

# Photosensitive polynorbornene containing the benzyl thiocyanate group—Synthesis and patterning

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## Abstract

In this paper, we report the synthesis of a new polymer based on polynorbornene containing the photosensitive benzyl thiocyanate group. The monomer ( $\pm$ )-*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-bis-(4-thiocyanatomethyl)benzyl ester (**2**) was prepared from (4-thiocyanatomethyl)benzyl alcohol (**1**) and ( $\pm$ )-*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarbonyl dichloride as starting materials. Compound **2** was polymerised via ring opening metathesis polymerisation using the Grubbs type initiator [RuCl<sub>2</sub>(H<sub>2</sub>IMes)(3-bromo-pyridine)<sub>2</sub>(CHPh)] providing a photoreactive polymer. The photoreactions of the low molecular compounds as well as of the polymer were investigated by FT-IR spectroscopy. The benzyl thiocyanate group undergoes photoisomerisation to the reactive benzyl isothiocyanate group when exposed to UV-light. Upon a post-modification process with gaseous propylamine, the isothiocyanate group is selectively transformed to the corresponding thiourea derivative. We show that these processes allow patterning of thin films of this polymer by lithographic techniques.  
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**Keywords:** Ring opening metathesis polymerisation; Photoreactive polymer; Photoisomerisation; Thiocyanate

## 1. Introduction

Photolithography is a versatile tool for 2D-structuring of polymer films. Over the last few years, we have shown that polystyrene based photoactive polymers containing the benzyl thiocyanate group are excellent materials for applications in optics, optoelectronics and for immobilisation of (bio)molecules [1–9]. The basic reaction behind is an irreversible photoisomerisation of the benzyl thiocyanate group via a radical mechanism to the corresponding isothiocyanate group, as sketched in Scheme 1 [10–12].

Due to this isomerisation, the refractive index of the material changes. Using interference lithography, it is possible to inscribe refractive index gratings into the polymeric matrix that can be used for distributed feed back (DFB) lasers [3,6,13]. Recently, we have produced a mechanically tunable DFB laser by preparing an elastomeric copolymer of vinylbenzyl thiocyanate, styrene and butadiene. The colour of the laser can be tuned continuously between 600 and 625 nm by mechanical force [2]. By incorporating benzyl thiocyanate groups into

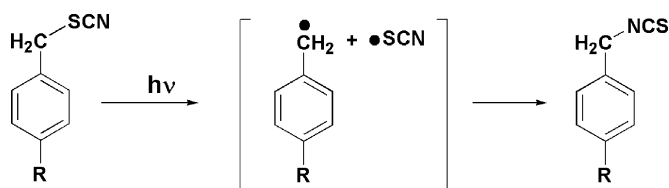
conjugated polymers it is possible to inscribe a refractive index pattern into an electroactive material [1].

A second feature of this isomerisation reaction is the different reactivity of the thiocyanate and the isothiocyanate group. While the isothiocyanate unit reacts readily with amines, e.g. ammonia or propylamine to give derivatives of thiourea, the thiocyanate remains inert. Thus it is possible to immobilise amino-functionalised molecules onto the illuminated area. At the same time an increase in film thickness can be observed. This reaction has been applied for the generation of surface relief structures and for the preparation of bio-chips [4,6,7].

With exception of the electroactive polymer all investigations up to now were made on vinylbenzyl thiocyanate polymers and copolymers prepared by radical polymerisation.

In this paper, we report for the first time the synthesis of a norbornene derivative carrying the benzyl thiocyanate group. Moreover, we wanted to investigate the possibility to polymerise this compound by ring opening metathesis polymerisation with ruthenium initiators. One crucial question is if the –SCN moiety is compatible with Ru, as it is known that CN-groups interact with the metal centre and hampers the reaction [14–16]. Using [RuCl<sub>2</sub>(H<sub>2</sub>IMes)(3-bromo-pyridine)<sub>2</sub>(CHPh)], the third generation Grubbs initiator [17], and optimising the reaction conditions, it is possible to obtain a defined polymer in good yield.

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With these new norbornene monomers, the versatile photochemistry of thiocyanates can be introduced to the ring opening metathesis toolbox [18–20].

