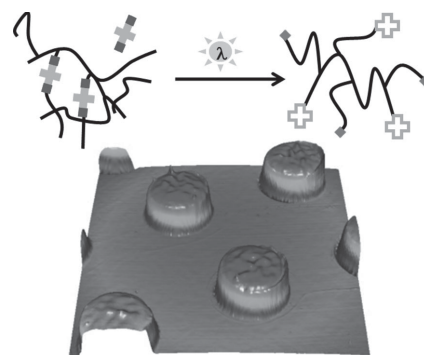


A Polyurethane-Based Positive Photoresist

Luis García-Fernández, Alexandre Specht, Aránzazu del Campo*

Polyurethane (PU) monomer mixtures containing commercially available *o*-nitrobenzyl-based photocleavable monomers have been formulated and tested as low-cost positive tone photoresists. The photolysis reaction is studied by UV spectroscopy. Well-defined micropatterns on 2 μm thick photodegradable PU films are obtained using 365 nm light exposure. This strategy is also extended to improved formulations based on synthesized *o*-nitrobiphenylpropyl derivatives with enhanced photochemical properties for single photon excitation and high two-photon absorption cross-sections. Improved pattern resolution in 2D and the capability of 3D resolution using a scanning laser at 780 nm is demonstrated. This work demonstrates the potential of PUs as readily available, versatile, and easy-to-use photoresist materials for low-cost lithography applications.



1. Introduction

Positive-tone photoresist materials used in photolithography effectively degrade upon exposure to UV light or e-beams.^[1] Most common positive photoresist formulations rely on mixtures of Novolac (a phenol formaldehyde resin) with diazonaphthoquinone (DNQ) for UV-sensitive lithography, or on poly(methylmethacrylate) for e-beam applications. Apart from effective response to light or e-beam irradiation, photoresist materials must present good film-forming properties, adequate viscosity for the spin-coating process, mechanical stability after processing, and low shrinkage during polymerization. All these factors are crucial for dimensional accuracy and stability of the lithographic features.

Polyurethanes^[2,3] (PUs) are widely used for coating applications due to their flexible design, rapid polycondensation at almost any temperature with no release of small molecules, and adjustable film properties (surface energy, hydrophilicity, viscosity, hardness, and viscoelasticity...) by changing the monomer composition over a great variety of low-cost commercially available candidates.^[4] PUs are self-priming and can be applied in a single coating step to any dry film thickness. They can be formulated with low to zero volatile organic content, facilitating the formation of compliant coatings on many different substrates. Their versatility and wide range of superior properties, such as solvent and abrasion resistance, impact strength, and low temperature flexibility are the driving forces to their continuously expanding usage in many applications. These are also interesting properties for the application of PUs as photoresist materials. However, no strategies for photodegradation or photopolymerization of PU chains are reported.

Over the last few years, photoremovable protecting groups (PPGs) have been increasingly used for light-mediated control of molecular architecture and derived properties in polymer coatings.^[5,6] PPGs or “cages” are chromophores that can be covalently attached to organic

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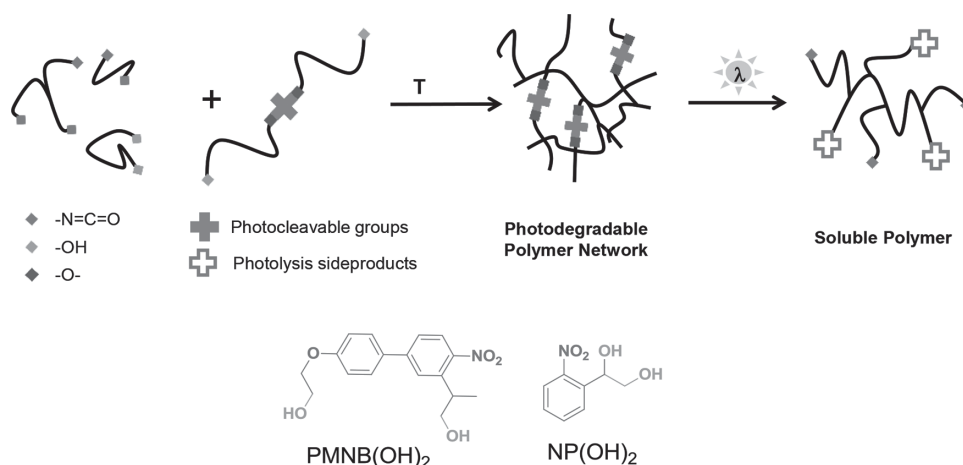


