ℙ periodica polytechnica

Chemical Engineering
58/1(2014)69-74
doi:10.3311/PPch.7206
http://www.periodicapolytechnica.org/ch

RESEARCH ARTICLE

UV-Induced Crosslinking of Poly[2-(2’-Norbornenyl)-2-Oxazoline]s

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RECEIVED 10 JUNE 2013; ACCEPTED AFTER REVISION 16 JULY 2013

Abstract

A 2-oxazoline monomer bearing a norbornenyl functionality in the side-chain was prepared from the reaction of 5-norbornene-2-carbonitrile and 2-ethanol amine. This monomer could be successfully polymerized using a 2-oxazolinium-based macroinitiator that was in-situ generated from the methyl cation-initiated oligomerization of 2-ethyl-2-oxazoline. This polymer could be subjected to polymeranalogous reactions involving the alkene groups of the norbornenyl side-chains: A proof-of-concept was established by utilizing the polymers in photoresists that were crosslinked by thiol-ene reactions involving bisfunctional thiols. Photoinitiators for the UV-induced thiol-ene reaction were required in catalytic amounts only. After development, the resists exhibited reproduction of the geometric patterns with a resolution of 30 µm.

Keywords

photoresist · thiol-ene reaction · cationic polymerization · polymer photochemistry · poly(2-oxazoline)s · microwave-assisted polymerization

Acknowledgement

This work was presented at AMSALS 2012.

This study was performed at the Institute for Chemistry and Technology of Materials of the Graz University of Technology and the Polymer Competence Center Leoben GmbH (PCCL) within the framework of the Kplus-program of the Austrian Ministry of Traffic, Innovation and Technology. PCCL is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

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1 Introduction

UV-induced crosslinking is a key strategy for the three-dimensional patterning of structures on substrate surfaces [1]. The patterns, which are preset by masks during illumination, can be reproduced either as positive or as negative image, and the formulations are referred to as positive or negative photoresists. Commonly used positive (negative) resists comprise the DNQ/Novolak system (the SU-8 system and acrylic photoresists) [2-4]. Proper adherence of the formulations on the substrates is a key prerequisite for high-resolution reproduction of the patterns.

2-Oxazolines are a class of monomers that can be polymerized in living cationic ring-opening polymerizations, yielding (block co-) poly(2-oxazoline)s with targeted properties [5-7]. Copoly(2-oxazoline)s bearing linear olefinic side-chains can be used in photoresist formulations: Polymeranalogous crosslinking of poly(2-oxazoline)s in the solid state by thiol-ene reactions has shown to meet the criteria of high yields, high reproducibility, and high resolution [5]. In addition it was shown that the statistical copoly(2-oxazoline)s exhibit good adhesion on various substrates, overcoming the challenges associated with some combinations of substrates and commercially available photoresists.

In order to further enhance the tool-box of poly(2-oxazoline)-based materials, this study aimed at the synthesis of a 2-oxazoline monomer bearing olefinic cyclic side-chains. The feasibility of polymeranalogous modifications of the corresponding polymer was proven on the example of UV-induced crosslinking of the olefinic moieties.

2 Materials and Methods

2.1 Chemicals and Instrumentation

All chemicals were purchased from Sigma Aldrich (Vienna, Austria) and used as received with the exception of 2-ethyl-2-oxazoline and methyl tosylate that were distilled prior to use and stored under argon. Lucirin TPO-L was provided by Ciba (now BASF). The monomer synthesis was performed in standard glassware. The polymerization reaction was conducted in the Biotage Initiator 8 single-mode microwave reactor in dedicated vials that were filled in inert atmosphere. NMR spectra were recorded with a Bruker Advance III 300 MHz NMR-Spectrometer with deuterated chloroform as solvent. Signals were referenced to the solvent peak at 7.26 and 77.0 ppm, respectively. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer in ATR mode with 32 scans per sample. The spectral range was set from 500 to 4000 cm^{-1}. Elemental analyses were carried out at the Institute of Analytical Chemistry & Food Chemistry of the Graz University of Technology. UV irradiation was supplied by a EFOS Novacure UV lamp by EXFO at 4500 $mWcm^{-2}$ for 300 s (at 12 cm distance). Images of the developed photoresists were recorded with an Olympus BX60 optical microscope. Average molecular weights and polydispersity indices were determined by size exclusion chromatography GPC using $CHCl_3/Et_3N/^{iso}PrOH$ (94/4/2) as eluent. The measurements were performed with a Merck Hitachi L-6000A pump, separation columns from Polymer Standards Service, 8x300 mm STV linear XL 5 µm-grade size, and a differential refractometer Waters 410 detector. Polystyrene standards from Polymer Standard Service were used for calibration.

