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Photoinduced Cross-linking of Dynamic Poly(disulfide) Films via Thiol Oxidative Coupling¹

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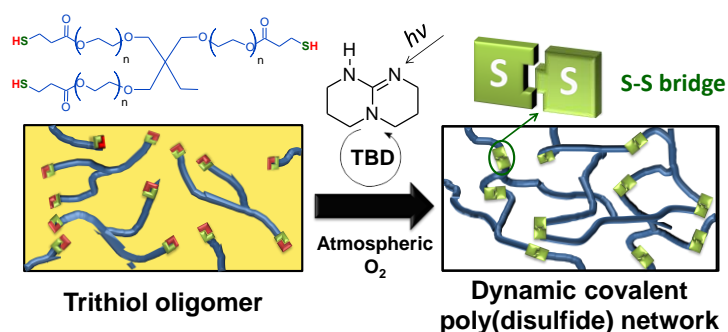
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Abstract

Initially developed as an elastomer with an excellent record of barrier and chemical resistance properties, poly(disulfide) has experienced a revival linked to the dynamic nature of the S-S covalent bond. We report a novel photobase-catalyzed oxidative polymerization of multifunctional thiols to poly(disulfide) network. Based solely on air oxidation, the single-

¹ **Supporting Information** is available online from the Wiley Online Library or from the author.

step process is triggered by the photodecarboxylation of a xanthone acetic acid liberating a strong bicyclic guanidine base. Starting with a 1- μm thick film based on trithiol poly(ethylene oxide) oligomer, the UV-mediated oxidation of thiols to disulfides occurs in a matter of minutes both selectively i.e. without over-oxidation, and quantitatively as assessed by a range of spectroscopic techniques. Thiolate formation and film thickness determine the reaction rates and yield. Spatial control of the photopolymerization serves to generate robust micropatterns, while the reductive cleavage of S-S bridges allows the recycling of 40 % of the initial thiol groups.



1. Introduction

Once considered a limitation, polymers consisting of repeated reversible covalent bonds — such as C=N bonds in imine or C-O bonds in alkoxyamine — are now highly praised for their adaptability and compositional diversity.^[1] Chemists progressively realized that such dynamic polymers able to reorganize structure and constitution on demand provides an avenue for smart stimulus-responsive materials with advanced properties such as reversible surface functionalization,^[2] recycling,^[3] self-repair,^[4, 5] or stress relaxation.^[6] One of the most intriguing and versatile examples of dynamic covalent bonds is the disulfide bond, which controls processes as important as protein folding and rubber vulcanization.^[7] The S-S bond reversibility is expressed through a number of pathways — thiol-disulfide exchange, reduction to thiol or metathesis — and using an extensive range of stimuli, e.g redox species, thiol nucleophiles,^[8] UV light.^[9] Of major importance is the reversible disulfide/thiol Red/Ox couple, which is ubiquitous in living organisms.^[10] Poly(disulfide)s are unique polymers because the dynamic character of the repeated S-S bridges does not prevent an excellent record of “static” properties, such as low vapor permeation, high resistance to solvents and environmental degradation.^[11] Accordingly, the major developments for sulfur-containing polymers have focused on high-performance industrial sealants,^[12] but also gene delivery^[13] through reductive depolymerization. Nevertheless, this unique combination of dynamic and static properties has not garnered so much attention, particularly when considering that the first products were released in the late 1920s.^[14]

To unlock the full potential of poly(disulfide)s, simple, eco-efficient and industrially scalable processing methods are needed. Three main synthetic routes to disulfide polymers are reported in the literature.^[11, 14] The first is the heat-induced ring-opening polymerization of cyclic (arylene disulfide) oligomers.^[15] The second brings together several polycondensations involving monomers with internal disulfide groups.^[16] The third is conceptually the most

simple because it relies on the base-catalyzed oxidation of multifunctional (≥ 2) thiol derivatives in presence of an oxidizing agent. In contrast to the first two methods, the disulfide bonds are generated in situ, and a broader range of affordable precursors is accessible.^[17-19] Industrially, the oxidative coupling of thiol-terminated oligomers is the reference process to cross-link poly(disulfide) rubbers, referred to as Thiokol® or Thioplast®.^[12] However, this methodology is plagued with several problems, including slow curing, 2-component formulation, toxic (metal) or harmful (organic peroxides) oxidative reagents. The linear polymerization of dithiol monomer solution is even more challenging with insolubility issues, formation of low-molecular-weight products and very long reaction times up to ten hours.^[20] Recently, Puskas et al. introduced a more sustainable and effective approach performed in water, thus demonstrating that there is scope for improved processing methods. Using triethylamine catalyst and a pair of oxidants (air and hydrogen peroxide), the oxidative polymerization of ethylene glycol dithiol resulted in a poly(disulfide) precipitate with $\bar{M}_n > 2.5 \times 10^5$ g/mol.^[21]

In this paper, we move forward in describing a fast and single-step light-mediated thiol oxidative polymerization to synthesize disulfide polymer as film. UV control enables the use of storable, ready-to-use, and cost-effective thiol formulations with no pot-life issue. In addition, a simplified and energy-saving photopolymerization procedure is implemented for the first time.

2. Results and Discussion

As depicted in Figure 1, our simple procedure starts with the application of a trifunctional poly(ethylene oxide) thiol oligomer (1300 g/mol, **1**) on a KBr or glass substrate to form a 1 μm -thick liquid film. This latter includes 4 wt. % of xanthone acetic acid quaternary salt of triazabicyclodecene (TBD) photobase generator (PBG) noted **PBG-A**, which is commercially available. Recently, Arimitsu et al. proved that this PBG was able to release a strong bicyclic

guanidine base via a photodecarboxylation reaction with high quantum yield.^[22] Herein, subsequent UV irradiation of the photolabile bicomponent **1/PBG-A** is performed in air and at ambient temperature with a filtered medium-pressure Hg-Xe lamp (290 mW/cm², $\lambda > 330$ nm) for 15 min, resulting in a dry film fully insoluble in conventional organic solvents. We present extensive characterization evidence, including Raman and real-time FTIR spectroscopies, XPS, NMR, TGA and DSC, which shows that a quantitative photobase-catalyzed air oxidation of thiol takes place, leading to the formation of a poly(disulfide) network film.