Figure 1. Scheme of a positive photoresist material based on a photodegradable polyurethane. The structure of the photocleavable monomers NP(OH)₂ and PMNB(OH)₂ is also shown.

functional groups and subsequent cleaved by light exposure. PPGs have been intercalated in the polymer backbones to allow photodegradation,^[7–10] or have been linked to polar side chain functional groups to mediate solubility changes after light-triggered chromophore removal.^[11–16] Here, we propose to use a photocleavable diol as comonomer in a PU formulation and show the formation of crosslinked coatings that can be effectively degraded and dissolved after light exposure using single- and two-photon excitation (Figure 1). The commercially available diol 1-(2-nitrophenyl)-1,2-ethanediol, NP(OH)₂, and the previously synthesized^[17] diol 2-(4'-(2-hydroxyethoxy)-4-nitro-[1,1'-biphenyl]-3-yl)propan-1-ol, PMNB(OH)₂, contain a PPG (*o*-nitrobenzyl and *o*-nitrobiphenylpropyl, respectively) flanked by two hydroxyl groups. The free hydroxyl groups can react with isocyanates to form PU. Light exposure induces cleavage of the intercalated PPGs and degradation of the polymer chain. Site-selective exposure allows spatial resolution of the photodegradation and the possibility of generating regions with differential solubility within the PU layer. This is the first example of a positive-tone PU-based photoresist that can be applied to obtain micropatterns using masked irradiation or scanning lasers.

2. Experimental Section

2.1. Composition of Monomer Mixture

The photoactive monomer 1-(2-nitrophenyl)-1,2-ethanediol, NP(OH)₂ was purchased from Sigma–Aldrich and was used without purification. The monomer 2-(4'-(2-hydroxyethoxy)-4-nitro-[1,1'-biphenyl]-3-yl)propan-1-ol, PMNB(OH)₂, was synthesized as previously reported.^[17] The rest monomers were commercially available: isophorone diisocyanate (IPDI; Sigma–Aldrich), triphenylmethane-4,4', 4''-triisocyanate (DRE, Bayer AG) and poly(propylene glycol) 1200 Mw (PPG; Dow Chemical).

Anhydrous tetrahydrofuran (THF; Sigma–Aldrich) was used as a reaction solvent. Dibutyltin dilaurate (DBTDL; Sigma–Aldrich) was used as a catalyst.

Mixtures containing variable ratios of the photocleavable monomers NP(OH)₂ or PMNB(OH)₂ and the commercially available diisocyanate IPDI, triisocyanate DRE, and dialcohol PPG were prepared using THF as solvent and 0.5% of DBTDL as initiator (Figure 2).

2.2. Preparation of Photoresist Film

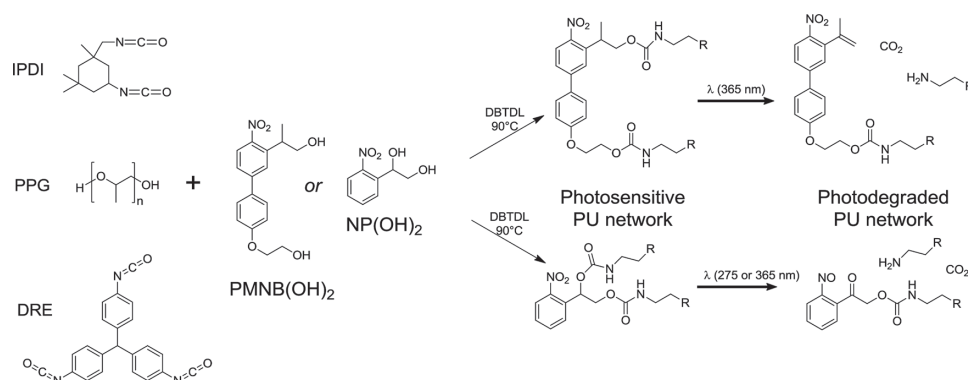
Quartz slides (1 × 2.5 cm², thickness 1 mm) or round-glass substrates (*d* = 13 mm, thickness = 0.16 mm) were cleaned by immersion in piranha solution overnight and washed with water and ethanol. In order to improve the adhesion of the PU film to the surface, substrates were modified by immersion in 3-aminopropyltriethoxysilane (APTS, ABCR) solution (1:1000) in distilled water for 30 min. The substrates were cleaned with water and dried under vacuum at 90 °C in order to stabilize the silane layer.