2.2 Synthesis of 2-(bicyclo[2.2.1]hept-5-en-2-yl)-4,5-dihydrooxazole, NbOx

To 5.98 g (1 eq) of bicyclo[2.2.1]-hept-5-ene-2-carbonitrile, 0.29 g (0.023 eq) cadmium(II) acetate dihydrate were added. The suspension was heated to 130 °C under constant stirring and reflux conditions. Subsequently, 2.66 g (1.03 eq) 2-ethanol amine were added. Heating was continued for 24 hours. The product was recovered by vacuum distillation and additionally purified on a silica column (eluent: chloroform). The product was obtained as a colorless clear liquid; yield: 2.40 g, 35%.

^{1}H-NMR (20 °C, $CDCl_3$, 300 MHz): The signal assignment has been included in the caption of Fig. 1.

^{13}C-NMR (20 °C, $CDCl_3$, 75 MHz): The signal assignment has been included in the caption of Fig. 2.

FT-IR (cm^{-1}): 3054 w, 2961 m, 1648 s, 1324 m, 1179 s, 988 s, 902 m, 717 s.

Elemental analysis: Calculated: 73.59% C, 8.03% H, 8.58% N. Experimental: 73.00% C, 8.05% H, 8.52% N.

2.3 Polymerization of NbOx

5.0 mg (1 eq) of methyl tosylate were dissolved in 1 mL of chloroform and 10.7 mg (4 eq) of 2-ethyl-2-oxazoline were added. The reaction mixture was heated at 145 °C for 0.5 h. Subsequently, 440 mg (99.9 eq) of NbOx were added, and the reaction mixture was heated at 140 °C for 1 h. After removal of the solvent and drying under reduced pressure, 0.44 g of a white solid were obtained in quantitative yield.

^{1}H-NMR (20 °C, $CDCl_3$, 300 MHz): δ (ppm) = 1.11 (12 H, m, H13), 1.35-1.61 (300 H, m, H9A, H10A, H10B), 1.76-1.95 (100 H, m, H9B), 2.14 (60 H, m, H4 endo), 2.30 (8 H, m, H12), 2.82 (40 H, m, H4 exo), 2.89-3.01 (200 H, m, H5, H8), 3.46 (428 H, H2), 5.92-6.13 (200 H, m, H6, H7), 7.15-7.18 (2 H, d, ArH), 7.67-7.69 (2 H, d, ArH).

^{13}C-NMR (20 °C, $CDCl_3$, 75 MHz): δ (ppm) = 31.2, 40.6, 41.6, 42.7, 44.5-47.0, 49.7, 135.8, 136.7, 138.4, 173.9-176.0.

2.4 Formulation and Application of the Photoresists

A solution of pNbOx and Lucirin TPO-L in chloroform (55 mg/0.1 mg in 0.5 mL) was prepared at 0 °C. Subsequently, either 1,4-butanedithiol (17.4 mg) or 3,4-dimercaptotoluene (25.2 mg) were added (ratio thiol:ene = 1:1). FR4 substrates were drop-coated with 0.2 mL of the photoresist formulation and left to dry under nitrogen flow for 3 min. The photoresists were illuminated through a glass mask with a preset geometric pattern and subsequently developed in chloroform.

