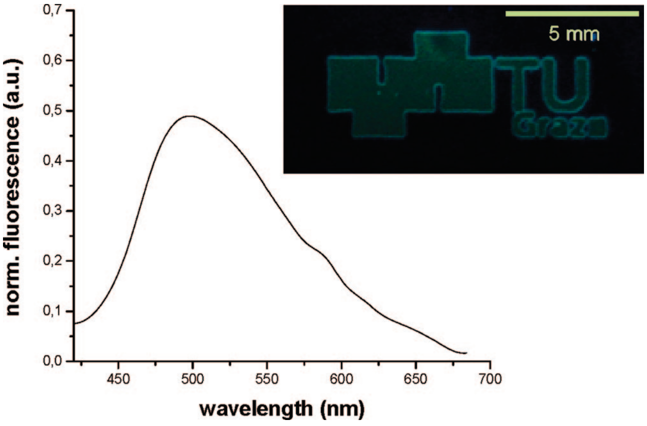
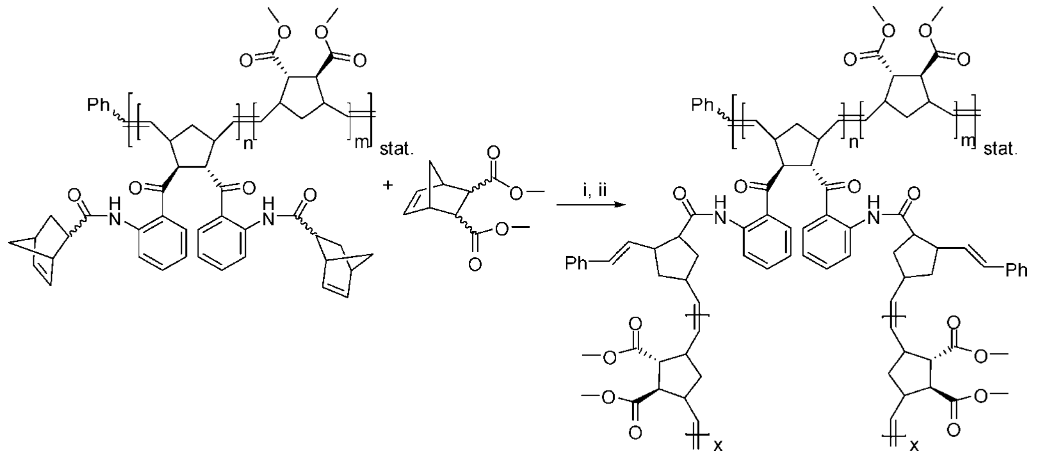


Figure 7. Photoluminescence spectra of a film of poly(**1**-*co*-DME) after illumination and postmodification reaction with fluorescamine (excitation wavelength λ = 390 nm) and an image of a patterned film prepared by the same procedure (the film was illuminated with 302 nm light while taking the photograph).

Scheme 4. Graft-Copolymerization of DME onto an Irradiated Film of Poly(1-*co*-DME) Bearing Pendant Norbornene Groups. (i) $RuCl_2(H_2IMes)(3\text{-pyridine})_2(CHPh)$, Dichloromethane; (ii) Dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate, Dichloromethane



of photoreactive groups can be adjusted by adding a comonomer during the polymerization step, as was shown in the preparation of poly(**1**-*co*-DME).

The polymers poly-**1** and poly(**1**-*co*-DME) were obtained in good yields of 96% for poly-**1** and 69% for poly(**1**-*co*-DME). The polymers exhibit a number averaged molecular weight M_n of 130.000 g mol^{-1} and 390.000 g mol^{-1}, respectively, and comparably high polydispersity indices PDI of 2.16 and 2.80. These PDI values are much higher than usually obtained for ROMP polymers using these Grubbs initiators. A possible explanation can be found in the NMR and FT-IR spectra, as in both a small amount of carboxylic acid groups are detected probably stemming from impurities of the acid chloride monomer. Free carboxylic acid groups are known to interfere with the ruthenium center.[24]

Both polymers have rather high glass transition temperatures (T_g). For the copolymer poly(**1**-*co*-DME) only one single glass transition is observed (T_g = 161 °C). This value is between the T_g of poly-**1** (206 °C) and poly-DME (approximately 81 °C; ref 24). Therefore it can be assumed that a statistical copolymer was obtained. Both polymers show excellent film forming properties when spin-cast from THF solutions. For the investigation of the photoisomerization and the postmodification reactions, homogeneous and transparent polymer films were prepared on optical substrates.