## 2. Experimental

### 2.1. Materials

All chemicals were purchased from commercial sources and used without further purification.  $\text{CH}_2\text{Cl}_2$  was distilled over  $\text{CaH}_2$  and THF was distilled over Na under nitrogen atmosphere. All experiments were carried out under argon atmosphere using Schlenk techniques.

### 2.2. Characterisation techniques

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 mm  $\times$  300 mm STV 5  $\mu\text{m}$  grade size ( $10^6$ ,  $10^4$ , and  $10^3$  Å), refractive index detector from Wyatt Technology, model Optilab DSP Interferometric Refractometer. Polystyrene standards purchased from Polymer Standard Service were used for calibration.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer operating at 499.803 MHz and 125.687 MHz, respectively, and were referenced to  $\text{SiMe}_4$ .

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer Pyris Diamond under a nitrogen flow of 20 mL/min. Glass transition temperatures ( $T_g$ ) were read as the midpoint of change in heat capacity.

FT-IR spectra were recorded with a Perkin-Elmer Spectrum One instrument (spectral range between 4000 and 450  $\text{cm}^{-1}$ ). All FT-IR spectra of the samples were recorded in transmission mode. Optical microscopy was carried out with an Olympus BX 60 instrument.

### 2.3. Synthesis and characterisation

#### 2.3.1. (4-Thiocyanatomethyl)benzyl alcohol (**1**)

About 1.580 g (10.1 mmol) of (4-chloromethyl)benzyl alcohol dissolved in 15 mL dichloromethane was added to a solution of 0.845 g (11.1 mmol) ammonium thiocyanate in 10 mL methanol and the mixture was refluxed for 4.5 h. The solvent was evaporated and the residue was treated with dichloromethane.

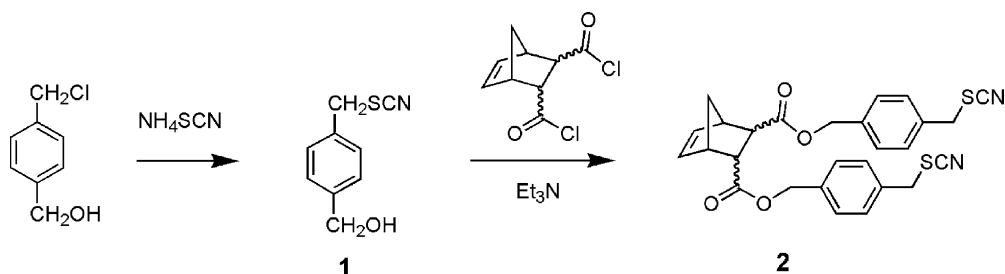
The remaining precipitate was filtered off, and the solution was evaporated in vacuo. The residual crude product was purified by column chromatography (silicagel, ethyl acetate/*n*-hexane 2/3) and recrystallised from dichloromethane/cyclohexane. Yield: 1.385 g (77%) white needles.  $^1\text{H}$  NMR (500 MHz, 20 °C,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd, 4H, Ph), 4.69 (s, 2H,  $-\text{CH}_2-\text{OH}$ ), 4.15 (s, 2H,  $-\text{CH}_2-\text{SCN}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 20 °C,  $\text{CDCl}_3$ )  $\delta$  141.9 (1C,  $\text{Ph}^4$ ), 133.7 (1C,  $\text{Ph}^1$ ), 129.3 (2C,  $\text{Ph}^{3,5}$ ), 127.7 (2C,  $\text{Ph}^{2,6}$ ), 112.1 (1C,  $-\text{SCN}$ ), 64.8 (1C,  $-\text{CH}_2-\text{OH}$ ), 38.2 (1C,  $-\text{CH}_2-\text{SCN}$ ). FT-IR (Si wafer,  $\text{cm}^{-1}$ ) 3401 (s,  $\nu_{\text{OH}}$ ), 3029 (m, aromatic  $\nu_{\text{CH}}$ ), 2930–2873 (m, aliphatic  $\nu_{\text{CH}}$ ), 2300 (w), 2153 (s,  $\nu_{\text{SCN}}$ ), 1914 (w), 1803 (w), 1614 (w), 1580 (w), 1513 (s), 1423 (s), 1246 (s), 1209 (s), 1109 (m), 1044 (s), 1017 (s), 891 (m), 822 (s), 761 (m), 719 (m), 635 (m), 591 (w), 522 (w). Elem. anal. (anal. calc.) C: 60.31% H: 5.06% N: 7.81% S: 17.89%. Found C: 59.04% H: 5.17% N: 7.45% S: 16.94%.