Proof for the formation of disulfide bonds is provided by analyzing the film with Raman spectroscopy at different irradiation times. As shown in Figure 2 (top), the spectrum of **1** (t = 0 min) shows significant differences compared to that of the resulting polymer **P1** (t = 15 min). The gradual decrease of the ν_{S-H} and ν_{C-SH} stretching mode features at 2570 cm⁻¹ and 672 cm⁻¹ respectively suggest a thiol consumption induced by UV exposure. After 15 min irradiation, these two characteristic SH signals completely vanish below the noise level. Concomitantly with their decay, we observe in the lower frequency range a large enhancement of the intensity ratio of the S-S stretching mode features at 643 cm⁻¹ (ν_{C-SS}) and 510 cm⁻¹ (ν_{S-S}). On the basis of these two significant and simultaneous changes (no other modifications is noticeable), it is likely that air oxidation of thiols to disulfide bridges occurs, both selectively i.e. without over-oxidation, and quantitatively (100 % conversion) despite the mobility restriction imposed by the network formation.

To our knowledge, the mild and chemoselective oxidative photopolymerization in air of polythiol is unprecedented. By contrast, the photodissociation in air of monothiol compounds has been previously investigated at shorter wavelength ($\lambda < 300$ nm), yielding a range of higher oxidation states species such as sulfonic acid, sulfone, thiosulfinate or thiosulfonate.^[23,24] By contrast, XPS surface analysis of the S_{2p} peaks (Fig. S1 of SI)

conclusively supports the minor role played by these highly oxidized sulfur species, arising at a distinctive higher binding energy than thiols or disulfides.^[25]

In addition, RT-FTIR spectroscopy was implemented to probe online the film compositional changes throughout the irradiation. The decreasing IR S-H stretching mode feature at 2555 cm^{-1} , shown in the inset plot of Figure 2 (bottom), gives essentially the same information as given by the Raman data, except that rapid scan acquisition provides in this case kinetic details. Thiol conversion–time plot in air (Figure 2, trace **a**) shows a fast and complete consumption with 90 % conversion accomplished after only 5 min irradiation. In contrast, no conversion was obtained without UV exposure (even after 4 h), demonstrating the photolateness of the reactive **1/PBG-A** mixture. Additionally, no reaction takes place upon removing the PBG (Figure 2, trace **b**), which emphasizes the crucial role of thiolates in triggering the oxidation process. To shed further light into the photo-oxidation mechanistic scheme, an experiment was conducted under nitrogen atmosphere (Figure 2, trace **c**). A strong inhibition is observed in this case, which argues for a prevalent role of atmospheric oxygen in the oxidation process. The air oxidation of thiols to disulfides is a well-established reaction (see Scheme S1 in SI), which has been harnessed to poly(sulfide) synthesis with mixed success.^[17] Our hypothesis is that the release of photobase causes the thiol groups to be converted to thiolate. The next step involves electron transfer with oxygen which results in the formation of thiyl radicals and subsequent dimerization to disulfides and step-growth polymerization, as documented by many studies. To complete this concise mechanistic description, two features seem critical for photopolymerization efficiency: (i.) film thickness, and (ii) photocatalyst basicity.

i. Upon increasing gradually the film thickness (1 – 10 μm), slower kinetics and limiting conversion are obtained (Fig. S2-3 of SI). A marked decrease in reactivity is noted above a threshold thickness of 4 μm , thus indicating an oxygen diffusion limitation effect. In addition,

at 10 μm , the final conversion is reduced to 90 % after 15 min irradiation whereas thinner samples reveal full thiol consumption. Although this result stresses a limitation, it positions this novel UV-curing process as a viable and complementary alternative to radical photopolymerization, in which oxygen inhibition makes the surface polymerization of submicrometer-thick films tricky.^[26]

ii. The release of base mediates the deprotonation of the trithiol **1** ($\text{pK}_a = 9.87$ in water at 25 C).^[27] The importance of basicity is evidenced by substituting TBD ($\text{pK}_a = 14.5$) for a less basic N-alkyl morpholine tertiary amine ($\text{pK}_a = 9.3$) photogenerated with a conventional α -aminoketone PBG noted **PBG-B** (see structure and photolysis mechanism in Scheme S2 of SI). Although quantum yields are different in both species and thus direct comparison difficult, the released tertiary amine led to only 40 % thiol conversion after 15 min irradiation (Figure 2, trace **d**).

To illustrate the industrial viability of this process, cross-linked films were also produced under a UV-conveyor equipped with a medium-pressure Hg arc lamp, which is the workhorse equipment for UV-curable coatings. Dry films were obtained after 10 passes (1.35 J/cm² per pass) corresponding to an exposure time of only 2.3 s. Raman analysis were consistent with previous results, yielding 95 % conversion of thiol to disulfides (Fig. S4 of SI). Despite the insolubility typical of highly cross-linked polymers, the transparent rubbery film yielded a gel after several days in CDCl₃. This allowed its characterization by High Resolution Magic Angle Spinning (HR-MAS) ¹H NMR technique. The spectra of **P1** and **1** are displayed in Figure 3. The feature at 1.67 ppm, straightforwardly attributed to thiol protons (H_a) of **1**, is almost no detectable in **P1**, thereby confirming the high conversion. In addition, the resonance assigned to methylene protons adjacent to the thiol group at 2.75 ppm (H_b) in **1** is significantly shifted to 2.92 ppm ($\text{H}_{b'}$) in the polymer product. These results provide clear evidences that disulfide bonds are created. Note that all these significant results were supported by ¹³C NMR

analysis (Fig. S5 of SI). In addition, TGA characterization (Fig. S6 of SI) indicated that the polymer **P1** was thermally stable up to 150 °C under nitrogen atmosphere. Finally, DSC analysis (Fig. S7 of SI) revealed an elastomeric behavior with a glass transition temperature of –45 °C fully consistent with the literature data of poly(disulfide).^[7]

One unique feature of UV-triggered catalyst is to allow spatially-controlled polymerization and surface modification, which are unattainable with a conventional latent catalyst. To demonstrate the photopatterning ability, the **1/PBG-A** film was irradiated using a commercial mask aligner equipped with a high-pressure Hg lamp (14 mW/cm²). After a UV exposure of 15 min, the solid **P1**-based film was washed several times with acetone to remove the unreacted or soluble parts. Figure 4 (top) shows two optical microscopy images of the developed film (right) and the original mask (left), indicative of the quality of the micro-scale photolithographic process. In addition, profilometry enabled to obtain a height profile of the pattern (Fig. S8 of SI). Thiol photooxidative polymerization thus represents another chemical amplification reaction for negative tone resist, because a single photon can initiate a cascade of chemical reactions.

