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## Wavelength selective refractive index modulation in a ROMP derived polymer bearing phenyl- and *ortho*-nitrobenzyl ester groups

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Patterning and tuning of the refractive index in polymers by means of UV-light is of great interest for optical applications such as polymeric waveguides or optical data storage devices. In this contribution, we report on the synthesis of a polynorbornene based copolymer bearing *ortho*-nitrobenzyl and phenyl ester groups capable of undergoing the photo-induced cleavage reaction and in a subsequent step optionally the photo-Fries rearrangement upon irradiation with UV-light. The photoreaction of these aromatic ester groups was investigated by means of FTIR, UV-VIS and spectroscopic ellipsometry. Due to the difference in UV absorption of the photoreactive units, the *o*-nitrobenzyl ester can be selectively excited by UV-light above 300 nm, while a subsequent illumination with 254 nm induces the photo-Fries rearrangement of the remaining phenyl ester groups. The structural changes in the chemical composition upon UV illumination lead to significant changes in the refractive index of the polymeric materials. Whilst the photo-Fries rearrangement of the phenyl ester groups causes a remarkable increase in the refractive index, it was found that the photo-induced cleavage reaction of *ortho*-nitrobenzyl ester moieties causes a decrease of the refractive index. This fact enables a selective tailoring of the refractive index by the choice of the applied wavelength. In addition, a two-step irradiation procedure using a sequence of different wavelengths provides the possibility of erasing and even inverting the index contrast.

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## Introduction

The modulation of the refractive index in polymeric materials by means of UV-light is still drawing much attention for applications in optical communication (e.g. polymeric waveguides and optical switches) and optical data storage devices.<sup>1</sup> For that purpose a large number of photoreactive polymers with tunable refractive index have been developed and investigated over the last few years. A commonly used technology is based on the photo bleaching process of dye-doped polymers, which results in required refractive index changes  $\Delta n$  for optical devices in the order of  $10^{-3}$ . Photochromic dyes that bleach upon UV irradiation can be dispersed in thermoplastic polymeric matrices,

e.g. polymethylmethacrylate (PMMA), polystyrene and polyethylene.<sup>2</sup> Alternatively, photoinduced refractive index modification can also be achieved with photosensitive polymers, in which photoreactive units such as benzylthiocyanate groups, cinnamate units or aromatic esters and amides are covalently attached to the polymer backbone.<sup>3</sup> These polymers have the advantage that a high chromophore concentration can be incorporated into the polymer system without crystallization, phase separation, or the formation of concentration gradients.

Such photosensitive groups are capable of undergoing defined photoreactions inducing structural changes in the chemical composition. As a consequence a shift in the refractive index is caused. Besides these photoreactive materials, other approaches are based on photo-polymerizable groups such as acrylates or methacrylates.<sup>4</sup>

In our previous work we reported on photo-induced refractive index changes in polymers containing aromatic ester groups that undergo the irreversible photo-Fries rearrangement upon irradiation with UV-light. Refractive index changes in the range of  $\Delta n = +0.03$  up to  $\Delta n = +0.08$  were obtained in these polymeric materials.<sup>3c,5</sup> In polymers bearing aryl ester groups the amount of the photoproduct directly determines the value of the refractive index change enabling a selective control by means of the applied UV dose. In this context it was demonstrated that in a copolymer bearing both naphthyl and phenyl

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ester groups the refractive index can be modulated using UV-light of different wavelengths.<sup>5</sup> Due to the different UV absorption behavior of both chromophores, the naphthyl ester group can be selectively excited with UV-light of 313 nm causing an increase in the refractive index by  $\Delta n = +0.010$ , whilst an illumination with 254 nm leads to a photoreaction in both esters ( $\Delta n = +0.036$ ). Interestingly, when already irradiated films of this copolymer (with UV-light of 313 nm) are subjected to a second illumination step with 254 nm, a significant decrease of the refractive index is observed. The reason for this behavior seems to arise from the formation of carboxylic acid groups, which are known as side products in the photo-Fries rearrangement.

In the present study we combine this photochemistry with that of photosensitive *ortho*-nitrobenzyl ester groups which undergo a defined photoreaction to yield carboxylic acid groups upon irradiation with UV-light, thus influencing the refractive index of the polymeric material. In the past years such photosensitive *ortho*-nitrobenzyl ester derivatives have gained tremendous attention in the area of polymer chemistry and beyond.<sup>6</sup> Some recent developments deal with cross-linkers for photodegradable hydrogels,<sup>7</sup> photo-cleavable block copolymers,<sup>8</sup> stimuli responsible micelles,<sup>9</sup> photopatterning of polymeric<sup>10</sup> and inorganic surfaces,<sup>11</sup> and photosensitive interfacial layer in organic electronics.<sup>12</sup>

The generally accepted photoisomerization mechanism of *o*-nitrobenzyl esters into the corresponding carboxylic acid group proceeds *via* a radical mechanism (see Scheme 1) based on a Norrish-type II reaction. Upon irradiation with UV-light an  $n-\pi$  transition occurs. The excited singlet state is transformed into a triplet state. An oxygen of the nitro group abstracts a proton from the methylene carbon in the  $\gamma$ -H position and an *aci*-nitro intermediate is formed. The subsequent rearrangement and cleavage of the resonance stabilized five-membered ring rapidly regenerates the parent carboxylic acid and affords nitroso aldehyde as an additional product.<sup>13</sup>

In the present contribution, a copolymer bearing *ortho*-nitrobenzyl ester and phenyl ester groups, capable of generating carboxylic acids (*via* the photocleavage of nitrobenzyl ester groups) and hydroxy ketones (*via* the photo-Fries rearrangement),