#### 2.3.2. ( $\pm$ )-endo,exo-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-bis-(4-thiocyanatomethyl)benzyl ester (**2**)

To a solution of 3.122 g (17.42 mmol) **1** and 3.64 mL (26.13 mmol) triethylamine in 15 mL dichloromethane 1.41 mL (8.71 mmol) ( $\pm$ )-endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-bis-(4-thiocyanatomethyl)benzyl ester dissolved in 5 mL dichloromethane were added dropwise. After refluxing for 16 h 1.21 mL (8.68 mmol) triethylamine were added. The obtained white precipitate was filtered off and the solution was extracted with HCl (5%) and subsequently with saturated  $\text{NaHCO}_3$ . The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness in vacuo. The residual crude product was purified by column chromatography (silicagel, cyclohexane/ethyl acetate 2/1) and recrystallised from cyclohexane/ethyl acetate 2/1. Yield: 1.492 g (34%) white powder.  $^1\text{H}$  NMR (500 MHz, 20 °C,  $\text{CDCl}_3$ )  $\delta$  7.36 (d, 8H, Ph), 6.27 (dd, 1H,  $\text{nb}^6$ ), 6.00 (dd, 1H,  $\text{nb}^5$ ), 5.2–5.1 (m, 4H,  $-\text{O}-\text{CH}_2-$ ), 4.16 (s, 4H,  $-\text{CH}_2-\text{SCN}$ ), 3.46 (t, 1H,  $\text{nb}^3$ ), 3.30 (s, 1H,  $\text{nb}^4$ ), 3.16 (s, 1H,  $\text{nb}^1$ ), 2.78 (m, 1H,  $\text{nb}^2$ ), 1.62, 1.47 (m, 2H,  $\text{nb}^7$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, 20 °C,  $\text{CDCl}_3$ )  $\delta$  174.2, 173.0 (2C,  $-\text{C}=\text{O}$ ), 137.8 (1C,  $\text{nb}^6$ ), 137.0, 136.9 (2C,  $\text{Ph}^{4,4'}$ ), 135.2 (1C,  $\text{nb}^5$ ), 134.5, 134.5 (4C,  $\text{Ph}^{1,1'}$ ), 129.4, 129.3 (4C,  $\text{Ph}^{3,3',5,5'}$ ), 128.8, 128.8 (2C,  $\text{Ph}^{2,2',6,6'}$ ), 112.0 (2C,  $-\text{SCN}$ ), 66.2, 65.9 (2C,  $-\text{O}-\text{CH}_2$ ), 48.2 (1C,  $\text{nb}^3$ ), 47.9 (1C,  $\text{nb}^1$ ), 47.5 (1C,  $\text{nb}^7$ ), 47.4 (1C,  $\text{nb}^2$ ), 45.9 (1C,  $\text{nb}^4$ ), 38.1 (2C,  $-\text{CH}_2-\text{SCN}$ ). FT-IR (Si wafer,  $\text{cm}^{-1}$ ) 3443 (w), 3061 (w, aromatic  $\nu_{\text{CH}}$ ), 2988–2878 (m, aliphatic  $\nu_{\text{CH}}$ ), 2153 (s,  $\nu_{\text{SCN}}$ ), 1917 (w), 1729 (s,  $\nu_{\text{C}=\text{O}}$ ), 1616 (w), 1515 (m), 1452 (m), 1424 (m), 1378 (m), 1358 (m), 1332 (m), 1308 (m), 1265 (s), 1176 (s), 1111 (m), 1067 (w), 1013 (m), 909 (w), 862 (w), 826 (m), 722 (m) 698 (w), 647 (w), 522 (w).