A second application made possible thanks to S-S bond reversibility is the reductive cleavage of the poly(disulfide) network as a means to recycle the starting thiol oligomer. To this purpose, the powdered product **P1** was stirred in a CHCl₃ solution containing 8 equivalents of dithiothreitol and 0.75 eq of triethylamine. Dithiothreitol forms a very stable six-membered ring in its oxidized state, and is currently the most widely used reducing agent of disulfide-based proteins.^[8] A gradual solubilisation was noted, and a slightly turbid solution was obtained after 12 days under stirring (see images in Fig. S9 of SI). The reaction progress was assessed using ¹³C NMR. Figure 4 (down) gives the ¹³C NMR spectra of **1**, **P1** and **P1R** the polymer after reduction. The extent of reduction is reflected by the integral ratios of the carbon signal of the methylene group (C_b) adjacent to the thiol group at 19.7 ppm to that of a

reference resonance, such as the CH₂ (C_j) in alpha position of the methyl group at 22.9 ppm. The initial ratio of 2.2 found in precursor **1** is reduced to less than 0.1 (5 % of thiol group remaining) after photopolymerization (**P1**), then rises back to 0.8 (40 % of thiol group regenerated) at the end of the reduction process (**P1R**). These data demonstrate a partial regeneration of thiol group despite **P1** cross-linked structure. Additionally, control experiments carried out without reductant have confirmed the immunity of the disulfide groups (Fig. S10 of SI).

3. Conclusion

In conclusion, we present the first UV-mediated pathway to cross-linked poly(disulfide) films based on thiol air oxidation. Significant advantages compared to previous methods include fast and complete thiol conversion, formation of chemically resistant film, and a one-step process starting from a simple and photolabile “thiol-PBG” formulation. There is no apparent limitation on substrate, and extension to a range of thiol oligomers and monomers will be examined in the near future. Critical to process efficiency are the photogenerated TBD strong base and thin film conditions ($\leq 1\ \mu\text{m}$), promoting respectively thiolate formation and oxygen permeation.

We think that this novel oxidative photopolymerization might revive interest in this remarkable polymer, with application areas far beyond the normal domains of UV-curing. For example, reductive cleavage of S-S bonds opens the doors to recycling, which is generally unattainable with UV-cured thermoset coatings. Additionally, the interest of UV-patterning extends beyond the fabrication of novel photoresist and may serve for generating robust protein biochips based on a thiol/disulfide exchange protein immobilization strategy.

Supporting Information

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Keywords: polysulfides, photopolymerization, recycling, photoresists, crosslinking

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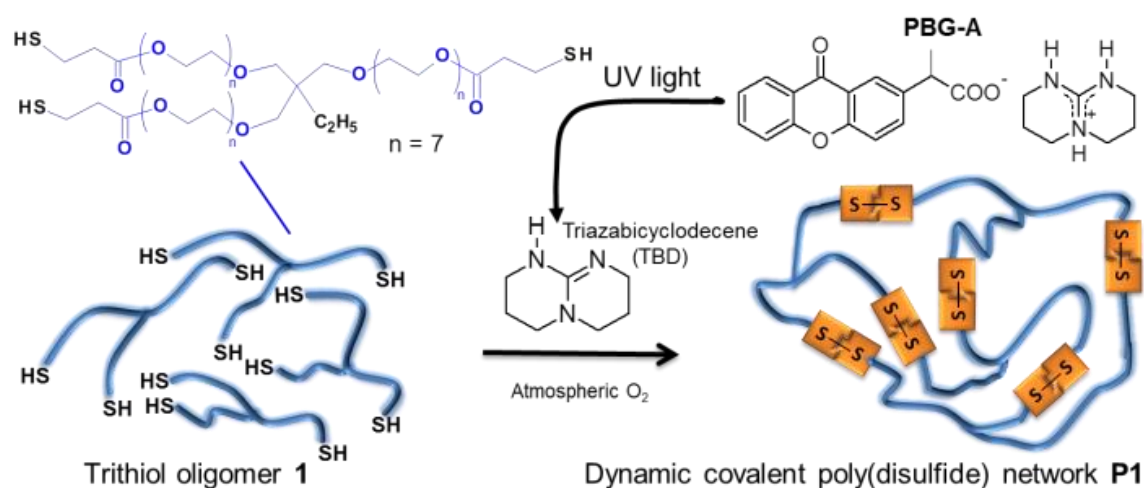


Figure 1. Photobase-catalyzed oxidative polymerization of trithiol oligomer 1.