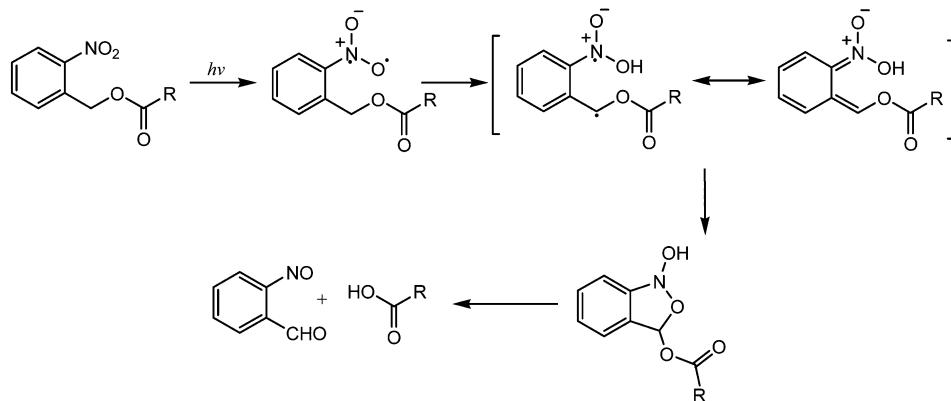
is investigated with respect to a wavelength selective refractive index modulation. The difference in UV absorption enables a selective excitation of the *ortho*-nitrobenzyl ester groups by using UV-light  $>300$  nm, while a subsequent illumination with 254 nm induces a photo-Fries rearrangement of the remaining phenyl ester groups.

## Experimental

### Preparation of materials

All chemicals were purchased from commercial sources and used without further purification. All experiments were carried out under an inert atmosphere using Schlenk techniques or a glove box. *Endo,exo*-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (mono-2)<sup>3c</sup> and  $(H_2IMes)(py)_2(Cl)_2Ru=CHPh$  ( $H_2IMes = N,N$ -di(mesityl)-4,5-di-hydroimidazolin-2-ylidene, py = pyridine)<sup>14</sup> were synthesized as previously reported. **Caution:** for 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!

*Endo,exo*-di(2-nitrobenzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (mono-1): (2-nitrophenyl)methanol (2.42 g; 15.8 mmol) was added to a stirred solution of bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl dichloride (1.56 g; 7.18 mmol) and pyridine (1.24 mL; 15.8 mmol) in dichloromethane. The reaction was stirred for 48 h at ambient temperature. The reaction mixture was filtered to remove the pyridinium salt and extracted with dichloromethane. The organic layer was extracted with  $3 \times 20$  mL of 5% hydrochloric acid solution to remove excess pyridine, and with 20 mL of saturated sodium bicarbonate solution, and then dried over sodium sulphate. The solvent was removed in a vacuum and subsequently a column separation using cyclohexane/ethyl acetate (10 : 1) for product purification was performed. Yield: 2.69 g of a white solid (83% of theoretical yield).  $^1H$ -NMR: ( $\delta$ , 400 MHz, 20 °C,  $CDCl_3$ ): 8.09 (m, 2H, ph<sup>3</sup>); 7.63 (m, 2H, ph<sup>4</sup>); 7.58 (m, 2H, ph<sup>5</sup>); 7.49 (d, 2H, ph<sup>6</sup>); 6.30, 6.11 (m, 2H, nb<sup>5,6</sup>); 5.55, 5.47 (m, 4H, O-CH<sub>2</sub>-ph); 3.51 (m, 1H, nb<sup>3</sup>); 3.36 (s, 1H, nb<sup>4</sup>); 3.21 (s, 1H, nb<sup>1</sup>); 2.83 (m, 1H, nb<sup>2</sup>); 1.67, 1.54 (d, 2H, nb<sup>7</sup>) ppm.  $^{13}C$ -NMR: ( $\delta$ , 125 MHz, 20 °C,  $CDCl_3$ ): 173.6, 172.4 (2C, COO); 137.71 (2C, ph<sup>2</sup>-NO<sub>2</sub>); 137.62, 135.16 (2C, nb<sup>5,6</sup>);



**Scheme 1** Reaction mechanism of *ortho*-nitrobenzyl esters upon irradiation with UV-light (ref. 13).

133.74, 133.63 (2C, ph<sup>5</sup>); 131.98, 131.67 (2C, ph<sup>1</sup>); 129.26, 129.15 (2C, ph<sup>4</sup>); 128.87 (2C, ph<sup>6</sup>); 125.87; 125.02 (2C, ph<sup>3</sup>); 63.31, 63.54 (2C, O-CH<sub>2</sub>-ph); 48.67 (1C, nb<sup>1</sup>); 47.60 (1C, nb<sup>4</sup>); 47.57 (1C, nb<sup>2</sup>); 47.20 (1C, nb<sup>3</sup>); 45.78 (1C, nb<sup>7</sup>) ppm. IR-data (CaF<sub>2</sub>, cm<sup>-1</sup>): 1733, 1613, 1578, 1525, 1447, 1342, 1306, 1163.

*Polymerization of mono-1 to give poly(*endo,exo-di(2-nitrobenzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*) (poly-1):* a solution of mono-1 (500 mg, 1.105 mmol) in 3 mL of dichloromethane was added to a solution of (H<sub>2</sub>IMes)(py)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (6.7 mg, 9.2  $\mu$ mol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> and the mixture was stirred at ambient temperature for 3 h. After complete conversion (TLC), the reaction was stopped by adding 0.15 mL of ethyl vinyl ether. The polymer was precipitated by dropping the solution into a tenfold excess of cold methanol. The precipitate was dried *in vacuo*. Yield: 420 mg of a white solid (84%). <sup>1</sup>H-NMR: ( $\delta$ , 400 MHz, 20 °C, CDCl<sub>3</sub>): 8.01–7.23 (8H, ph); 5.6–5.1 (2H, (CH=CH)+4H, (O-CH<sub>2</sub>-ph)); 3.74–3.03 (4H, nb<sup>1,2,3,5</sup>); 1.91–1.55 (2H, nb<sup>4</sup>) ppm. FTIR (film on CaF<sub>2</sub>, cm<sup>-1</sup>): 2963–2850, 1736, 1611, 1576, 1518, 1448, 1336, 1164, 1002. SEC: (CHCl<sub>3</sub>):  $M_n$  = 45 600 g mol<sup>-1</sup>;  $M_w$  = 47 900 g mol<sup>-1</sup>; PDI = 1.05.  $T_g$  = 57.9 °C.