20 μL of the monomer mixture was deposited on the APTS-modified substrates by spin-coating (Model WS-400B-6NPP; Laurell Technologies Corporation). A two-step program was used with the following values of acceleration, rate, and time: a first step at 150 rpm s^{−1}, 2000 rpm, 30 s for distributing the monomer solution across the substrate, and a second step at 1500 rpm s^{−1}, 5000 rpm, 10 s for obtaining homogeneous films of 2 μm thickness. The spin-coater chamber was blown with Ar to maintain dry atmospheric conditions.

The spin-coated film was heated in an oven to 90 °C during 30 min in order to activate the polycondensation reaction and form the crosslinked PU network. Under these conditions, the PU film was not soluble in THF, water, or ethanol and it was slightly swellable in acetone.

2.3. Characterization of the Spin-Coated Films

The thickness of the film was measured by the scratch method using a 3D optical measurement system based on white-light



■ Figure 2. Polymerization and photodegradation reactions of the PU photoresists containing PMNB(OH)₂ and NP(OH)₂ as monomers.

confocal microscopy of the disk-scanning type (μ surf, NanoFocus AG, Oberhausen, Germany). The UV spectra of the PU films spin-coated on quartz substrates was measured using a Cary 4000 spectrometer (Varian Inc., Palo Alto, USA).

2.4. Photoinduced Depolymerization

The crosslinked PU film was irradiated at 365 nm (1.35 mW cm⁻²) using a LED (LTFR36/UV365 from Opto Engineering) or at 275 nm (1.65 mW cm⁻²) using a LUMOS 43 (Atlas Photonics Inc., Fribourg, Switzerland) irradiation source. Irradiation time was 15 min. For the masked irradiation, a quartz mask (2.5 × 2.5 cm²) with different gold patterned features (lines or dots from 10 to 200 μ m in size) was placed in contact with the film during exposure. The development step was done in THF/EtOH (1:1). Exposed areas were removed from the substrate.

For the two-photon experiments, a confocal microscope (Zeiss Axiovert 200M + LSM 510 + ConfoCor 2) equipped with a Titanium-Sapphire laser (780 nm–920 nm–max. 1 W, <100 fs) was used. A 780 nm laser was used to scan squares of 1 mm² area of the crosslinked PU film with 100% intensity (960 mW), a resolution of 2048 × 2048 (px per line) and a pixel time exposure of 51.7 μ s. Under these conditions, three scans were enough for completion of photocleavage.^[17] The micropattern was developed in THF/EtOH (1:1).

3. Results and Discussion

3.1. Selection of Photosensitive Monomers

Two diols (NP(OH)₂ and PMNB(OH)₂) containing two different intercalated PPGs were used in our studies (Figure 1b). NP(OH)₂ was commercially available and PMNB(OH)₂

was obtained in three synthesis steps as previously reported.^[17] NP(OH)₂ contains a nitrobenzyl unit and present a $\lambda_{\text{max}} = 264$ nm (Table 1). NP(OH)₂ shows a similar chromophore as the common 1-(2-nitrophenyl)ethyl (NPE) group and does only weakly absorb at wavelengths greater than 340 nm, thus limiting applications in the range of 320–400 nm. The photolytical mechanism of NP(OH)₂ derivatives is most probably analogous to that of NPE leading to the formation of a α -hydroxy-*o*-nitrosoacetophenone by-product.^[18]

The diol PMNB(OH)₂ contains the methoxynitrophenyl (PMNB) chromophore, a derivative of the *o*-nitrophenylethyl family^[19–25] using the donor–acceptor biphenyl core and a –OR substituent in the *p*-position. It presents a $\lambda_{\text{max}} = 317$ nm with an increased molar absorption coefficient together with a good photolysis quantum yield and an efficient yield of carboxylate release, leading to superior photophysical and photochemical properties than NPE under single-photon excitation in the range of 320–400 nm (Table 1 and Figure 3).^[22] More interestingly, this chromophore can be seen as methoxynitrobiphenyl platforms, which are known to be efficient in two-photon absorption, leading to an high improvement of the two-photon uncaging cross-section (Table 1). Therefore, this photoremovable group has been used for the release of carboxylate^[22] and phenol^[25] groups.

3.2. Formulation of Monomer Mixtures and Crosslinked PU Films

Monomer mixtures containing different ratios of NP(OH)₂ or PMNB(OH)₂ and di-/tri-isocyanates and a dialcohol were

■ Table 1. Photochemical properties of donor–acceptor biphenyl PMNB^[22] and NPE^[27] cages for carboxylate release.