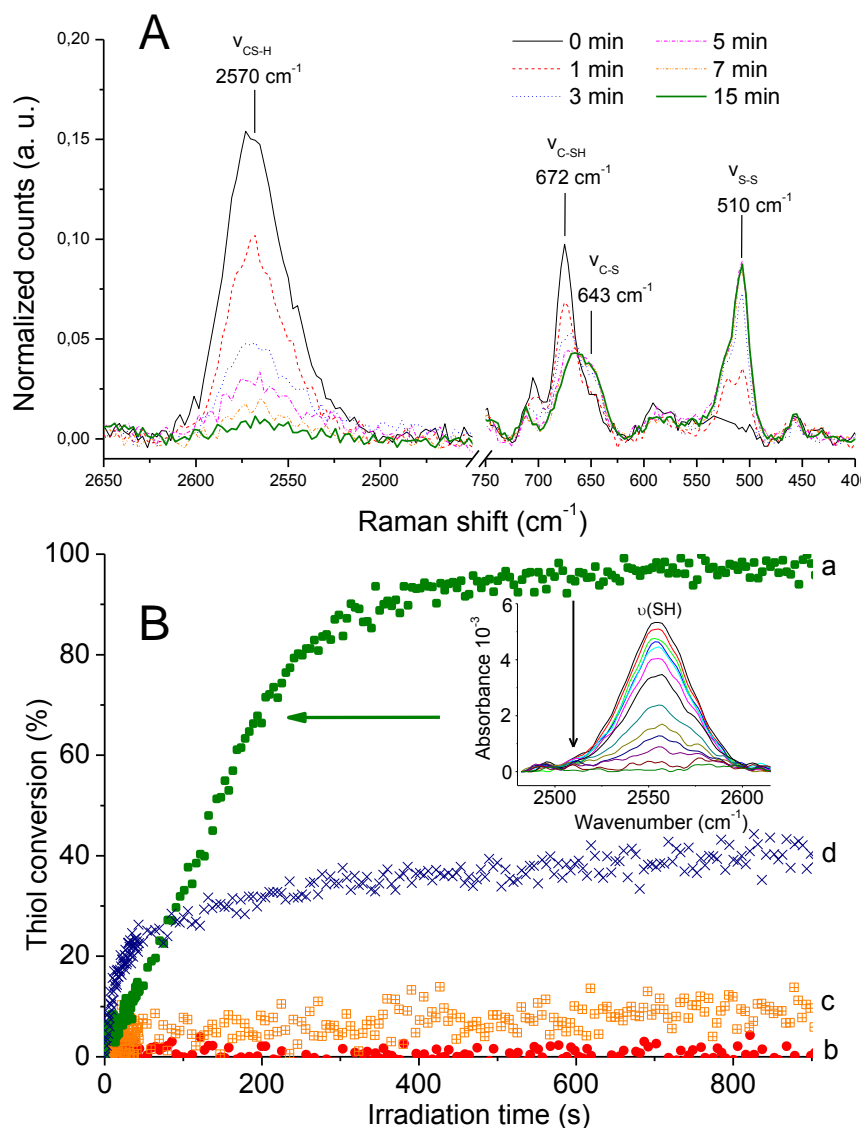


Figure 2. A (top) Raman spectra of **1/PBG-A** trithiol film after different UV exposure times: 0, 1, 3, 5, 7 and 15 min. **B (bottom)** Thiol conversion-time plot obtained from RT-FTIR data during photopolymerization of oligomer **1** under different conditions: **(a)** with **PBG-A** in air; **(b)** without **PBG-A** in air; **(c)** with **PBG-A** under nitrogen atmosphere; and **(d)** with **PBG-B** in air. The inset shows the temporal evolution of the IR S-H stretching mode feature at 2555 cm^{-1} in run **a**. Irradiation conditions: Hg-Xe lamp (330-500 nm), irradiance = 290 mW/cm^2 .

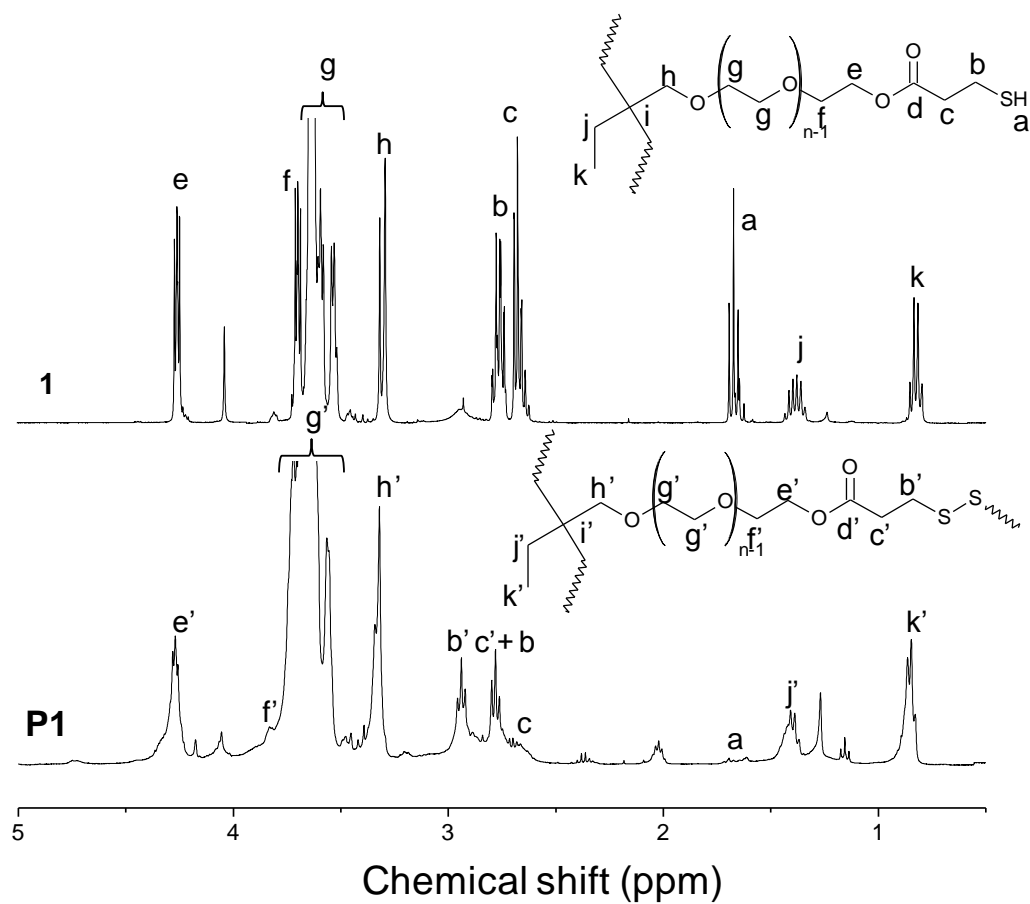
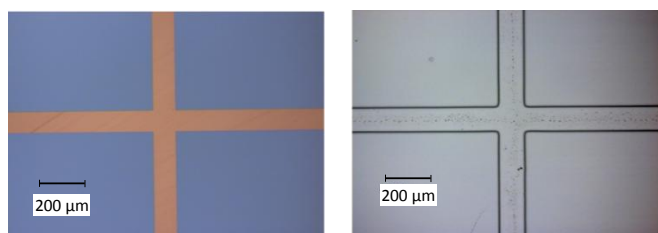


Figure 3. ^1H NMR spectrum of the starting trithiol oligomer **1** and HR-MAS ^1H spectrum of polymer **P1**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm^2 , UV exposure time = 2.3 s.