*Copolymerization of mono-1 and mono-2 to give poly[*(endo,exo-di(2-nitrobenzyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate)-co-(endo,exo-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate*)] (poly(1-co-2):* a solution of H<sub>2</sub>IMes)(py)<sub>2</sub>(Cl)<sub>2</sub>Ru=CHPh (2.7 mg, 3.7  $\mu$ mol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to a mixture of mono-1 (50.2 mg, 0.11 mmol) and mono-2 (110.5 mg, 0.33 mmol) in 3 mL of dichloromethane and the mixture was stirred at RT for 24 h. After complete conversion (TLC), the reaction was stopped by adding 0.15 mL of ethyl vinyl ether. The polymer was precipitated by dropping the solution into a tenfold excess of cold methanol. The precipitate was dried *in vacuo*. Yield: 0.132 g (82%) of a white solid. SEC (CHCl<sub>3</sub>):  $M_n$  = 37 000 g mol<sup>-1</sup>;  $M_w$  = 39 900 g mol<sup>-1</sup>; PDI = 1.08;  $T_g$  = 79.9 °C. ( $\delta$ , 400 MHz, 20 °C, CDCl<sub>3</sub>): 8.01–7.37 (18H, ph); 5.6–5.1 (4H, CH=CH) (4H, O-CH<sub>2</sub>-ph); 3.74–3.03 (8H, nb<sup>1,2,3,5</sup>); 1.91–1.55 (4H, nb<sup>4</sup>) ppm. Composition: 28 mol% mono-1 and 72 mol% mono-2 as estimated from elemental analysis measurements; FTIR (film on CaF<sub>2</sub>, cm<sup>-1</sup>): 3125–2800, 1747, 1591, 1528, 1491, 1456, 1380, 1340, 1198, 1160, 1142.

## Physico-chemical measurements

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded with a Varian 400-NMR spectrometer operating at 399.66 MHz and 100.5 MHz, respectively, and were referenced to Si(CH<sub>3</sub>)<sub>4</sub>. A relaxation delay of 10 s and 45° pulse were used for acquisition of the <sup>1</sup>H-NMR spectra. Solvent residual peaks were used for referencing the NMR spectra to the corresponding values given in the literature.<sup>15</sup>

For UV-VIS and FTIR measurements a 10 mg mL<sup>-1</sup> solution of the corresponding polymer dissolved in tetrahydrofuran (THF) was spin cast on CaF<sub>2</sub> discs. The film thickness was in the range of 20–25 nm for ellipsometry. For UV-VIS and FTIR-spectroscopy measurements 100 nm thick polymer films have been applied.

UV-VIS spectra were recorded with a Varian Cary 50 UV-VIS spectrophotometer. All UV-VIS spectra were taken in the absorbance mode. Differential scanning calorimetry (DSC)

measurements were carried out on a Perkin Elmer "Pyris Diamond" under a nitrogen flow of 20 mL min<sup>-1</sup> and a heating rate of 10 °C min<sup>-1</sup>. Glass transition temperatures ( $T_g$ ) from the second heating run were read as the midpoint of change in heat capacity.

For ellipsometric measurements a 10 mg mL<sup>-1</sup> solution of the corresponding polymer dissolved in anisole was spin cast on silicon wafers. Ellipsometric measurements were carried out with a Woollam VASE spectroscopic ellipsometer (Xenon short arc lamp, wavelength range 240–1100 nm, and spectral bandwidth 4 nm). The implemented software uses the Levenberg–Marquardt fit algorithm. FTIR spectra were recorded with a Perkin Elmer "Spectrum One" instrument (spectral range between 4000 and 450 cm<sup>-1</sup>). All FTIR spectra were recorded in transmission mode.

*Size exclusion chromatography:* 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 tetrahydrofuran (THF) as the solvent using the following arrangement: Merck Hitachi L6000 pump, separation columns of Polymer Standards Service, 8 × 300 mm STV 5  $\mu$ m grade size (10<sup>6</sup> Å, 10<sup>4</sup> Å, and 10<sup>3</sup> Å), combined refractive index–viscosity detector from Viscotec, Viscotec 200. Polystyrene standards purchased from Polymer Standards Service (PSS) were used for calibration.