#### 2.3.3. Preparation of poly-**2**

To a solution of 500 mg (0.99 mmol, 100 equiv.) of monomer **2** in 2.5 mL dichloromethane, 8.76 mg (0.0099 mmol, 1 equiv.) of the initiator  $[\text{RuCl}_2(\text{H}_2\text{IMes})(3\text{-bromo-pyridine})_2(\text{CHPh})]$  dissolved in 1.5 mL dichloromethane were added at room temperature. The polymerisation was monitored by TLC (cyclohexane/ethyl acetate 2/1). After 3 h the solution was treated with some drops of ethyl vinyl ether for 15 min and subsequently precipitated into 50 mL of cooled methanol. The light brown



Scheme 2.

polymer was reprecipitated in cooled methanol and dried under vacuum. Yield: 345 mg (69%) poly-**2**. GPC:  $M_n$  33,800 g mol<sup>-1</sup> ( $M_n$  calc.: 49,141 g mol<sup>-1</sup>), PDI ( $M_w/M_n$ ) 1.36.  $T_g$ : 44.2 °C (second heating run, 10 °C min<sup>-1</sup>). <sup>1</sup>H NMR (500 MHz, 20 °C, CDCl<sub>3</sub>)  $\delta$  7.2 (s, 8H, Ph), 5.5–4.8 (m, 6H, nb<sup>5,6</sup>, -CH<sub>2</sub>-O), 4.0 (s, 4H, -CH<sub>2</sub>SCN), 3.4–2.9 (m, 4H, nb<sup>1,2,3,4</sup>), 2.1–1.3 (m, 2H, nb<sup>7</sup>). <sup>13</sup>C NMR (125 MHz, 20 °C, CDCl<sub>3</sub>)  $\delta$  173.4 (2C, C=O), 136.8–134.8 (6C, nb<sup>5,6</sup>, Ph<sup>1,1',4,4'</sup>), 129.3–128.4 (8C, Ph<sup>2,2',3,3',5,5',6,6'</sup>), 112.2 (2C, -SCN), 65.9 (1C, -CH<sub>2</sub>-O), 52.8–40.2 (5C, nb<sup>1,2,3,4,7</sup>), 37.9 (1C, -CH<sub>2</sub>-SCN). FT-IR (Si wafer, cm<sup>-1</sup>) 2953, 2928, 2858 (w, aliphatic  $\nu_{CH}$ ), 2153 (m,  $\nu_{SCN}$ ), 1731 (s,  $\nu_{C=O}$ ), 1515 (w), 1449 (w), 1424 (w), 1391 (w), 1252 (m), 1169 (m), 1110 (w), 979 (w), 825 (w), 734 (w), 647 (w).

#### 2.4. UV-irradiation and post-modification

UV irradiation experiments were carried out with an unfiltered medium pressure Hg lamp (Heraeus, 1000 W) in nitrogen atmosphere. For these experiments, the light intensity (power density) at the sample surface was measured with a spectroradiometer (Solatell, Sola Scope 2000TM, spectral range from 230 to 470 nm). The light intensity was 4.23 mW cm<sup>-2</sup> for the spectral range 250–254 nm. These values were obtained directly from the polychromatic spectrum of the Hg lamp. Typical UV illumination times were between 60 and 180 s. After UV illumination of the samples, post-modifications with propylamine were performed by exposing the irradiated sample films to the vapours of a solution of propylamine in toluene (10 wt.%). Patterned structures were obtained by placing a contact mask (Cr pattern on quartz) directly onto the polymer film prior to illumination.

### 3. Results and discussion

The photosensitive norbornene derivative, ( $\pm$ )-endo,exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid-bis-(4-thiocyanatomethyl)benzyl ester (**2**), was synthesised as depicted in Scheme 2. Starting from (4-chloromethyl)benzyl alcohol, substitution of the chlorine by the thiocyanate anion leads to the photoreactive compound **1**. This molecule itself undergoes a photoisomerisation from the thiocyanate to the isothiocyanate group. The benzyl thiocyanate group absorbs UV-light up to 280 nm.