Investigation of the Photoreaction and Refractive Index Modulation. The monochromatic irradiation (254 nm) of the photoreactive polymers poly-**1** and poly(**1**-*co*-DME) under inert gas conditions causes a significant change in their chemical structure which can be easily followed with spectroscopic techniques such as UV/vis and FTIR spectroscopy. Figure 1 shows detailed FTIR spectra of a film of poly-**1** before (a) and after illumination (b) with UV light (254 nm, 9.7 J cm^{-2}). The film thickness was in the range of 0.3 μm. In the spectrum of the nonirradiated film the signals at 1662 cm^{-1} (C═O stretch) and 3313 cm^{-1} (N−H stretch) are typical of *N*-phenylamides. After UV irradiation, the vibration band at 1662 cm^{-1} has almost disappeared. Instead, two new bands evolve at 3469 cm^{-1} and 3344 cm^{-1} which arise from the N−H stretching vibration of the amino groups. The new signal at 1628 cm^{-1} can be attributed to the carbonyl stretching vibration of an *o*-aminoketone. These signals indicate the formation of the expected photo-Fries rearrangement product. A quantification of the yield was not possible as it is difficult to distinguish between the aminoacetophenone units (i.e., the photo-Fries rearrangement product), aniline and other side products of the photoreaction.[17] However, the conversion of the *N*-phenylamide groups is higher than 90% as derived from the depletion of the corresponding amide signals (1662 cm^{-1} and 1370 cm^{-1}) in the FTIR spectrum of poly-**1**. A comparatively high energy density (9.7 J cm^{-2}) is required to achieve the conversion of the *N*-aryl amide groups. This is explained by the low quantum yield of the photo-Fries rearrangement in *N*-aryl amides.[14c]

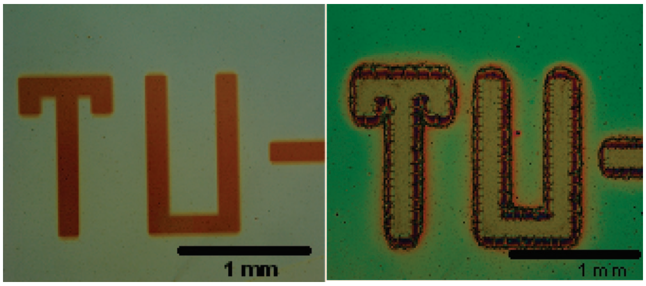


Figure 8. Micrographs of a film of poly(**1**-*co*-DME) showing a pattern obtained after site-selective reaction with norbornene carboxylic acid chloride (left image), and after the subsequent graft-copolymerisation of DME (right image).

Moreover, the UV absorbance spectra of the polymer changes upon illumination. As shown in Figure 2, the film of poly-**1** with a thickness of approximately 0.3 μm absorbs light up to 300 nm with an absorption maximum at 245 nm. This peak can be attributed to the *N*-phenylamide moieties in the polymer. The UV spectrum resembles that of acetanilide which displays a peak at 240 nm.[25] The illumination with light of 254 nm leads to a significant decrease of the UV-absorption maximum at 245 nm. Concomitantly three new absorption maxima at 230, 320, and 380 evolve upon irradiation. These changes indicate the formation of aminoketones, and the peaks are comparable to those in the UV spectra of *o*- and *p*-aminoacetophenones.[25]

The refractive index changes in thin films of poly-**1** and poly(**1**-*co*-DME) were investigated by means of spectroscopic ellipsometry. Figure 3 displays the Cauchy fits of the dispersion of the refractive index for the pristine and the UV illuminated films of the polymers. In these experiments, the duration of UV irradiation was adjusted to obtain a maximum yield of ketone formation. In both polymers a large increase of the refractive index *n* is observed upon irradiation with UV-light of 254 nm.