1. Photolithography



2. Reductive depolymerization

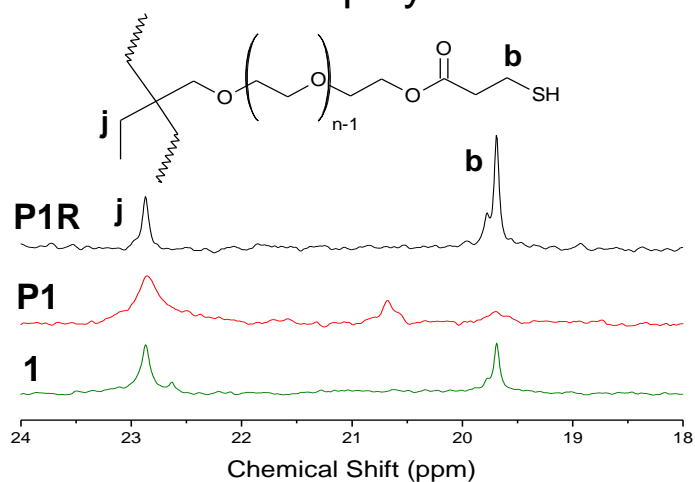


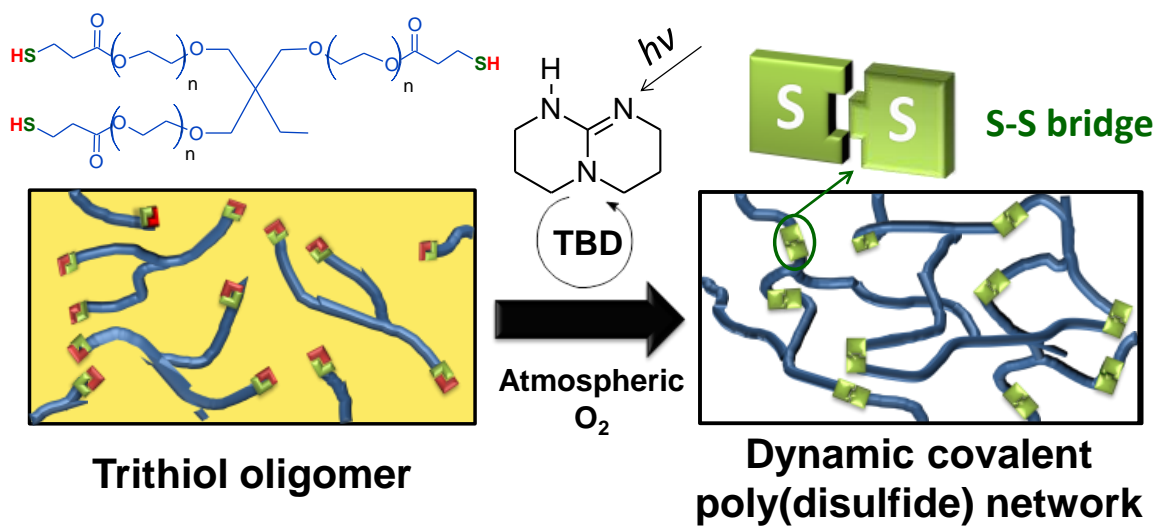
Figure 4. Top. Optical microscopy images of photolithography mask (left) and **P1** photopatterned film (right). **Bottom.** ¹³C NMR spectra of thiol oligomer **1**, poly(disulfide) **P1**, and the latter polymer after reduction **P1R**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm², UV exposure time = 2.3 s.

Table of contents entry

The first oxidative photopolymerization of polythiol film to poly(disulfide) network is described. The process is simple, efficient (100 % conversion in the matter of minutes), highly selective (no over-oxidation), and occurs under ambient conditions. The essential chemistry relies on photogenerated superbases promoting the formation of thiolate anion, which are then subjected to air oxidation.

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Supporting Information

for *Macromol. Rapid Commun.*, DOI: 10.1002/marc.2013#####

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General methods and materials

Materials

Ethoxylated trimethylolpropane tri(3-mercaptopropionate) (**1**, 1300 g/mol) was provided by Bruno Bock. 2-(9-Oxoxanthen-2-yl)propionic acid 1,5,7-triazabicyclo[4.4.0]dec-5-ene salt (**PBG-A**) and DL-dithiothreitol were purchased from TCI. Irgacure 907 (**PBG-B**) is a gift from BASF Specialty Chemicals. Triethylamine (> 99 %) and chloroform (> 99.5 %) were purchased from Sigma-Aldrich. All reagents were used as received without further purification.

Poly(disulfide) films via photobase-catalyzed air oxidation of thiol

The formulation was prepared by adding 20 mg of **PBG-A** to a chloroform solution ($V = 4$ mL) containing 0.48 g of oligomer **1**. The homogeneous and photolabile mixture was then deposited on a KBr or glass substrate using a spin-coater to achieve a 1 μm thick film assessed by profilometry measurements (3D surface profiler Bruker). Two UV irradiation devices were implemented for oxidation photopolymerization yielding poly(disulfide) **P1**. First, UV irradiation in air was performed at ambient temperature during 900 s using a medium-pressure Hg-Xe arc lamp (Hamamatsu L8251, 200 W) coupled with a flexible light-guide. The emitted light was filtered ($\lambda > 330$ nm) to prevent self-dissociation of thiol functions, and directed perpendicular to the specimen film placed 3 cm away. A total irradiance of 290 mW/cm^2 was

measured at the surface of the film sample by conventional radiometric techniques. The irradiation device was also equipped with an elliptical reflector (365 nm) that efficiently reflects the UV light, and lets heat rays pass through, preventing any significant increase of temperature. Using this cold reflector cutting off heat, the local temperature during the process may be increased of ca. 3 °C. For experiments performed under nitrogen, the sample was performed in a controlled-environment chamber where temperature and atmosphere were finely adjusted. Light entry into the chamber was enabled by a KBr window transparent to UV light. This focalized UV lamp was used to conduct in situ RT-FTIR experiments. Alternatively, UV exposure was carried out at by ten successive passes under a UV conveyor (Qurtech) equipped with an H-bulb lamp (Fusion). The belt speed of the conveyor was set to 10 m/min. Under these conditions, the emitted light dose for each pass is 1.35 J/cm² (UVA [320-390 nm]: 0.46 J/cm², UVB [280-320 nm]: 0.31 J/cm², UVC [250-260 nm]: 0.08 J/cm² and UVV [395-445 nm]: 0.50 J/cm²) and corresponds to an exposure time of 0.23 s.

Photopatterning of poly(disulfide) film

A similar **1/PBG-A**/CHCl₃ formulation was deposited on glass substrate with a spin-coater to achieve an effective thickness of 1 μm. The substrate was then placed at 40 μm of a cross-patterned mask in a SUSS MicroTech mask aligner and irradiated for 15 min under a HBO Osram UV lamp (14 mW/cm²). After irradiation, the substrate was dipped into an acetone bath for 5 s to remove the unpolymerized parts.

Reduction of poly(disulfide) P1 in presence of DTT

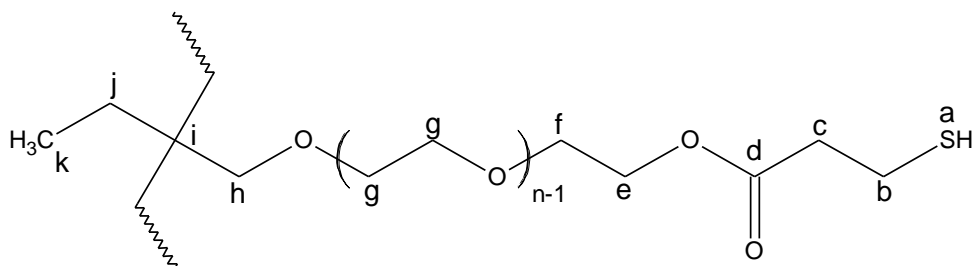
0.1 g of polymer **P1** (0.12 mmol of disulfide bonds) was added as powder to 50 mL of chloroform under vigorous stirring. Subsequently, 0.15 g of dithiothreitol (0.96 mmol) and 9 mg of Et₃N (0.09 mmol) were added to the latter insoluble mixture. After 12 days of reaction, the

solid aggregates disappeared, and a turbid solution was formed. The resultant organic solution was washed with 50 mL of saturated NaCl aqueous solution to extract the water-soluble oxidized and reduced DTT species. The organic phase was evaporated and the sticky resin was analyzed by NMR.