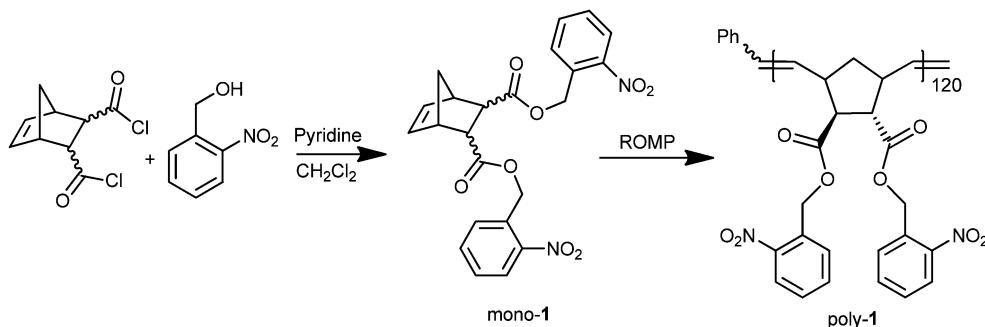
## UV irradiation experiments

UV irradiation experiments were carried out with a medium pressure Hg lamp (100 W, from Newport, model 66990) equipped with a filter which excludes UV-light <300 nm, and an ozone free low pressure Hg lamp (Heraeus Noblelight; 254 nm). In these experiments, the light intensity (power density  $P$  in  $\mu$ W cm<sup>-2</sup>) at the sample surface was measured with a spectroradiometer (Solatell, Sola Scope 2000<sup>TM</sup>, spectral range from 230 to 470 nm). The power density was 13.2 mW cm<sup>-2</sup> for 300–450 nm and 178  $\mu$ W cm<sup>-2</sup> for 254 nm, respectively. All UV illumination methods were carried out under an inert gas atmosphere (N<sub>2</sub>). **Caution:** UV irradiation causes severe eye and skin burns. Precautions (UV protective goggles, gloves) must be taken! Photolithographic patterning was carried out with a mask aligner (model MJB4 from SUSS, Germany) using a 500 W HgXe lamp equipped with a filter transmissive for the wavelength range from 270 nm to 353 nm ( $P$  = 37 mW cm<sup>-2</sup>).

## Results and discussion

### Synthesis of the polymers poly-1 and poly(1-co-2)

The photoreactive monomer mono-1 is easily accessible by an esterification reaction of norbornene-2,3-dicarboxylic acid dichloride with (2-nitrophenyl)methanol (see Scheme 2), analogous to the synthesis of *endo,exo-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate* as reported previously.<sup>3c</sup> Mono-1 was purified by column chromatography and was obtained in high yield (82.3%). <sup>1</sup>H NMR, <sup>13</sup>C NMR and FTIR-spectroscopy are in accordance with the proposed structure. Details are given in the Experimental section.



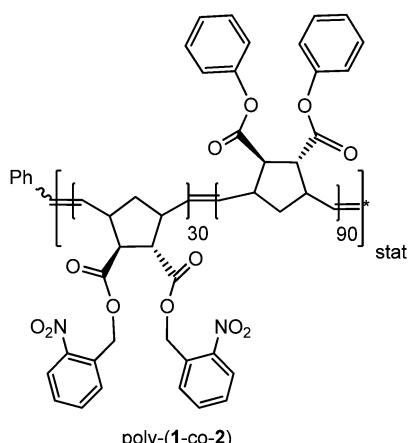
Scheme 2 Synthesis of poly-1.

The polymers were prepared by ring opening metathesis polymerization (ROMP) using  $(H_2IMes)(py)_2(Cl)_2Ru=CHPh$  ( $H_2IMes = N,N$ -di(mesityl)-4,5-di-hydroimidazolin-2-ylidene, py = pyridine) as an initiator for ROMP. The polymerization reactions were performed in dichloromethane under an inert atmosphere at room temperature in a glove box. A homopolymer, poly-1, with a theoretical polymerization degree  $X_n = 120$  as well as a statistical copolymer poly(1-co-2) (Scheme 3,  $X_n = 120$ , mono-1 : mono-2 = 30 : 90) were prepared by this method.

Both polymers were obtained in high yields of 84% and 82%, respectively. Due to overlapping NMR signals, elemental analysis was performed to determine the content of mono-1 and mono-2 in poly(1-co-2). The found value for the molar ratio of the incorporated monomers mono-1 and mono-2 amounts to be 1 : 2.5. The physico-chemical data of the investigated polymers are compiled in Table 1.

For poly(1-co-2) only one glass transition is observed ( $T_g = 79.9$  °C), which is between the  $T_g$  of poly-1 (57.9 °C) and poly(*endo,exo*-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (96.5 °C, ref. 3c) which is expected for a statistical copolymer. Both polymers show excellent film forming properties when spin-cast from  $CH_2Cl_2$  and anisole solutions and fully transparent films with optical quality were obtained.

Fig. 1 shows the UV absorption spectra of the new polymers poly-1 and poly(1-co-2) compared to the absorption spectrum of poly(*endo,exo*-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate).



Scheme 3 Structure of poly(1-co-2).

Table 1 Physico-chemical data of poly-1 and poly(1-co-2)

Polymer	Molar ratio <sup>a</sup>	Yield (%)	$M_n$ (theor.) ( $g\ mol^{-1}$ )	$M_n$ (exp.) ( $g\ mol^{-1}$ )	PDI ( $M_w\ M_n^{-1}$ )	$T_g$ (°C)
Poly-1	1 : 120	84	54 300	45 600	1.05	57.9
Poly(1-co-2)	1 : 120 <sup>b</sup>	82	43 700	37 000	1.08	79.9

<sup>a</sup> Molar ratio of initiator to monomer. <sup>b</sup> Molar ratio of monomers mono-1 : mono-2 = 1 : 3.

While the phenyl ester groups in poly(*endo,exo*-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) absorb light up to a wavelength  $\lambda \sim 280$  nm which is typical of a  $\pi-\pi^*$  transition, the UV absorption spectra of the new polymers poly-1 and poly(1-co-2) exhibit a maximum at around 265 nm which extends the absorption to >300 nm as expected for *ortho*-nitrobenzyl ester units.