3 Results and Discussion

3.1 Monomer Synthesis and Characterization

2-(2’-Norbornenyl)-2-oxazoline NbOx was chosen as the monomer of this study due to the assumingly high reactivity of its olefinic side-chain in orthogonal block copolymer synthesis and polymeranalogous reactions. NbOx was synthesized from the solvent-free one-pot reaction of 5-norbornene-2-carbonitrile and 2-ethanol amine according to the synthetic routine described by Witte and Seeliger (Fig. 1) [8]. The commercially available reactant 5-norbornene-2-carbonitrile can be prepared from the Diels-Alder reaction of cyclopentadiene and acrylonitrile and is obtained as a mixture of the endo- and the exo-isomer. Throughout this manuscript, the classification of exo- and endo-isomer is referred to the position of the nitrile or 2-oxazoline substituent, respectively. The monomer was obtained in high purity after distillation and subsequent flush column chromatography. However, due to comparably low reactant conversion, only a yield of 35% of the purified product could be achieved. ^{1}H- and ^{13}C-NMR as well as FT-IR and elemental analyses confirmed its successful synthesis. According to ^{1}H-NMR analyses, the monomer was recovered with an exo:endo ratio of 0.4:0.6. In particular the proton H2’ (Fig. 1) revealed a pronounced difference in shifts in the exo- compared to the endo-isomer (2.84 vs. 2.17 ppm).

3.2 Polymerization of NbOx Using Macroinitiators

Polymerizations were performed in a microwave reactor dedicatedly designed for chemical syntheses, approaching the concept of green chemistry associated with this heating technique [9]. The first attempts to synthesize linear pNbOx with methyl tosylate as initiator failed: An insoluble precipitate was obtained from a polymerization mixture with a targeted polymerization degree of 100. Presumably, the initiating methyl cation did not only attack the 2-oxazoline ring at the nitrogen position [10], but also attacked the double bond of the