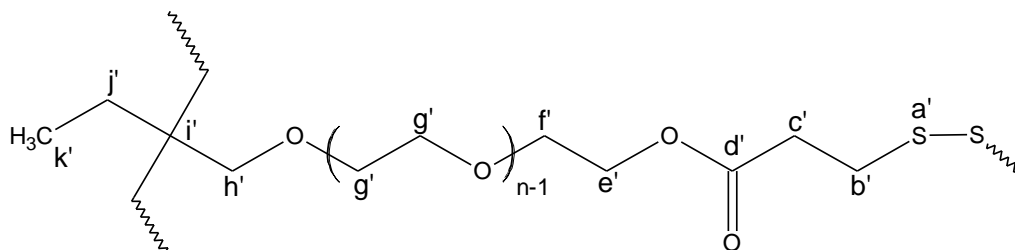
Characterization

Raman spectra were collected using an In via Raman reflex microscope from Renishaw. The excitation wavelength was provided by a He-Ne laser from Renishaw emitting 17 mW/cm^2 at 633 nm. The objective used was N PLAN 50x Leica with a numerical aperture of 0.75. A 600 l/mm grating optimized for visible light was used to disperse the light on a CCD NIR deep depletion Peltier cooled detector camera. A 30 s exposure and 10 spectra accumulation were needed to obtain a reasonable signal-to-noise ratio. The conversion rate of thiol functions was determined by integration of the Raman SH stretching band at 2570 cm^{-1} before and after irradiation. **X-ray photoelectron spectrometry (XPS)** analysis was carried out using a Gammatdata Scienta SES 2002 X-ray photoelectron spectrometer under ultra-high vacuum ($P < 10^{-9} \text{ mbar}$). The monochromated Al $K\alpha$ source was operated at a current of 30 mA and 14 kV, with a 90° nominal take-off angle (angle between the sample surface and photoemission direction). During acquisition, the pass energy was set to 200 eV for high-resolution spectra. Classical Scofield sensitivity factors were used for peak fitting procedures with CASAXPS software: S2p 1.68. All line shapes used in peak fitting procedures were a mix of 30% Gaussian and 70% Lorentzian shapes. **Real-time Fourier transform infrared (RT-FTIR)** spectra were obtained with a Bruker Vertex 70 spectrophotometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector working in the rapid scan mode. The resolution of the spectra was 4 cm^{-1} with an average of 4 scans/s. The conversion rate of thiol functions over time was determined by integration of the SH stretching band at 2555 cm^{-1} . **Thermal**

gravimetric analysis (TGA) was carried out with a TGA Q500 (TA Instruments) under nitrogen atmosphere (20 mL/min). 9 mg of poly(disulfide) film was placed in an open aluminum pan and heated from ambient conditions to 900 °C at 10 °C/min⁻¹. **Differential scanning calorimetry** (DSC) was carried out on a TA Q2000 DSC using a heat-cool-heat thermal cycle. 5 mg of poly(disulfide) film was placed in an hermetic aluminum pan. The first cycle started by heating the sample from –90 to 100 °C at 10 °C/min. The second cycle cooled the sample back to –90 °C. The third step heated the sample again from –90 to 100 °C at 10 °C/min. **¹H NMR** (400 MHz) and **¹³C NMR** (100 MHz) spectra were recorded at room temperature on a Bruker Advance 400 spectrometer equipped with 5 mm Z-gradient QNP (¹H, ¹³C) probe for routine spectroscopy or 4 mm (¹H, ¹³C) Z-gradient HR-MAS probe for supramolecular gel. The chemical shifts were referenced to the residual proton signal of the solvents CHCl₃ at 7.26 ppm for ¹H and 77.03 ppm for ¹³C.

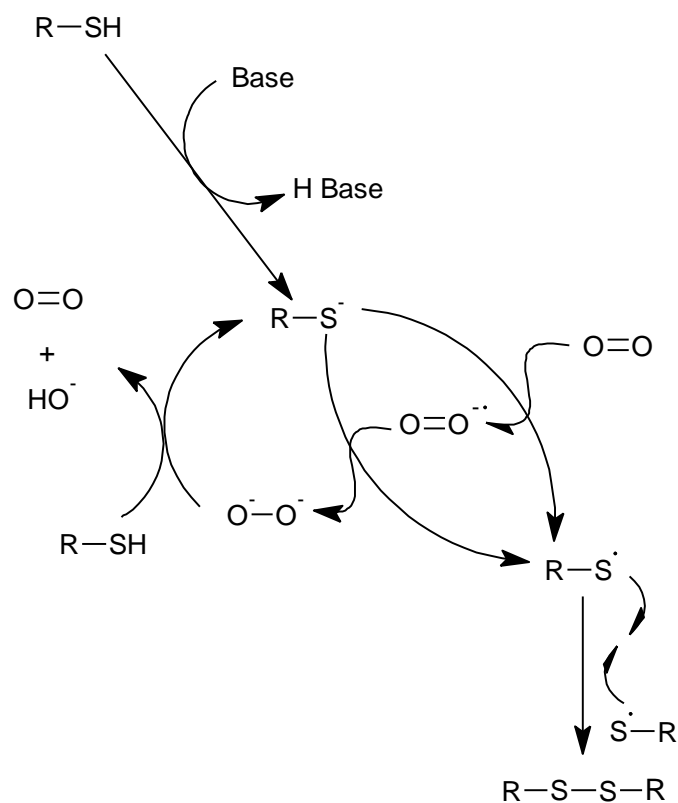


Oligomer 1. ¹H NMR (400 MHz, CDCl₃), δ 4.25ppm (m, 2H, H_e), 3.69ppm (m, 2H, H_f), 3.66-3.5ppm (m, (n-1)×2H, H_g), 3.32 and 3.29ppm (s, 2H, H_h), 2.75 ppm (m, 2H, H_b), 2.67ppm (m, 2H, H_c), 1.67ppm (t, J=8.3Hz, 1H, H_a), 1.38ppm (m, 2H, H_j), 0.82ppm (m, 3H, H_k). ¹³C NMR (100 MHz, CDCl₃), δ 171.5ppm (C_d), 71.5ppm (C_h), 70.6ppm (C_g), 69.0ppm (C_f), 63.7ppm (C_e), 43.2ppm (C_i), 38.4ppm (C_c), 22.9ppm (C_j), 19.7ppm (C_b), 7.6ppm (C_k).