### Photoreactions of poly-1

The UV irradiation of thin films of poly-1 causes a cleavage of the *o*-nitrobenzyl ester groups to give the corresponding carboxylic acid groups as shown in Scheme 4. Because of this

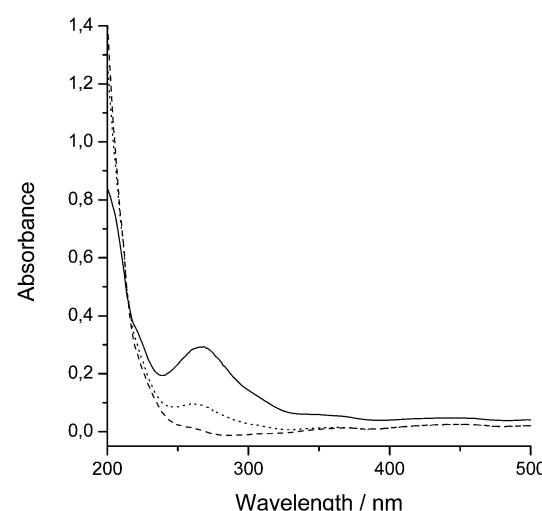


Fig. 1 UV spectra of films of poly-1 (solid line), poly(1-co-2) (dotted line) and poly(*endo,exo*-diphenyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate) (dashed line) on  $CaF_2$ . Film thicknesses are in the range of 100 nm.

significant change in the chemical structure of the polymer's side chain, the photoisomerization can be easily followed by spectroscopic methods such as UV-VIS and FTIR spectroscopy. It is well known that the formed 2-nitrosobenzaldehyde is chemically not stable and undergoes a dimerization reaction to generate the corresponding azobenzene (displayed in Scheme 4) derivative almost quantitatively.<sup>16</sup>

In Fig. 2A the UV-VIS spectra of a film of poly-1 prior to and after UV illumination (energy density  $E = 19.8 \text{ J cm}^{-2}$ ,  $\lambda > 300 \text{ nm}$ ) under a nitrogen atmosphere are shown. The film thickness was in the range of 100 nm. Upon illumination a significant increase in the UV absorption can be observed. This behavior can be attributed to the formation of 2-nitrosobenzaldehyde and the subsequent formation of the corresponding azobenzene moieties.<sup>16</sup> Additionally, these photo-generated azobenzene groups lead to a discoloration of the polymeric film from transparent to a yellow shade in the illuminated areas. Regarding optical applications the increase of the UV-VIS absorption between 210 and 550 nm has to be taken into account. However, higher wavelengths typically used for optical data communication ( $\lambda > 800 \text{ nm}$ ) are not affected (see Fig. 2A).

Fig. 2B shows detailed FTIR spectra of a film of poly-1 before (solid line) and after illumination (dotted line) with UV-light ( $E = 19.8 \text{ J cm}^{-2}$ ,  $\lambda > 300 \text{ nm}$ ). The film thickness was in the range of 100 nm. In the spectrum of the non-irradiated film the signals at  $1728 \text{ cm}^{-1}$  (C=O stretch) and at  $1165 \text{ cm}^{-1}$  (asym. C–O–C stretch) are typical for the ester units. Additionally, strong signals

at  $1528 \text{ cm}^{-1}$  (asym.  $\text{NO}_2$  stretch) and  $1342 \text{ cm}^{-1}$  (sym.  $\text{NO}_2$  stretch) are observed, which can be attributed to the nitro group.

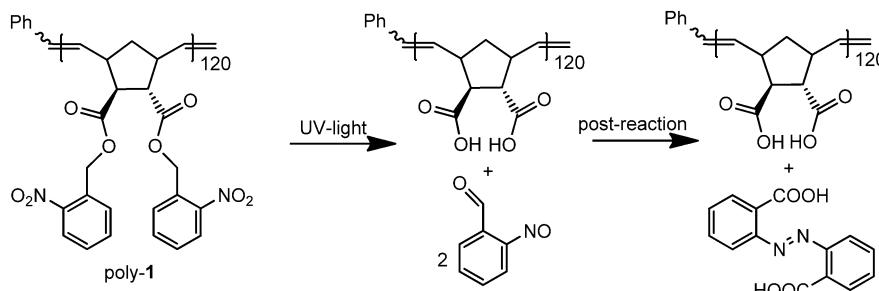
After UV irradiation, the vibrational bands of the ester (at  $1728 \text{ cm}^{-1}$  and  $1165 \text{ cm}^{-1}$ ) as well as the nitro group (at  $1528 \text{ cm}^{-1}$  and  $1342 \text{ cm}^{-1}$ ) decreased considerably. Instead, a new broad band at  $3400 \text{ cm}^{-1}$  that can be assigned to the O–H stretching vibration of the carboxylic acid group is observed. Additionally, a broad shoulder at approximately  $1705 \text{ cm}^{-1}$  is clearly discernible. This signal indicates the formation of the expected carboxylic acid group (C=O stretching vibration), partially overlapping with the carbonyl vibration of the remaining ester.

A quantification of the yield was not possible from FTIR data as it is difficult to distinguish between the formed carboxylic acid groups, the remaining ester groups and the side products (*i.e.* the azobenzene derivative) of the photoreaction.

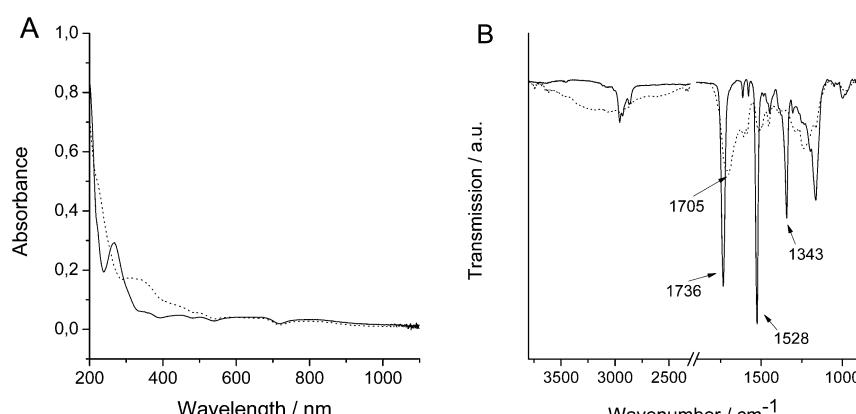
Due to the overlap of the C–O signal of the photo-product with the ester band, the  $\text{NO}_2$  stretching vibration at  $1528 \text{ cm}^{-1}$  was used for kinetic investigations in poly-1 as well as poly(1-*co*-2).