Caging group	λ_{max} [nm]	ϵ [M ⁻¹ cm ⁻¹]	Photo-release carboxylate [%]	Φ_u	$\delta\Phi_u$ (GM) [λ]
PMNB	317	9900	90	0.09	3.2 (740 nm)
NPE	264	5100	100	0.14	<0.03 (740)

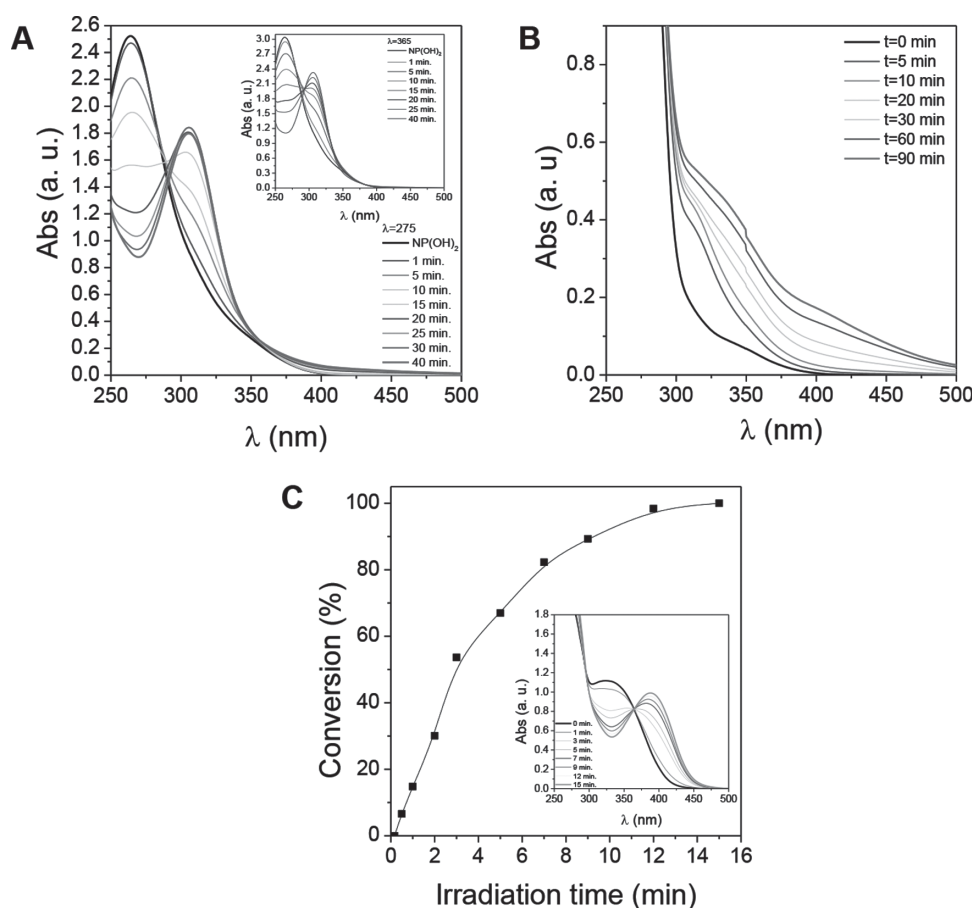


Figure 3. A) UV–Vis spectra of NP(OH)_2 in DMF solution (50×10^{-6} M) after irradiation at 275 nm for increasing times. The inset shows the UV–Vis spectra after irradiation at 365 nm. B) UV–Vis spectra of the NP(OH)_2 -based photodegradable PU before and after irradiation at 365 nm for increasing times. C) Photoconversion curve of the PMNB(OH)_2 -based photodegradable PU extracted from the UV data. The inset shows the UV–Vis spectra of the positive photoresist after irradiation at 365 nm for increasing time.

prepared (Figure 2). The mixtures were spin-coated onto glass substrates and heated in an oven to 90 °C during 30 min in order to activate the polycondensation reaction and form the crosslinked PU network. Different conditions were tested in order to obtain PU films with good film-forming properties and convenient crosslinking degree for avoiding swelling under conditions used for pattern development (THF/EtOH mixtures). The concentration of photocleavable monomer was also minimized. The best results were obtained with a mixture of 40 mol% IPDI, 38 mol% PPG, and 12 mol% of the photodegradable diol (NP(OH)_2 or PMNB(OH)_2) THF with 10 mol% triisocyanate DRE as crosslinker and 0.5 mol% of DBTDL initiator. Under these conditions, homogeneous films of ca. 2 μm thickness were obtained. PU films with lower concentrations of DRE swelled in THF/EtOH after polymerization (see Table SI1, Supporting Information). Monomer solutions with higher dilution did not render homogeneous films. The viscosity of the solution was too low and almost no material remained on the substrate during spin-coating. We speculate that a different formulation including monomers with

higher molecular weight would allow extension of our approach to thinner photoresist films. Photoresist layers with good planarity with thickness up to 500 μm were also obtained with the concentrated solutions of the same monomer mixture and slower spin-coating rates.