Its photosensitivity is demonstrated by the infrared spectra taken before and after illumination with UV-light, see Fig. 1 and

Table 1. The sharp peak of the vibration of the C≡N triple bond at 2153 cm<sup>-1</sup> decreases and two broad peaks emerge at 2180 and 2095 cm<sup>-1</sup> due to vibration of the cumulative double bonds of the N=C=S group. A small fraction of the thiocyanate groups is not converted.

The thereby formed reactive isothiocyanate group easily forms the thiourea derivative **1b** when exposed to vapours of propylamine. The two vibrational bands of the isothiocyanate unit completely vanish, and concomitantly the thiourea band at 1554 cm<sup>-1</sup> evolves. Unreacted SCN groups are detectable by the signal at 2153 cm<sup>-1</sup>.

This low-molecular-weight compound is an interesting new building block for the preparation of photosensitive molecules in general. Due to the alcohol functionality it can be coupled to carboxylic acids, e.g. by reacting compound **1** with carboxylic acid chlorides as carried out in this work. In an analogous reaction, we have also prepared a photoactive acrylate based monomer recently [21].

Reaction of compound **1** with norbornene dicarboxylic acid dichloride in the presence of triethylamine as HCl scavenger leads to the photosensitive norbornene derivative **2**. The photosensitivity of this compound as well as the post-modification with propylamine were verified by FT-IR spectroscopy. The IR

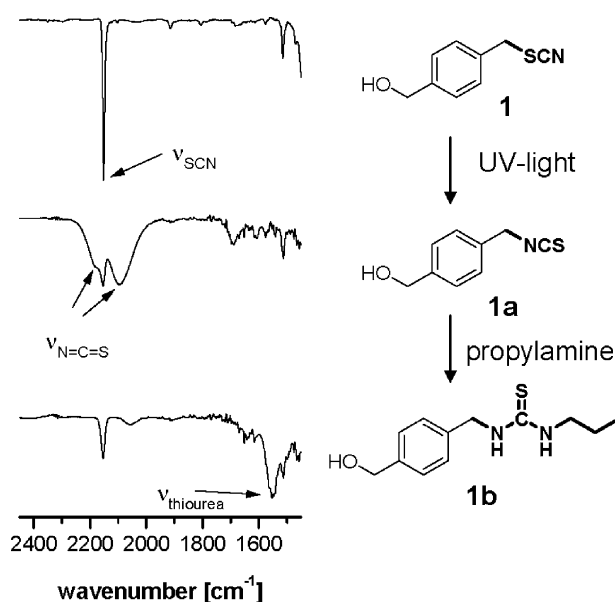
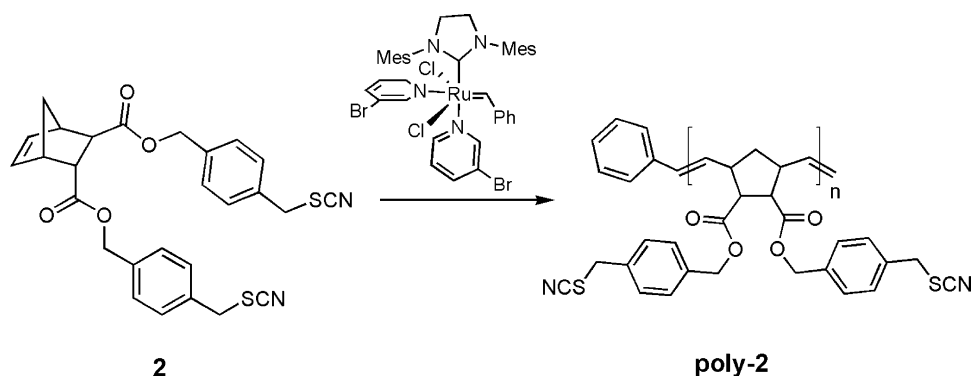


Fig. 1. IR-spectra of compound **1**, after illumination (**1a**), and post-treatment with propylamine (**1b**).

Table 1  
Comparison of IR vibrations (values in  $\text{cm}^{-1}$ )

	1	2	Poly-2	Comments
Original	2153	2153	2153	CN stretching vibration
Illuminated	2180, 2095	2180, 2095	2180, 2096	Asymmetric stretching vibration of NCS
PrNH <sub>2</sub>	– <sup>a</sup> , 1554	3368, 3262, 1554	3363, 3260, 1554	N–H stretching vibration coupling between C=S and C–N vibration

<sup>a</sup> Overlap with O–H stretching vibrations.