Fig. 3 shows the decrease of the  $\text{NO}_2$  groups during UV illumination ( $\lambda > 300 \text{ nm}$ ) of poly-1. A quantitative conversion of the nitro-groups can be observed upon irradiation with  $E = 20 \text{ J cm}^{-2}$ .

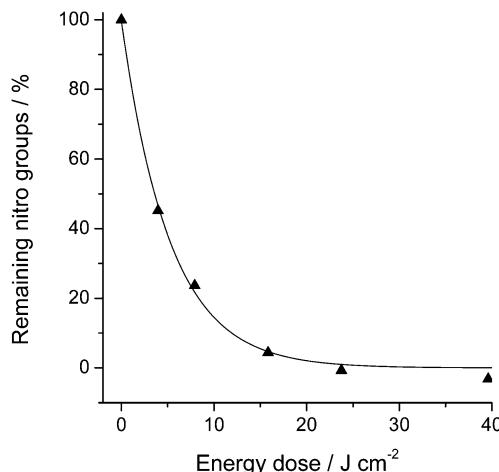
The refractive index change in a thin film of poly-1 was investigated by means of spectroscopic ellipsometry. Fig. 4A displays the Cauchy fits of the dispersion of the refractive index for the pristine and the UV illuminated films of the polymers. In these experiments, the duration of UV irradiation was adjusted to obtain a maximum conversion of the ester groups.



**Scheme 4** Photo-reaction in poly-1 containing o-nitrobenzyl ester units and post-reaction of o-nitrosobenzaldehyde.



**Fig. 2** (A) UV spectra of a film of poly-1 on  $\text{CaF}_2$ . Solid line: prior to irradiation; dotted line: after UV irradiation ( $E = 19.8 \text{ J cm}^{-2}$ ,  $\lambda > 300 \text{ nm}$ ). (B) FTIR spectra of poly-1 on  $\text{CaF}_2$  prior to illumination (solid line) and after illumination (dotted line) with UV-light of  $>300 \text{ nm}$  (energy density  $E = 20 \text{ J cm}^{-2}$ ).



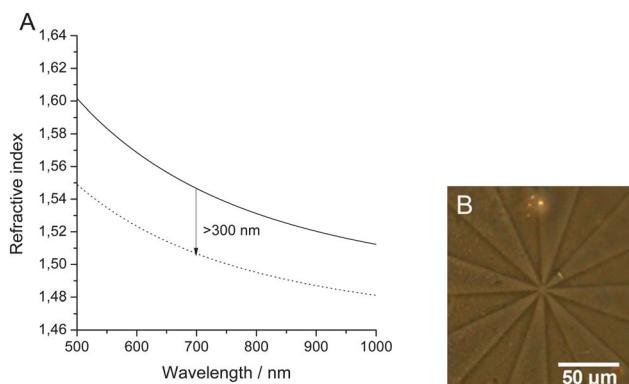
**Fig. 3** Monitoring the photo-reaction in poly-1 by FTIR spectroscopy: depletion of the  $\text{NO}_2$  band at  $1528\text{ cm}^{-1}$  during UV illumination (power density  $P = 13.2\text{ mW cm}^{-2}$ ).

The refractive index of poly-1 decreased by  $\Delta n = -0.047$  at 589 nm, which is remarkably high and more than sufficient for optical applications. This expected result can be explained by the formation of carboxylic acid groups. In general, carboxylic acids possess comparably low refractive indices, which explains the observed decrease after the photo-induced acid formation.<sup>5</sup>

Further support for this assumption is provided by a comparison of known refractive indices of low-molecular-weight model compounds. *o*-Nitrobenzyl acetate – the model compound for the pristine polymer – has a refractive index of  $\Delta n_{589} = 1.545$ , whilst acetic acid, the analogue for the formed carboxylic acid group, has a very low refractive index of  $\Delta n_{589} = 1.371$ .

Although the side product of the photoreaction, see Scheme 4, also influences the refractive index, it can be assumed that the additional carboxylic acid groups of this azobenzene derivative also contribute to the refractive index decrease.

The observed decrease in the refractive index can also be followed by optical microscopy using a phase contrast set-up for visualization. In Fig. 4B, a phase contrast image of a patterned



**Fig. 4** (A) Cauchy fits of the dispersion of the refractive index of poly-1 before (solid line) and after (dotted line) illumination with UV-light  $>300\text{ nm}$  ( $E = 15.8\text{ J cm}^{-2}$ ). (B) Phase contrast image of a film of poly-1 after UV patterning with a mask aligner, (MJB4 from SUSS) using a 500 W HgXe lamp equipped with a filter for the range 270–353 nm.

sample is shown. Areas with higher refractive indices appear dark (non-illuminated), while areas with lower refractive indices appear bright (illuminated). To create the pattern, a thin film of poly-1 was illuminated by using a mask aligner system and a suitable quartz-chromium mask (contact lithography). Without any optimization, a resolution of 5  $\mu\text{m}$  was achieved in this experiment.

### Photoreactions in poly(1-*co*-2)

The different UV absorption behaviour of the two chromophores (see Fig. 1) in the statistical copolymer poly(1-*co*-2) should allow selective excitation of the *ortho*-nitrobenzyl ester with UV-light  $>300\text{ nm}$ . Moreover, using UV-light of 254 nm in a subsequent illumination step, the reaction of the remaining phenyl ester groups (photo-Fries rearrangement) to the corresponding hydroxy ketones is expected. A scheme of this two step illumination procedure is shown in Fig. 5.