3.3. Spectroscopic Analysis of the Photodegradation Reaction in the PU Film

The UV spectrum of the chromophore NP(OH)_2 in solution is shown in Figure 3a. An absorbance maximum at $\lambda_{\text{max}} = 264$ nm is clearly observed. Upon light exposure at 275 or at 365 nm, a decrease in the absorbance at λ_{max} and the appearance of a new maximum around 305 nm was observed. The new band has been previously associated to the light-induced formation of the nitrosobenzaldehyde photoproduct.^[18,26] Similar changes were observed in the UV spectrum of a PU film containing NP(OH)_2 , as shown in Figure 3b. Upon exposure, a new shoulder appeared between 300 and 350 nm with increasing intensity as the exposure dose increased. These results suggest that

the monomer undergoes similar phototriggered changes in solution and in the polymerized state (although the leaving groups are different: H_2O vs carbamate).

PMNB(OH)₂ films showed similar changes (inset Figure 3c),^[17] though in this case λ_{max} shifted to 325 nm as a consequence of the phenyl substituent at 4' position of the nitrophenylethyl ring, and the vinylnitrophenyl photolytic byproduct appeared at 385 nm.^[22] The decrease in absorbance at 325 nm was used to calculate the degree of photoconversion for the different exposure times (Figure 3c). The photoconversion versus time curve allowed us to estimate the irradiation dose required for completing the photocleavage reaction, that is, at which no further changes were observed in the spectrum. Obviously, the dose for full photocleavage varied with the chromophore concentration in the mixture and the thickness of the film.

3.4. Surface Patterns Using Single- and Two-Photon Excitation

In order to demonstrate the possible application of the PU films as positive photoresists, site-selective irradiation experiments were performed in order to obtain surface patterns. Films were either irradiated through a mask (single-photon excitation) or selected areas were scanned with the laser (two-photon excitation). The photodegraded exposed areas are expected to dissolve, while the not exposed areas are expected to remain on the substrate.

After washing with a good solvent, a surface pattern was expected.

Preliminary experiments were performed with varying chromophore and DRE crosslinker was performed in order to optimize the monomer composition for efficient degradation/polymerization at the minimum exposure dose. Monomer mixtures containing 15% molar percentage DRE as trifunctional crosslinker and 12% PMNB(OH)₂ showed incipient patterns (Table SI1, Figure SI1, Supporting Information). The best results were obtained with a mixture of 40% IPDI, 10% DRE, 38% PPG, and 12% PMNB(OH)₂ after development in THF/EtOH (1:1). With this composition, micropatterns with lines and holes of 200 μm width and cones with 10 μm diameter at their base and 1 μm height were obtained from 2 μm thick resist films (Figure 4 and SI2, Supporting Information). Analogous patterns were obtained with the NP(OH)₂ photodegradable PU, though these patterns were rougher (Figure 4) and the photoresist film retained a residual layer of 1 μm on the exposed areas. Note that NP(OH)₂ absorbs weakly at 365 nm and photocleavage might significantly improve at shorter wavelengths. These results demonstrate the superior performance of the PMNB chromophore to mediate effective photolysis at 365 nm. Overall, these results demonstrate the capability of photocleavable diols to mediate photodegradation of a PU network and their possible application in the formulation of PU-based photoresist films.