For poly-**1** the refractive index increased by $\Delta n = +0.10$ at 450 nm and $\Delta n = +0.075$ at 1000 nm, respectively. An increase of *n* by $\Delta n = +0.10$ is remarkably high and more than sufficient for optical applications. Usually, refractive index variations in the range from 0.003 to 0.03 are already considered to be high.[26] It is interesting to compare the Δn value for poly-**1** to Δn values obtained for other photoreactive systems. For polymeric materials containing photoreactive benzyl thiocyanate groups[27] a value $\Delta n = +0.03$ was found, and for polymers containing aryl ester groups (photo-Fries rearrangement, and photodecarboxylation)[6,7,28] refractive index changes Δn up to +0.07 have been observed.

Compared to the homopolymer poly-**1**, the increase Δn in the refractive index of poly-(**1**-*co*-DME) is +0.04 at 450 nm and +0.028 at 1000 nm. The increase Δn of the refractive index of poly-(**1**-*co*-DME) is approximately one-third of the value observed for poly-**1**, which exactly corresponds to the molar fraction of the photoreactive monomer **1** in the copolymer (the comonomer DME is photochemically inert under 254 nm light). This fact supports the idea that the change in refractive index in these polymers is mainly caused by the photoisomersation of the aromatic amide groups. Further support is given by a comparison of literature values of low-molecular-weight reference compounds. The difference Δn of the refractive indices of *N*-butylacetanilide ($n_D^{20} = 1.5146$)[29] and 2-aminoacetophenone ($n_D^{20} = 1.6160$)[29] amounts to 0.1 and is in the same range as the Δn value found for poly-**1**. Since a direct comparison with the refractive index of neat acetanilide is not possible due to its high melting point (114 °C; ref 29), the refractive indices of acetone solutions (30 wt %) of acetanilide and 2-aminoacetophenone were measured. For the solution of acetanilide $n_D^{20} = 1.368$ was found, and for the solution of 2-aminoaetophenone $n_D^{20} = 1.461$. Also these data indicate that the photoinduced increase in the refractive index of the polymers poly-**1** and poly(**1**-*co*-DME) is caused by the rearrangement reaction. Photocross-linking which is generally observed as a side reaction[18] in these polymers is expected to further increase the refractive index as cross-linking is usually accompanied by a slight reduction in volume. Regarding optical applications such as waveguiding, the high absorption up to 450 nm as well as a possible discoloration due to oxidation of the generated amino groups should be taken into account.

The proposed cross-linking reaction is supported by the fact that—in analogy to poly(phenylmethacrylamide)[18]—poly-**1** becomes insoluble upon UV irradiation. This polymer is a negative-toned photoresist, and Figure 4 shows the patterning of a film of poly-**1** by contact lithography (development with THF).

Selective Surface Functionalization. Due to the photochemical generation of aminoketones the chemical reactivity in the illuminated areas is increased. Consequently this offers the possibility of functionalizing the polymer surface. This approach was demonstrated by two selective reactions as depicted in Scheme 3, the reamidification and the reaction with fluorescamine. In these reactions, poly(**1**-*co*-DME) was employed because this copolymer generally swells more strongly than poly-**1** in the organic solvents used which enhances the reaction rate during the postmodification. This can be explained by the lower cross-link density of irradiated poly(**1**-*co*-DME) as this polymer contains only a third of the reactive groups present in poly-**1**.

In the first selective post modification reaction with acetyl chloride the amino groups react with acetyl chloride to give a new amide functionality. This reamidification can be monitored by FT-IR spectroscopy, see Figure 5a. After exposure to a solution of acetyl chloride in dichloromethane, the formation of amides leads to the reappearance of the C=O stretch signal at 1662 cm^{-1}. In addition, the N−H signals at 3469 cm^{-1} and 3344 cm^{-1} disappear. In combination with lithographic methods, this postmodification reaction can be applied for the generation of patterned polymer films and surfaces. For that purpose, a contact mask was placed onto the polymer film prior to illumination. The following postmodification step with acetyl chloride leads to the evolution of structural features, see Figure 6. Without any optimization, a resolution in the micrometer range was achieved. The features are detectable since the reaction with acetyl chloride is accompanied by an increase in film thickness. This process leads to different optical pathlengths and interference colors in nonilluminated and in illuminated and subsequently modified areas of the polymer film.