Fig. 6 shows a comparison of the FTIR spectra prior to (A) and after illumination with UV-light  $>300\text{ nm}$  (B) and after a subsequent illumination with 254 nm (C), respectively. The first illumination step ( $>300\text{ nm}$ ) causes the formation of carboxylic acid groups as indicated by the formation of the shoulder at  $1705\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretch) and also a decrease of the ester vibration ( $1750\text{ cm}^{-1}$ ). This FTIR spectrum also reveals that no photo-product of the photo-Fries rearrangement (*i.e.* hydroxy ketone, which would appear at  $1630\text{ cm}^{-1}$ ) is formed. This fact is expected as only the *ortho*-nitrobenzyl ester absorbs light above 300 nm. Also a significant decrease of the corresponding  $\text{NO}_2$  vibrations at  $1528\text{ cm}^{-1}$  (asym. stretching vibration) and  $1342\text{ cm}^{-1}$  (sym. stretching vibration) is observed. After irradiation of poly(1-*co*-2) with UV-light of  $>300\text{ nm}$  a subsequent illumination with 254 nm light was performed. Hence, the formation of hydroxy ketone moieties ( $1631\text{ cm}^{-1}$ ,  $\text{C}=\text{O}$  stretch) and also a further decrease of the ester signal at  $1750\text{ cm}^{-1}$ , attributed to the photo-induced photo-Fries rearrangement of the phenyl ester groups, can be detected.

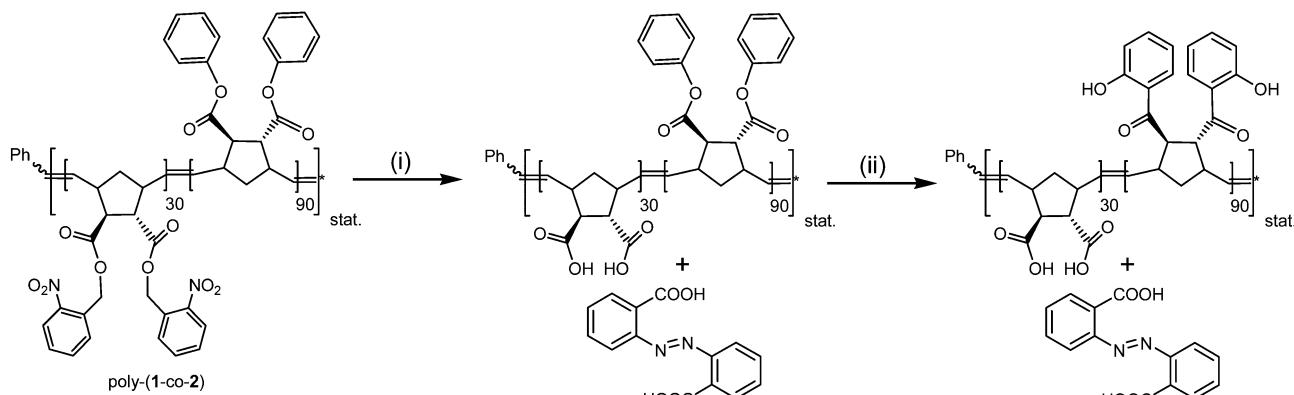
In Fig. 7 the depletion of the nitro peak during illumination with UV-light of  $>300\text{ nm}$  (first illumination step) and the evolution of a ketone band during the subsequent second illumination step with UV-light of 254 nm are depicted as a function of the irradiation time. This graph also reveals the wavelength selective photo-reactivity of poly(1-*co*-2), *i.e.* no photo-product of the photo-Fries rearrangement is formed in the first illumination procedure.

Although, the exact amount of photo-generated carboxylic acid groups cannot be determined due to overlapping infrared signals, an estimation of the yield of hydroxy ketones can be performed using the infrared absorbance coefficients of low molecular model compounds as described in previous contributions.<sup>36,5</sup>

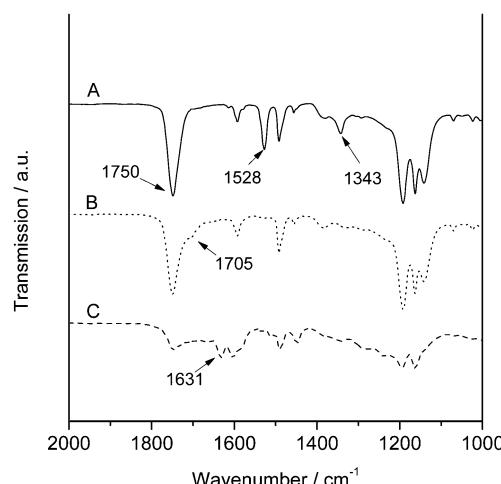
For that purpose, hydroxy acetophenone ( $A_{1631} = 345\text{ L mol}^{-1}\text{ cm}^{-1}$ ) and phenyl acetate ( $A_{1750} = 420\text{ L mol}^{-1}\text{ cm}^{-1}$ ) were used as model compounds. Using this method a maximum yield of *ortho*-hydroxy ketone was estimated to be 30% after the second illumination step (see Fig. 7).

### Refractive index changes in poly(1-*co*-2)

Spectroscopic ellipsometry was used to investigate the changes of the refractive index of poly(1-*co*-2) based on the different



**Fig. 5** Two step irradiation procedure: (i) irradiation using UV-light of  $\lambda = >300$  nm ( $E = 20 \text{ J cm}^{-2}$  and  $\lambda > 300$  nm) and (ii) irradiation using UV-light of  $\lambda = 254$  nm ( $E = 0.85 \text{ J cm}^{-2}$  and  $\lambda = 254$  nm).