The quality of the patterns was significantly improved by previous treatment of the supporting substrate with

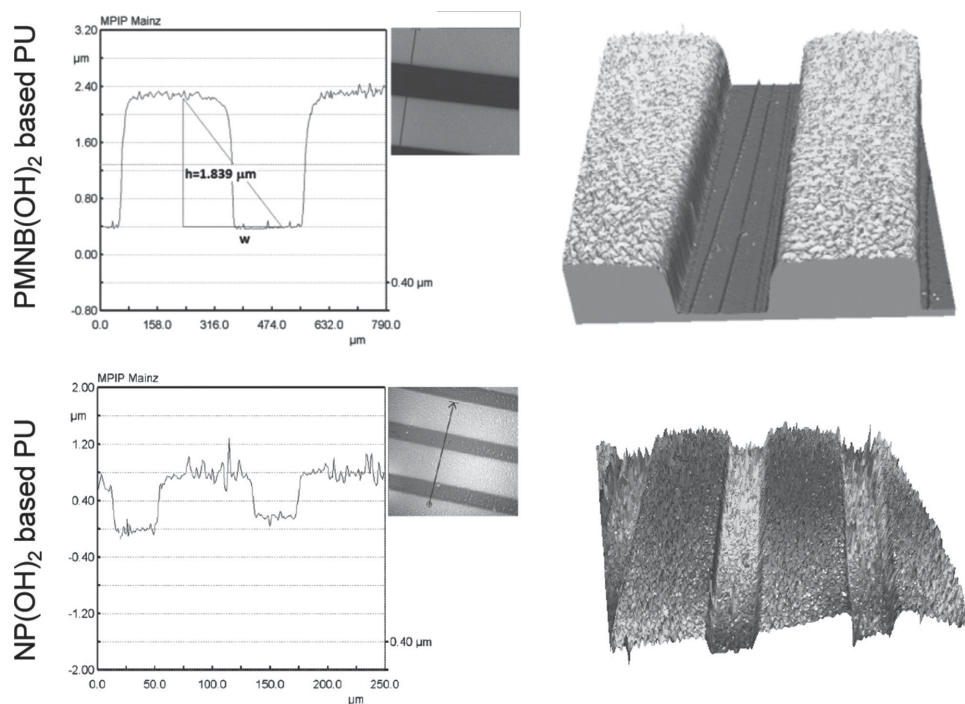


Figure 4. Confocal and microscopic pictures of micropatterns obtained with the PMNB(OH)₂ and NP(OH)₂ photodegradable polyurethanes after exposure at 365 nm. The initial film thickness was 2 μm in both cases.

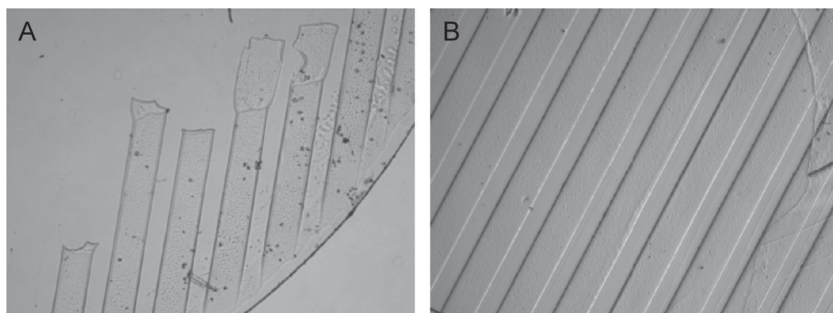


Figure 5. Microscope pictures of the PMNB-based PU photoresist after irradiation at 365 nm and washed with THF/EtOH. A) On glass substrate without modification. B) On glass substrate with APTS-modification.

APTS (Figure 5). The surface attached amine groups react with the isocyanate monomer and this improves the adhesion of the microfeatures to the silica substrate. However, it is important to note that a $< \text{nm}$ residual layer is expected to remain after development after full exposure as a consequence of the covalent coupling of the photoresist to the amino groups of the silane layer.

Patterning experiments were also performed on thicker photoresist films. Feature sizes of 2–3 μm were obtained independently of the photoresist thickness for the same exposure dose. Taking into account that the photoproduct

shows a significant absorbance, we do not envision application of this strategy for high aspect ratio lithography.

Pattern generation was also tested using two-photon excitation with the $\text{PMNB}(\text{OH})_2\text{PUs}$. For this purpose, a square of 1 mm^2 was scanned with a 780 nm laser in the spin-coated film. Development with EtOH revealed a 0.2 μm deep hole in the 2 μm film (Figure 6b), demonstrating successful site-selective two-photon depolymerization of the sample (Figure 6a and S13a, Supporting Information). Using

lower exposure doses (i.e., by changing the resolution of the laser scanning from 1024×1024 (Figure 6a and S13a, Supporting Information) to 512×512 (Figure 6c and S13b, Supporting Information), partial photodegradation of the crosslinked areas was obtained. As a consequence, a surface pattern of 0.3 μm pillars of swollen photoresist was generated (Figure 6d). A second scan over the first irradiated area allowed us to create pyramidal structures (Figure 6c,d). In summary, the photocleavable diol $\text{PMNB}(\text{OH})_2$ can mediate two-photon, site-selective degradation of a PU network and has potential interest as a key