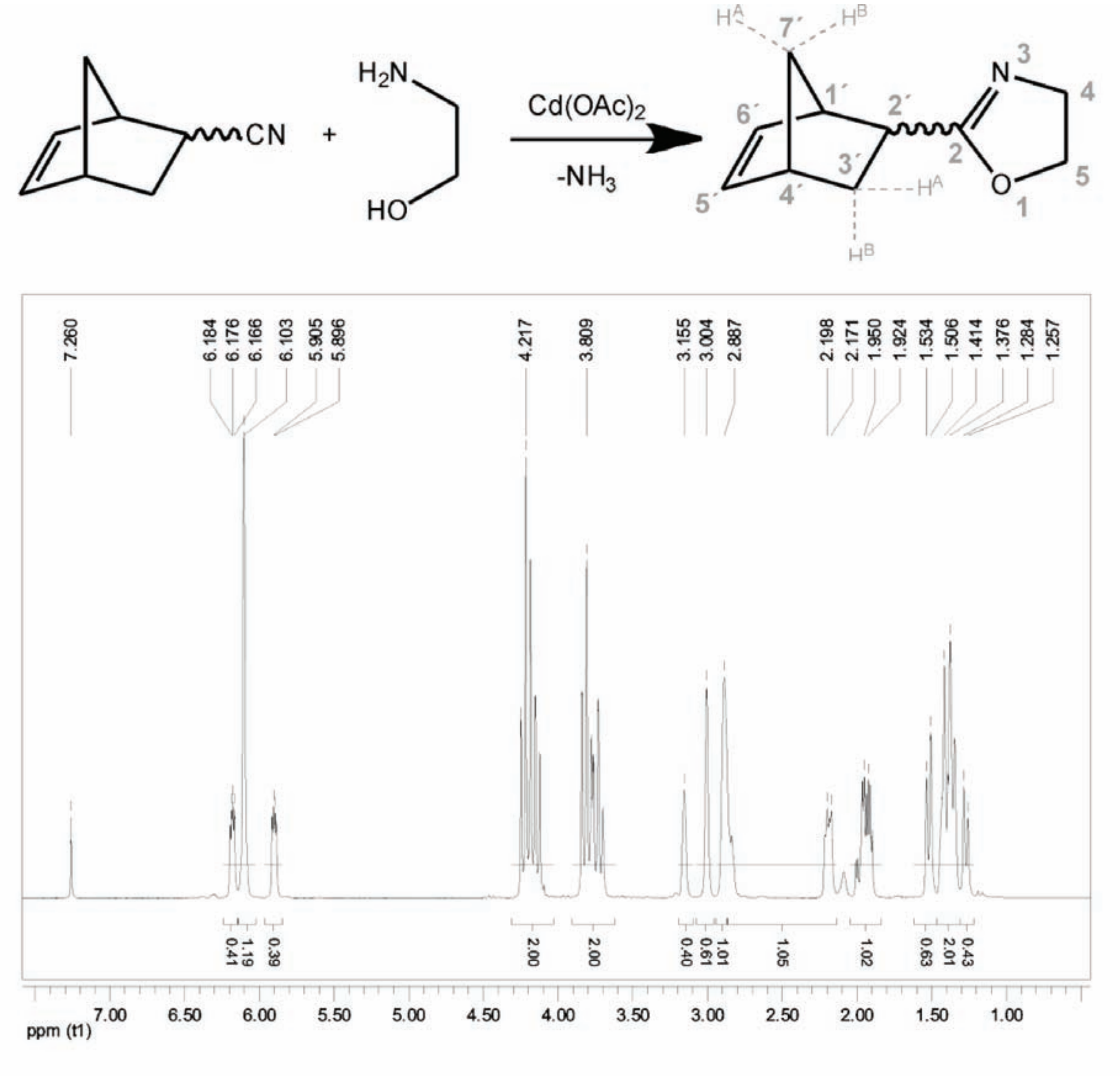


Fig. 1. Synthesis of NbOx (incl. atomic numbering) from 5-norbornenyl-2-carbonitrile and 2-ethanol amine according to the Witte and Seeliger protocol (top) and the ^{1}H-NMR spectrum of the purified NbOx (bottom). Signal assignment: δ (ppm) = 1.26 (0.4 H, m, H7’A exo), 1.38 (2 H, m, H3’A, H7’B), 1.52 (0.6 H, m, H7’A endo), 1.93 (1 H, m, H3’B), 2.17 (0.6 H, m, H2’ endo), 2.84 (0.4 H, m, H2’ exo), 2.89 (1 H, m, H4’), 3.00 (0.6 H, m, H1’ endo), 3.16 (0.4 H, m, H1’ exo), 3.81 (2 H, m, H4), 4.22 (2 H, m, H5), 5.91 (0.4 H, m, H6’ exo), 6.10 (1.2 H, bs, H5’ endo, H6’ endo), 6.18 (0.4 H, m, H5’ exo).

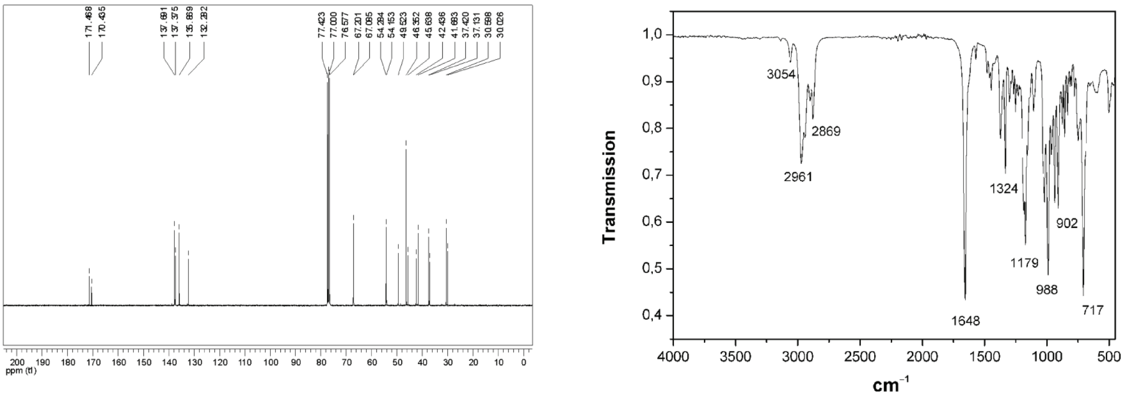
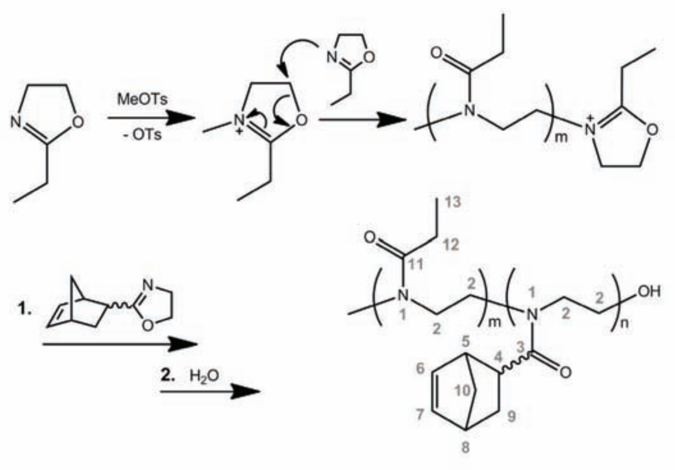