Scheme 3.

vibrations are almost identical with those of compound **1**, as listed in Table 1.

Polymerisations of nitrile containing monomers with ruthenium initiators are known to cause problems. In general this class of monomers cannot be polymerised in a controlled way with the classical “Grubbs”  $\text{RuCl}_2(\text{PCy}_3)_2(\text{CHPh})$ , ( $\text{Cy}$  = cyclohexyl) or “Super-Grubbs” initiator,  $\text{RuCl}_2(\text{H}_2\text{IMes})(\text{PCy}_3)(\text{CHPh})$  ( $\text{H}_2\text{IMes}$  = *N,N*-di(mesityl)-4,5-dihydroimidazolin-2-ylidene), due to strong interactions of the nitrile group with the metal centre.

The recently described bromopyridine initiator  $[\text{RuCl}_2(\text{H}_2\text{IMes})(3\text{-bromo-pyridine})_2(\text{CHPh})]$ , a derivative of the “Super-Grubbs” catalyst lacking the phosphine ligand, can polymerise such monomers in a controlled manner, as it has been shown by the synthesis of liquid crystalline polynorbornene polymers based on the cyanobiphenyl system [14–16]. However, the reaction conditions are very crucial for polymerisation, and the polydispersity of the polymers is higher than usual for these initiators due to these interactions.

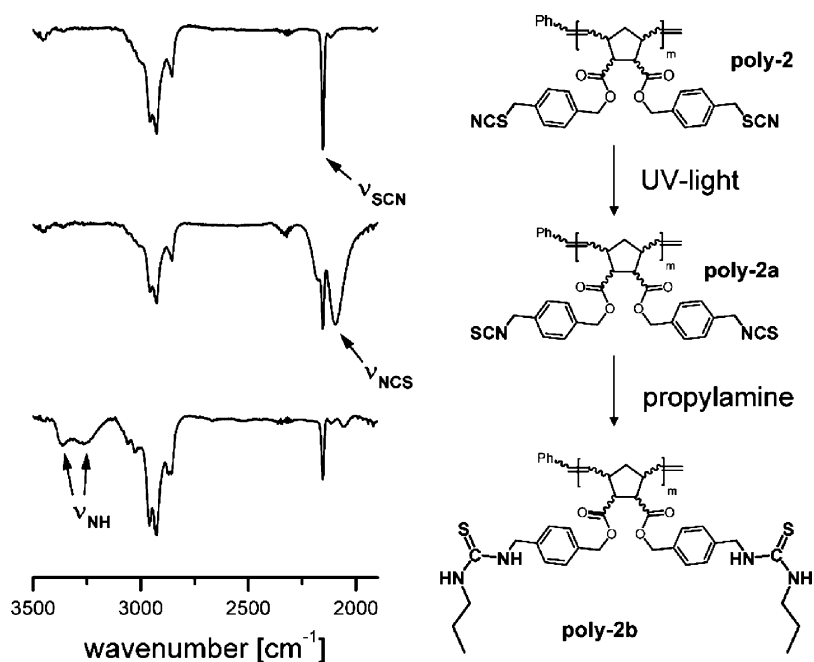


Fig. 2. IR-spectra of compound poly-2, after illumination (poly-2a), and post-treatment with propylamine (poly-2b).

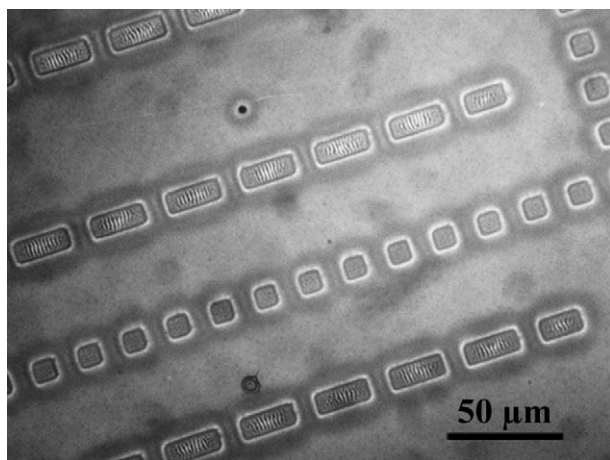


Fig. 3. Optical microscope image of a thin film of poly-2 after structured illumination followed by a post-treatment with gaseous propylamine.