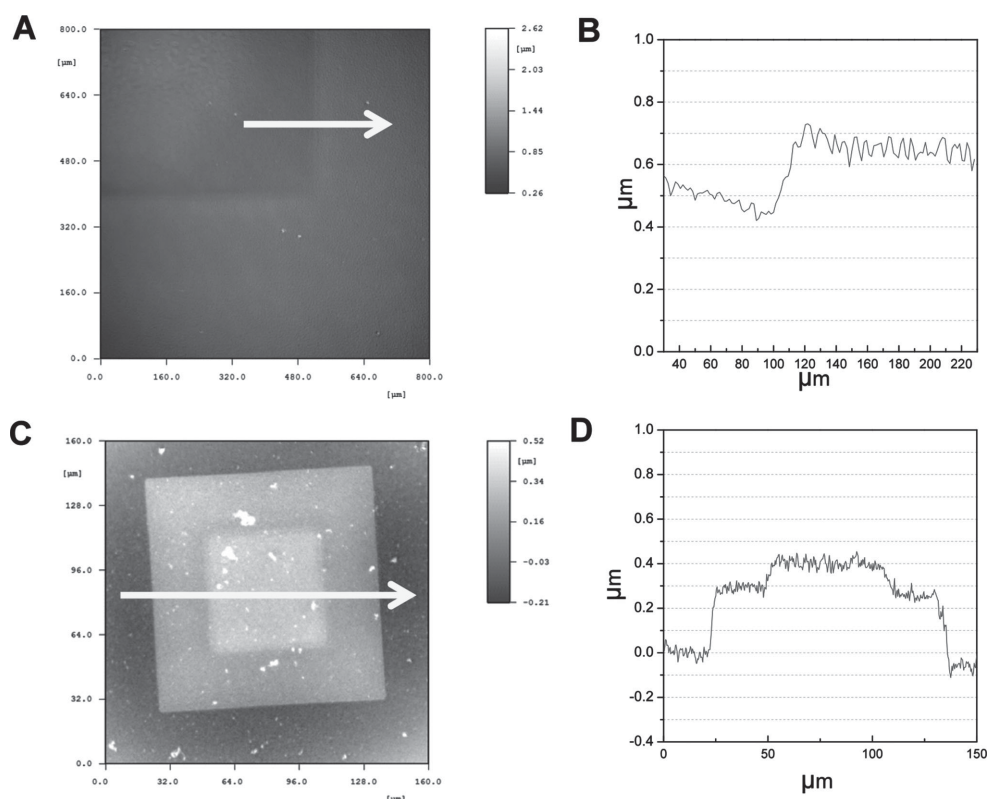


Figure 6. A,B) Photodegraded PU pattern after scanning with laser at 780 nm. The image (A) shows the edge of a $1 \times 1 \text{ mm}$ square after development and the profile (B) shows the deep of the pattern. C,D) Pyramidal structures made by a square of 100 μm with an inner square of 50 μm . C) Detail at high magnification of a pyramidal structure. D) Profile of the pyramidal structure.

component in positive photoresist materials for application in laser scanning lithography.