Fig. 2. ^{13}C-NMR (left) and IR spectrum (right) of the purified NbOx. For atomic numbering, see Fig. 1. Signal assignment: δ (ppm) = 30.0/30.6 (C3’), 37.1/37.4 (C2’), 41.7/42.5 (C4’), 45.6/46.4 (C1’), 46.4/49.5 (C7’), 54.1/54.3 (C4), 67.1/67.2 (C5), 132.3/135.9 (C6’), 137.4/137.7 (C5’), 170.4/171.5 (C2).

norbornenyl side-chain, opening the pathway to crosslinking of the polymer involving the olefinic moieties. This limitation could be overcome by employing a less reactive macroinitiator, namely oligo(2-ethyl-2-oxazoline)-2-ethyl-2-oxazolinium tosylate, which was prepared in-situ from the reaction of 2-ethyl-2-oxazoline and methyl tosylate (DP = 4). NbOx was added to the freshly prepared solution of the macroinitiator maintaining inert conditions, and, due to the significantly lower reactivity compared to methyl cations, the sterically more demanding macroinitiator preferentially attacked the nitrogen atom of the 2-oxazoline rings and yielded soluble pNbOx (Scheme 1). Similar findings were reported for the polymerization of a 2-oxazoline monomer with a pendant amino group [11]. According to ^{1}H-NMR analyses of the polymerization of NbOx, no residual monomer was present in the polymerization mixture after reaction times of 1 h; the polymerization was quenched with water. Completion of the targeted average polymerization degree of 100+4 (NbOx and 2-ethyl-2-oxazoline, respectively), could be confirmed by ^{1}H-NMR analysis (Fig. 3). Size-exclusion chromatography, however, revealed significant deviation from narrow monomodal molecular weight distribution: In fact, the molecular weight distributions of all investigated pNbOx samples (PDI ≥ 6) exhibited trimodal distribution in varying extent (Fig. 3). According to ^{1}H-NMR analyses, double bonds of the norbornenyl moieties were not consumed during the reaction; in addition, no insoluble polymer fractions were observed. However, due to the resolution of ^{1}H-NMR analyses, it cannot be excluded that a minor fraction of the double bonds was consumed during the polymerization and, correspondingly, side-reactions such as crosslinking were induced, which broadened the molecular weight distribution. In addition, the occurrence of chain transfer and subsequent chain coupling by-reactions must be assumed [6]. Notably, this type of by-reaction has been reported to occur preferably in the synthesis of block copoly-(2-oxazoline)s if the first block was composed of (short side-chain) 2-methyl- or 2-ethyl-2-oxazoline and the second block was composed of (long side-chain) 2-nonyl-2-oxazoline.



Sch. 1. Cationic ring-opening polymerization of NbOx: In-situ preparation of the macroinitiator oligo(2-ethyl-2-oxazoline)-2-ethyl-2-oxazolinium tosylate (top), polymerization of NbOx (middle), and termination with water (bottom). The copolymer is shown with atomic numbering.