As a second example, irradiated thin films of poly(**1**-*co*-DME) were immersed in a solution of fluorescamine, a selective reagent for free amino groups. This reaction leads to a highly fluorescent derivative (Scheme 2). After the immersion step, the polymer film exhibits photoluminescence with the maximum of fluorescence emission at 500 nm at an excitation wavelength of 390 nm (cf. Figure 7). This reaction is another proof that free amino groups have been generated by the photo-Fries reaction, as further evidenced by the FTIR spectrum shown in Figure 5b.

The decrease of the NH stretching vibrations at 3469 cm^{-1} and 3344 cm^{-1} is accompanied by the appearance of a new band at 1802 cm^{-1} attributable to the C=O stretching vibration of the 1,2-dihydropyrrol-3-one ring formed. Using lithographic techniques, this post modification reaction can be used to prepare fluorescencent patterns on polymer films. The result of a patterned modification, using a contact mask during the illumination step, is shown in Figure 7.

Graft-Polymerization from the Surface. The photochemically activated areas of films of poly(**1**-*co*-DME) can act as a reactive layer for graft copolymerizations. This approach is exemplified by the reaction of the photogenerated amino groups with *endo,exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid chloride. This reaction creates a polymer surface bearing pendant norbornene units. Using the ring opening metathesis polymerization technique (ROMP) the immobilized norbornene moieties are employed in the grafting-from polymerization of norbornene monomers (Scheme 4).

In a first step the functionalized polymer surface was immersed in a solution of Grubbs catalyst (third generation). In this step, the ruthenium based catalyst opens the double bonds of the immobilized norbornene molecules. After a washing step to remove excess catalyst, the graft-polymerization was carried out by immersing the polymer film in a solution of (±)*endo,exo*-dimethylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (DME). After 60 min the film was removed and washed carefully. The FTIR spectrum of the polymer film displays a strong increase of the C=O stretching vibration of the ester at 1750 cm^{-1} (Figure 5c) which stems from the additional polymer layer. Ellipsometric measurements showed that a 300 nm thick additional layer of poly-DME was formed on the film of (**1**-*co*-DME).

Due to the insolubility of poly(**1**-*co*-DME) in dichloromethane (prior to and after illumination) the whole graft polymerization can be performed in this common solvent.

Figure 8 (left image) shows a pattern on a polymer film of poly-(**1**-*co*-DME) after post exposure treatment with (±)*endo,exo*-bicyclo[2.2.2]hept-5ene-2-carboxylic acid chloride. The "blurred" pattern in Figure 8 (right image) was obtained after subsequent graft-copolymerization of DME.

Conclusion

In the present contribution, we have demonstrated that the photo-Fries rearrangement of *N*-phenylamide groups in polymers provides a versatile and convenient method for (1) achieving a modulation of the refractive index and (2) for obtaining functionalized and patterned surfaces. The prepared polymers, poly-**1** and poly(**1**-*co*-DME) contain photoreactive anilide functionalities, have excellent film-forming properties and display high glass transition temperatures (206 and 161 °C, respectively). The optical properties of these films change significantly upon irradiation with UV light of 254 nm resulting in a change in the optical absorption spectrum as well as in the refractive index. In particular, the achieved modulation Δn of the refractive index n amounts up to 0.10 and is extremely high for polymeric materials and more than sufficient for optical applications. FT-IR-spectroscopy proves that these effects originate from the photo-Fries rearrangement of the aryl-amide moieties to the corresponding aromatic aminoketones. Due to the photogenerated aminoketones, the chemical reactivity after the irradiation step is enhanced which can be applied in selective postmodification reactions. In combination with photolithographic techniques, structured surface functionalities are accessible. Exemplarily, this was shown by the immobilization of the amino-sensitive fluorophore fluorescamine, resulting in patterned fluorescent surfaces. The reaction of the amino groups with carboxylic acid chlorides to give new amides is a further possibility to create functionalized surfaces. By immobilizing norbornene functionalities at the activated surface of these polymers, graft copolymerizations via ROMP can be performed.

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