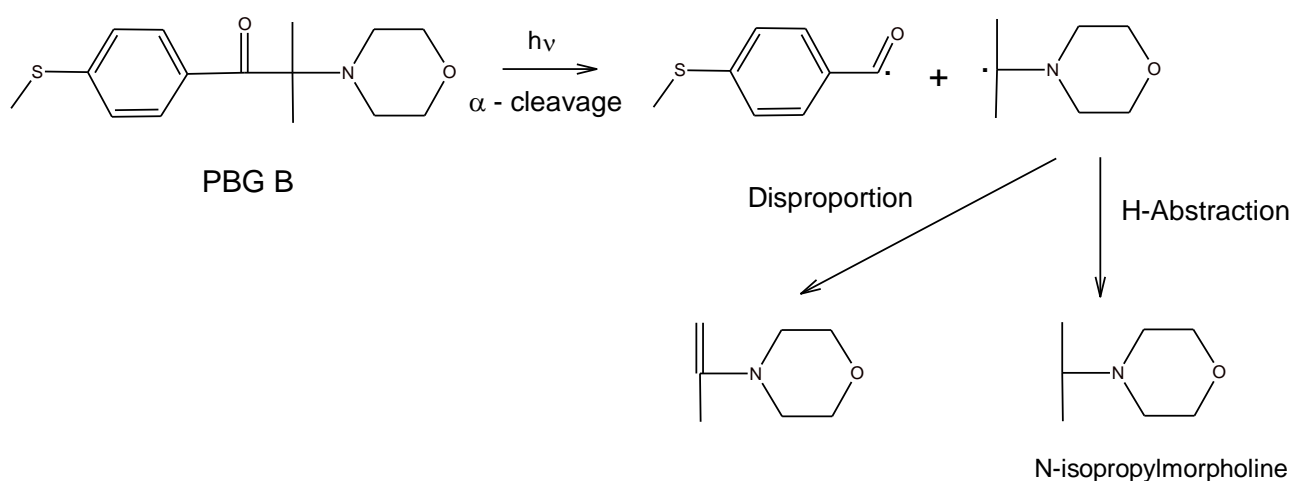


Poly(disulfide) P1. ¹H NMR (400 MHz, CDCl₃), δ 4.25ppm (m, 2H, H_{e'}), 3.7ppm (m, 2H, H_{f'}), 3.66-3.5ppm (m, (n-1)×2H, H_{g'}), 3.33 - 3.22ppm (m, 2H, H_{h'}), 2.92ppm (m, 2H, H_{b'}), 2.76ppm (m, 2H, H_{c'}), 1.39ppm (m, 2H, H_{j'}), 0.83ppm (m, 3H, H_{k'}). ¹³C NMR (100 MHz,

CDCl₃), δ 171.6ppm (C_d'), 71.5ppm (C_h'), 70.6ppm (C_g'), 69.1ppm (C_f'), 63.9ppm (C_e'), 43.3ppm (C_i'), 34.0ppm (C_b'), 33.0ppm (C_c'), 22.9ppm (C_j'), 7.7ppm (C_k').



Scheme S1. Mechanism of base-catalyzed thiol oxidation with oxygen as an oxidative reactant



Scheme S2. Mechanism of photoinduced generation of N-isopropylmorpholine photobase from PBG-B

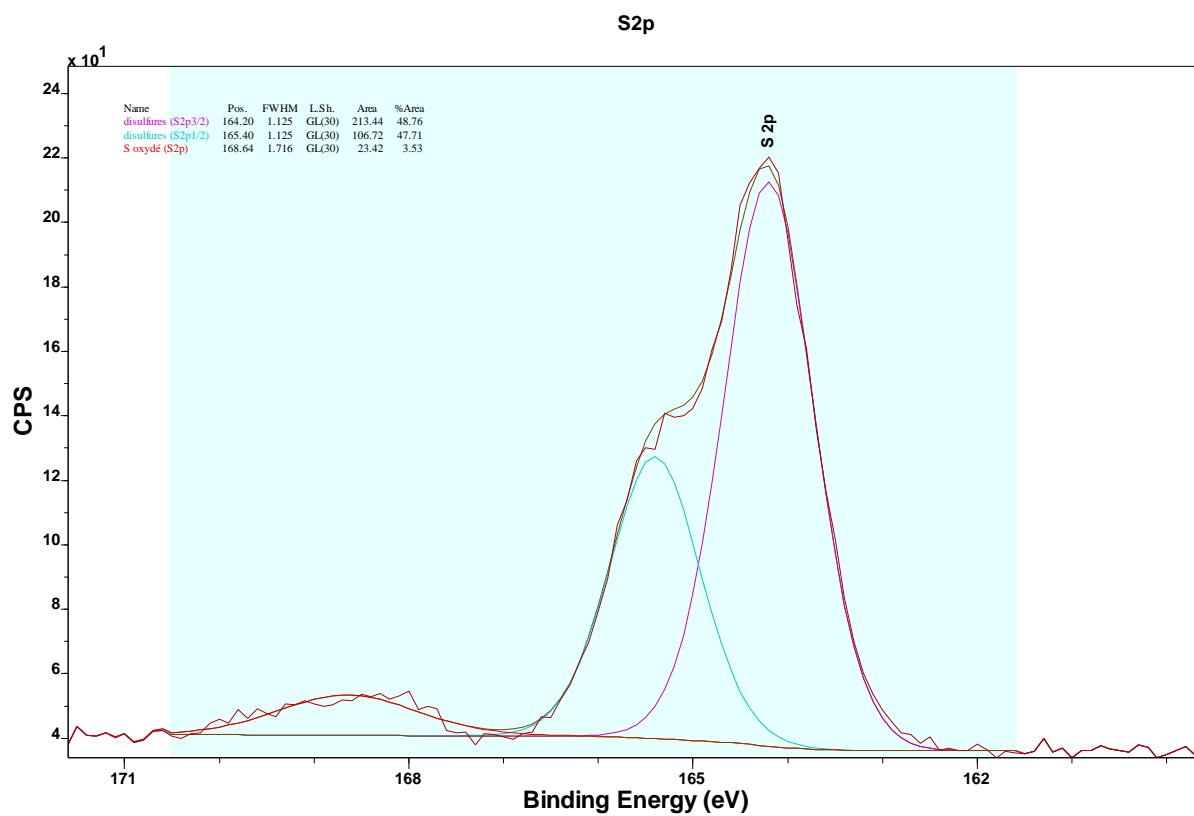


Figure S1. S_{2p} spectra of polymer **P1**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13. 5 J/cm², UV exposure time = 2.3 s.