Consequently, polymerisation of compound **2** was carried out with the bromopyridine initiator in THF, see Scheme 3. The resulting polymer was precipitated from methanol and reprecipitated from THF/methanol to remove residual ruthenium. Gel permeation chromatography (GPC) evidenced a polymer with a molecular weight  $M_n$  of about  $34,000 \text{ g mol}^{-1}$  with a polydispersity index of 1.36 as measured against polystyrene standards. This value is quite acceptable for this class of polymer. DSC measurements showed a glass transition temperature of poly-2 at  $44.2 \text{ }^\circ\text{C}$ .

It was possible to cast homogeneous polymer films (thickness between  $0.5$  and  $1.0 \text{ }\mu\text{m}$ ) onto silicon wafers and glass slides by using spin coating with polymer solutions in dichloromethane. Again, the photoreaction was followed by FT-IR-spectroscopy (see Table 1 and Fig. 2). By illuminating the sample film with UV-light, the sharp peak of the vibration of the  $\text{C}\equiv\text{N}$  triple bond at  $2153 \text{ cm}^{-1}$  decreases and two broad peaks emerge at  $2180$  and  $2096 \text{ cm}^{-1}$  due to vibration of the cumulative double bonds of the  $\text{N}=\text{C}=\text{S}$  group.

After exposure to vapours of propylamine, the isothiocyanate bands vanish completely and the thiourea band at  $1554 \text{ cm}^{-1}$  and two broad bands at  $3363$  and  $3260 \text{ cm}^{-1}$  (due to  $\text{N-H}$  stretching vibrations) appear. It becomes clear that FT-IR spectroscopy is an ideal tool to monitor both the progress of photoisomerisation and the post-exposure reaction with amines. In a similar fashion, the addition reaction can be carried out with thiols to give derivatives of dithiocarbamates.

The  $\text{SCN-NCS}$  photoisomerisation reaction was carried out in combination with lithographic techniques to give patterned polymer surfaces. The illuminated areas are then capable of reacting with amines. For patterning of thin films of poly-2, a contact mask was placed onto the polymer film. After UV illumination the polymer layer was still optically transparent and no structural features were detectable by optical microscopy. After exposure to vapours of propylamine for 180 s, the structures of the mask pattern became visible under the optical microscope, see the image in Fig. 3. The features are detectable because the reaction with propylamine is accompanied by an increase in film thickness. This process leads to different optical pathlengths and

interference colours in non-illuminated and in modified areas of the polymer film. The structural features of the used mask were in the micrometer range.

#### 4. Conclusion

In this paper, we have presented a new photosensitive benzyl alcohol **1**, a new norbornene derivative **2**, and the corresponding photoactive polymer, poly-2, all of them carrying the benzyl thiocyanate group. We have shown that the photoisomerisation of the thiocyanate to the isothiocyanate is possible in all of the three compounds. Post-reaction with propylamine then leads to the formation of thiourea compounds.

The low-molecular-weight-compound **1** is a very interesting precursor for preparing benzyl thiocyanate based photoactive substances, due to the fact, that it can be coupled to carboxylic acids by a simple esterification procedure. Following this route, compound **2** is obtained which introduces this photoisomerisation chemistry to the ROMP toolbox for the first time. We have successfully prepared a photosensitive polynorborne poly-2 via ROMP with the third generation Grubbs initiator. Moreover, we have shown that it is possible to pattern the surface of a polymer film by this chemistry and to inscribe relief structures with a resolution in the micrometer range.

Since ROMP provides all possibilities of living polymerisation techniques, this photochemistry can now be combined with a broad variety of different monomers. We expect that this will lead to very interesting photoreactive materials with possible applications in optics, optoelectronics, patterned surface modification, and immobilisation techniques, e.g. for the preparation of DNA chips.

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