3.3 Application of pNbOx as Negative Photoresist

In order to verify the applicability of the olefinic moieties in the side-chains of pNbOx for polymeranalogous reactions, the polymer was used in chloroform-based photoresist formulations. Crosslinking of the polymer chains was attempted by thiol-ene reactions employing bisfunctional thiols, namely 1,4-butanedithiol or 3,4-dimercaptotoluene. Thiol:ene ratios of 1:1 were maintained in both cases. Precipitation of crosslinked polymers was observed within 5 (20) min in the formulations based on 1,4-butanedithiol (3,4-dimercaptotoluene); this precipitation was found to be quantitative within 2 h. In order to prevent instant crosslinking of the polymer, the individual components were added to the formulation while cooling with ice and protection from light were maintained.

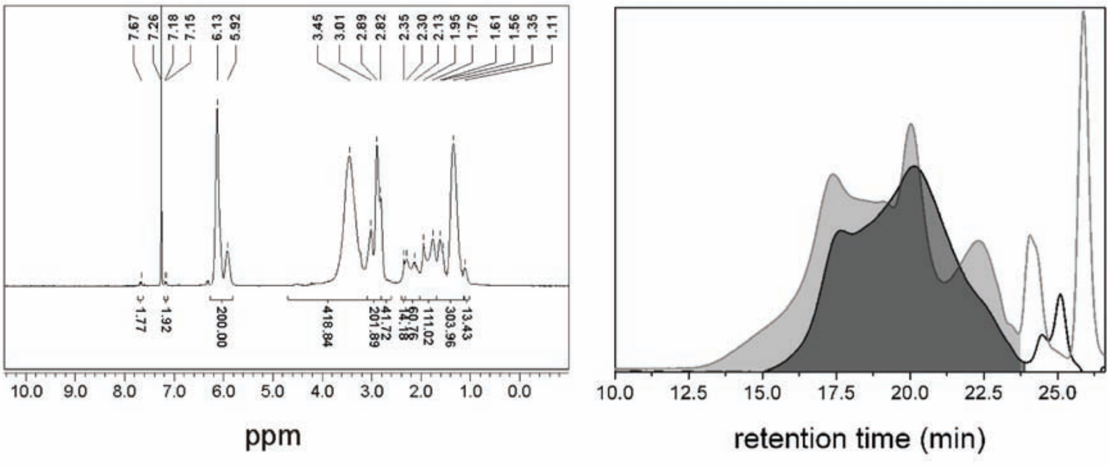
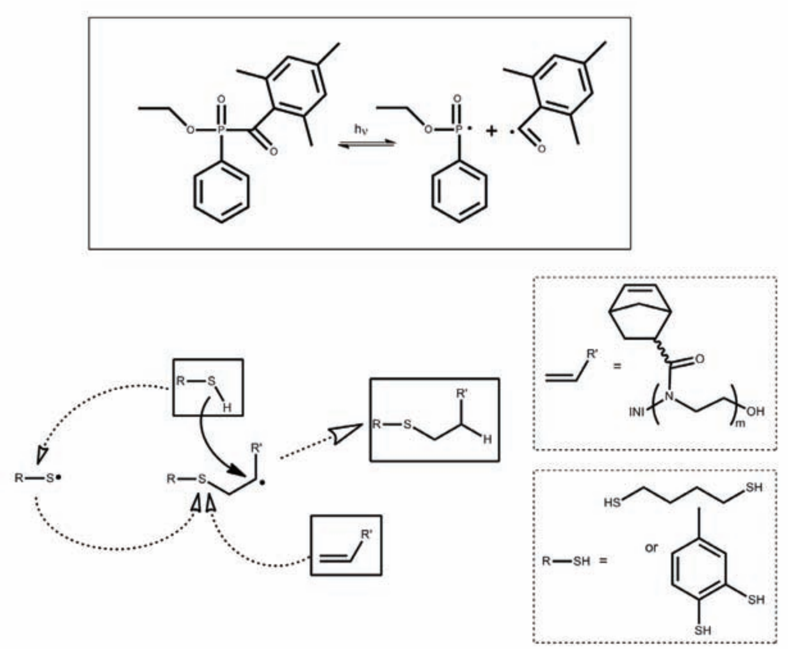


Fig. 3. ^{1}H-NMR spectrum (left) and size exclusion chromatograms (right) of one/two sample(s) of pNbOx with a targeted polymerization degree of 100. The number average molecular weight and PDI value are 5.4 kDa / 20.3 (colour code: light grey) and 6.5 kDa / 6.2 (colour code: dark grey).