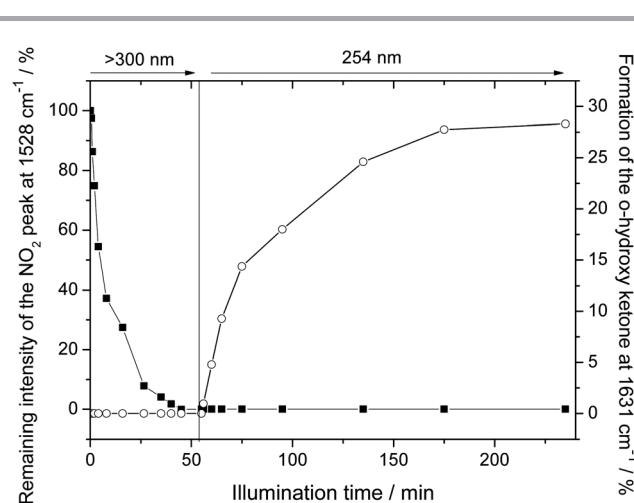


**Fig. 6** Comparison of FTIR spectra of poly(1-co-2) obtained by different illumination steps: solid line: prior to irradiation; dotted line: after UV irradiation ( $E = 20 \text{ J cm}^{-2}$  and  $\lambda > 300$  nm); dashed line: after 2<sup>nd</sup> illumination step ( $E = 0.85 \text{ J cm}^{-2}$  and  $\lambda = 254$  nm).

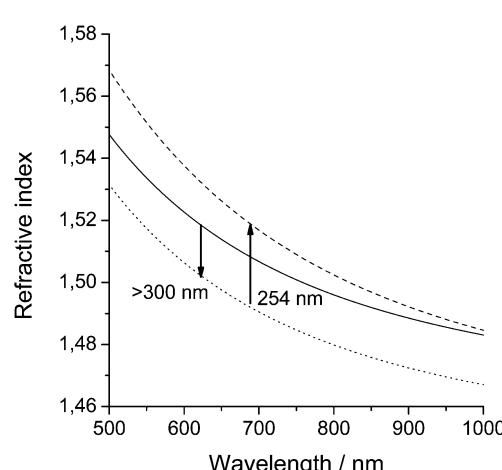
photoreactions. Fig. 8 displays the Cauchy fits of the dispersion of the refractive index of thin films of poly(1-co-2) for the pristine copolymer, for the copolymer after  $>300$  nm illumination, and for the copolymer after double illumination, first with  $>300$  nm and subsequently with 254 nm light. In these experiments, the film thickness of poly(1-co-2) was approximately 25 nm.

According to the investigations on poly-1, the irradiation of poly(1-co-2) with UV  $>300$  nm leads to a significant decrease of the refractive index, which can be attributed to the formation of carboxylic acid groups. The value of the decrease ( $\Delta n_{589} = -0.017$ ) is approximately 1/3 of the change observed in the homopolymer poly-1 ( $\Delta n_{589} = -0.047$ ) and is in good accordance with the molar fraction of *o*-nitrobenzyl groups in poly(1-co-2). This fact reveals the possibility of a selective tailoring of the expected refractive index change in ROMP derived polymers by the choice of the molar ratio of the applied monomers.

The second irradiation of this film with UV-light of 254 nm wavelength results in an increase of the refractive index by approximately  $\Delta n_{589} = +0.031$ , which can be assigned to the photo-induced generation of *o*-hydroxy ketones. The finding is consistent



**Fig. 7** Conversion of nitro groups (squares,  $P = 13.2 \text{ mW cm}^{-2}$ ) and formation of *o*-hydroxy ketone (circles,  $P = 178 \mu\text{W cm}^{-2}$ ) during the two step irradiation. (1<sup>st</sup> step  $\lambda > 300$  nm and 2<sup>nd</sup> step  $\lambda = 254$  nm).



**Fig. 8** Cauchy fits of the dispersion of the refractive index of poly(1-co-2) before (solid line) and after the 1<sup>st</sup> illumination step (dotted line) with UV-light of  $>300$  nm ( $E = 18.2 \text{ J cm}^{-2}$ ); after 2<sup>nd</sup> illumination step (dashed line) using UV-light of 254 nm ( $E = 4.1 \text{ J cm}^{-2}$ ).

with the observed refractive index changes in previously reported polymeric materials (considering that poly(1-*co*-2) contains approximately 66 mol% of photo-Fries reactive groups).<sup>3c,5</sup>

## Conclusion

In this contribution, we report on the synthesis of a polynorbornene based polymer bearing two photoreactive aromatic ester groups which are capable of undergoing the photo-induced cleavage reaction and in a subsequent step optionally the photo-Fries rearrangement upon irradiation with UV-light. Due to the difference in UV absorption of both ester groups, the *o*-nitrobenzyl ester can be selectively excited by UV-light above 300 nm, while a subsequent illumination with 254 nm induces the photo-Fries rearrangement of the remaining phenyl ester groups. Both photoreactions lead to significant changes in the refractive index of the polymeric materials, which can be attributed to the photo-induced structural change in the chemical composition. While the photo-induced cleavage reaction of *ortho*-nitrobenzyl esters causes a decrease by  $\Delta n_{589} = -0.017$ , it was found that the photo-Fries rearrangement of the phenyl ester in copoly(1-*co*-2) leads to a remarkable increase in refractive index by  $\Delta n_{589} = +0.031$ . Moreover, it turned out that the value of this decrease depends on the amount of photoreactive nitrobenzyl ester groups in the polymer chain, which allows an adjustment of the expected refractive index change in ROMP derived polymers by the choice of the molar fraction of the used monomers. Additionally, the selective excitation of the photoreactions by UV-light of different wavelengths enables a specific tuning of the refractive index, which paves the way towards erasing and even inverting the index contrast. The feasibility of a selective tailoring of the refractive index by the choice of (1) the applied wavelengths and (2) the ratio of the used monomers makes this material an interesting candidate for applications in modern optical devices.

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