4. Conclusions

The photocleavable monomers NB(OH)_2 (commercially available) and PMNB(OH)_2 can be mixed with commercially available isocyanates to formulate simple and cheap PU-based positive photoresist materials. Surface micropatterns can be obtained by light exposure of the films at typical wavelengths available in optical lithography equipments. Additionally, PMNB(OH)_2 -based PU films can also be photodegraded using near IR lasers, opening the possibility of generating 3D structures with optimized photoresist compositions. These materials represent the first example of PU-based photoresists.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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- [1] A. del Campo, E. Arzt, *Chem. Rev.* **2008**, *108*, 3.
- [2] D. Randall, S. Lee, *The Polyurethanes Book*, Wiley, Chichester, NY, USA **2002**.
- [3] M. Ionescu, *Chemistry and Technology of Polyols for Polyurethanes*, Rapra Technology Shawbury, Shrewsbury, Shropshire, UK **2005**.
- [4] H. W. Engels, H. G. Pirkel, R. Albers, R. W. Albach, J. Krause, A. Hoffmann, H. Casselmann, J. Dormish, *Angew. Chem. Int. Ed.* **2013**, *52*, 36.
- [5] J. Cui, V. S. Miguel, A. Del Campo, *Macromol. Rapid Commun.* **2013**, *34*, 4.
- [6] H. Zhao, E. S. Sterner, E. B. Coughlin, P. Theato, *Macromolecules* **2012**, *45*, 4.
- [7] M. A. Azagarsamy, D. L. Alge, S. J. Radhakrishnan, M. W. Tibbitt, K. S. Anseth, *Biomacromolecules* **2012**, *13*, 8.
- [8] D. R. Griffin, J. L. Schlosser, S. F. Lam, T. H. Nguyen, H. D. Maynard, A. M. Kasko, *Biomacromolecules* **2013**, *14*, 4.
- [9] K. J. R. Lewis, K. S. Anseth, *MRS Bull.* **2013**, *38*, 3.
- [10] Z. Shafiq, J. Cui, L. Pastor-Pérez, V. San Miguel, R. A. Gropeanu, C. Serrano, A. Del Campo, *Angew. Chem. Int. Ed.* **2012**, *51*, 18.
- [11] A. Brunsen, J. Cui, M. Ceolín, A. D. Campo, G. J. A. A. Soler-Illia, O. Azzaroni, *Chem. Commun.* **2012**, *48*, 10.
- [12] J. Cui, T. H. Nguyen, M. Ceolín, R. Berger, O. Azzaroni, A. Del Campo, *Macromolecules* **2012**, *45*, 7.
- [13] J. Erath, J. Cui, J. Schmid, M. Kappl, A. D. Campo, A. Fery, *Langmuir* **2013**, *29*, 39.
- [14] C. De Gracia Lux, C. L. McFearin, S. Joshi-Barr, J. Sankaranarayanan, N. Fomina, A. Almutairi, *ACS Macro Lett.* **2012**, *1*, 7.
- [15] W. Lu, C. Tian, P. Thogaripally, J. Hu, P. Wang, *Chem. Commun.* **2013**, *49*, 83.
- [16] J. M. Schumers, O. Bertrand, C. A. Fustin, J. F. Gohy, *J. Polym. Sci., Part A* **2012**, *50*, 3.
- [17] L. García-Fernández, C. Herbivo, V. S. M. Arranz, D. Warther, L. Donato, A. Specht, A. del Campo, *Adv. Mater.* **2014**, *26*, 5012.
- [18] C. Lv, Z. Wang, P. Wang, X. Tang, *Langmuir* **2012**, *28*, 25.
- [19] S. Bühler, I. Lagoja, H. Giegrich, K. P. Stengele, W. Pfleiderer, *Helv. Chim. Acta* **2004**, *87*, 3.
- [20] L. Donato, A. Mourrot, C. M. Davenport, C. Herbivo, D. Warther, J. Léonard, F. Bolze, J.-F. Nicoud, R. H. Kramer, M. Goeldner, A. Specht, *Angew. Chem. Int. Ed.* **2012**, *51*, 8.
- [21] S. Gug, F. Bolze, A. Specht, C. Bourgogne, M. Goeldner, J.-F. Nicoud, *Angew. Chem. Int. Ed.* **2008**, *47*, 49.
- [22] S. Gug, S. Charon, A. Specht, K. Alarcon, D. Ogden, B. Zietz, J. Léonard, S. Haacke, F. Bolze, J.-F. Nicoud, M. Goeldner, *ChemBioChem* **2008**, *9*, 8.
- [23] C. Herbivo, Z. Omran, J. Revol, H. Javot, A. Specht, *ChemBioChem* **2013**, *14*, 17.
- [24] A. Specht, J. S. Thomann, K. Alarcon, W. Wittayanan, D. Ogden, T. Furuta, Y. Kurakawa, M. Goeldner, *ChemBioChem* **2006**, *7*, 11.
- [25] D. Warther, F. Bolze, J. Léonard, S. Gug, A. Specht, D. Puliti, X. H. Sun, P. Kessler, Y. Lutz, J. L. Vonesch, B. Winsor, J. F. Nicoud, M. Goeldner, *J. Am. Chem. Soc.* **2010**, *132*, 8.
- [26] F. Yan, L. Chen, Q. Tang, R. Wang, *Bioconj. Chem.* **2004**, *15*, 5.
- [27] T. Furuta, S. S. -H. Wang, J. L. Dantzker, T. M. Dore, W. J. Bybee, E. M. Callaway, W. Denk, R. Y. Tsien, *Proc. Natl. Acad. Sci.* **1999**, *96*, 4.