Sch. 2. Structures of the photinitiator Lucrin TPO-L and the radicals formed by homolytic cleavage (top), and the mechanism of the thiol-ene reaction, highlighting the thiyl-thiol cycle (bottom).

The thiol-ene reaction of pNbOx proved to proceed with catalytic amounts of the photoinitiator Lucirin TPO-L in a ratio of thiol:ene:Lucirin TPO-L = 1000:1000:1. Lucirin TPO-L decomposes upon irradiation with UV light such that two free radicals are formed [12], and the in-situ formed phosphinoyl radicals are more reactive than the benzoyl radicals [5]. Due to the low amount of photoinitiator required, additional radical formation by homolytic dissociation of a thiol into a thiyl radical and a proton radical must be considered, too: Notably, while it was found almost a century ago that light accelerates thiol-ene reactions [13], the thiol-ene reaction of norbornenes without the use of a dedicated photoinitiator at 254 nm was investigated recently and found to correlate with the number of thiol groups [14]. Regardless of the type of radicals formed, they abstract the protons of thiol functions and yield thiyl radicals. These thiyl radicals react with the unsaturated side-chains of the norbornenyl moieties in pNbOx, while the carbon radicals abstract the protons of unreacted thiol functions and deliver the next generation of thiyl radicals (Scheme 2).

For photoresist applications, the photoresist formulations were dropcoated onto FR4-substrates. The coated substrates were dried for some minutes under nitrogen flow and subsequently irradiated with polychromatic UV-light through a glass mask exhibiting a preset geometric pattern. The geometric pattern of the mask was reproduced in negative fashion by development of the resists in chloroform for 30 s (Fig. 4). For both formulations, the one containing 1,4-butanedithiol as well as the one containing 3,4-dimercaptotoluene, resolutions in the range of 30 µm were detected by optical microscopic measurements.

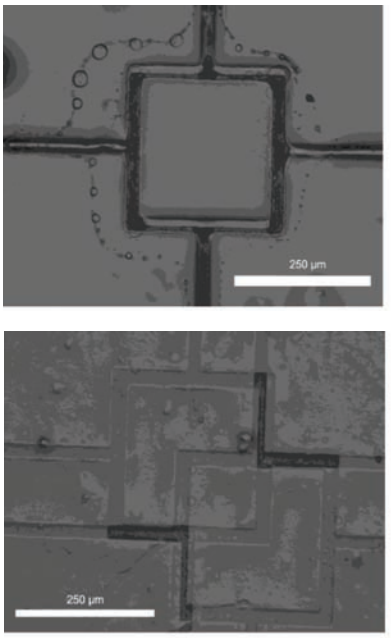


Fig. 4. FR4 substrates coated with pNbOx-based resists after illumination and development. Top: Formulation with 3,4-dimercaptotoluene and single illumination; bottom: formulation with 1,4-butanedithiol and double illumination.

4 Conclusions

In this report, we described the successful synthesis of a novel 2-oxazoline monomer bearing a norbornenyl functionality in the side-chain, NbOx. This monomer could only be polymerized without the occurrence of in-situ crosslinking of significant degree if a 2-oxazolinium-based macroinitiator was used; methyl tosylate as initiator failed to yield soluble polymers. Due to by-reactions in the course of the polymerization, namely chain transfer and subsequent chain coupling, broad and trimodal distributions of the molecular weight were observed. Because of the high reactivity of the norbornenyl side-chains, pNbOx can be successfully subjected to polymeranalogous transformations. This concept was proven on the example of pNbOx-based negative photoresist formulations. Photoinduced crosslinking of the polymers was accomplished by thiol-ene reactions of the norbornenyl moieties with bisfunctional thiols. Photoinitiators needed to be added in catalytic amounts only (ratio of thiol:ene:photoinitiator = 1000:1000:1), providing resolutions of the reproduced patterns in the range of 30 µm. Further investigations will focus on the applicability of NbOx in orthogonal ROMP/CROP strategies aiming at the synthesis of block copolymers.

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