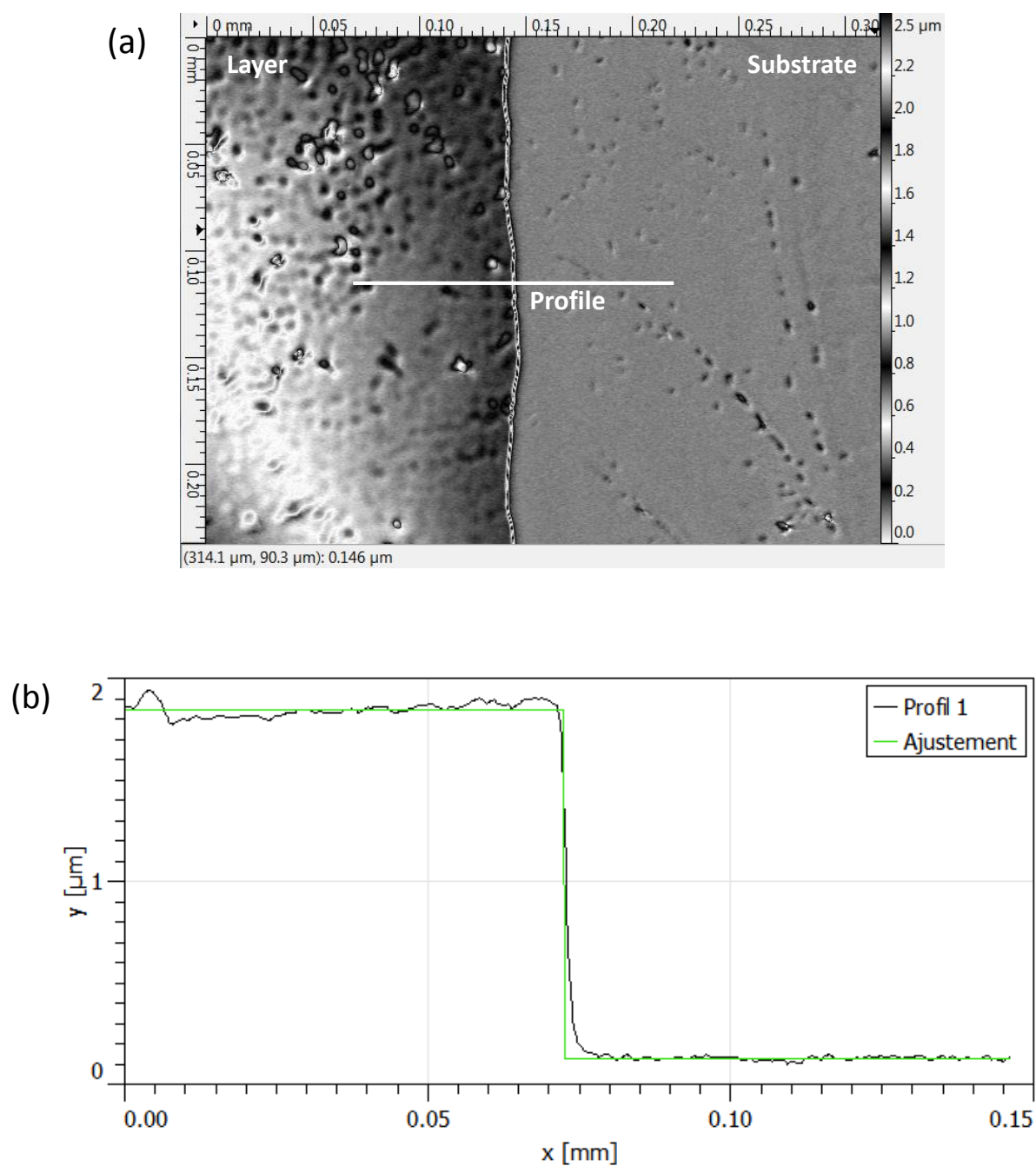


Figure S2. Thickness measurement of the trithiol film **1** before UV exposure using 3D optical profilometry. (a) Initial scanned surface; (b) fit to access the thickness value.

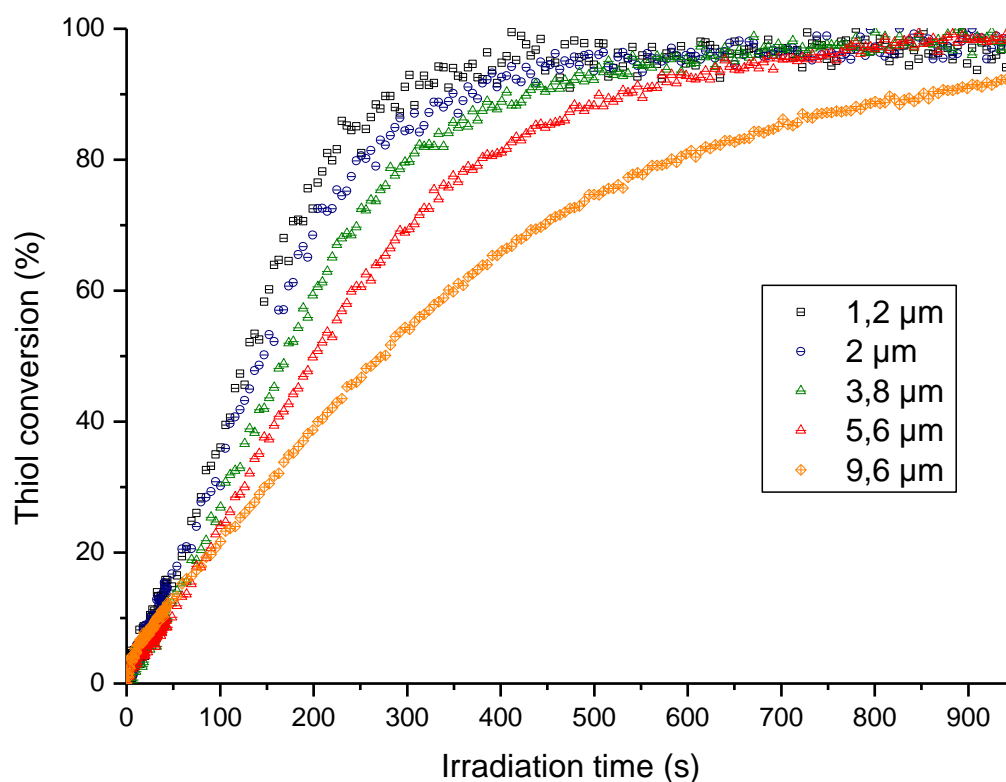


Figure S3. Effect of **1/PBG-A** film thickness on thiol oxidation kinetics (RT-FTIR data). Irradiation conditions: Hg-Xe lamp (330-500 nm), irradiance = 290 mW/cm².

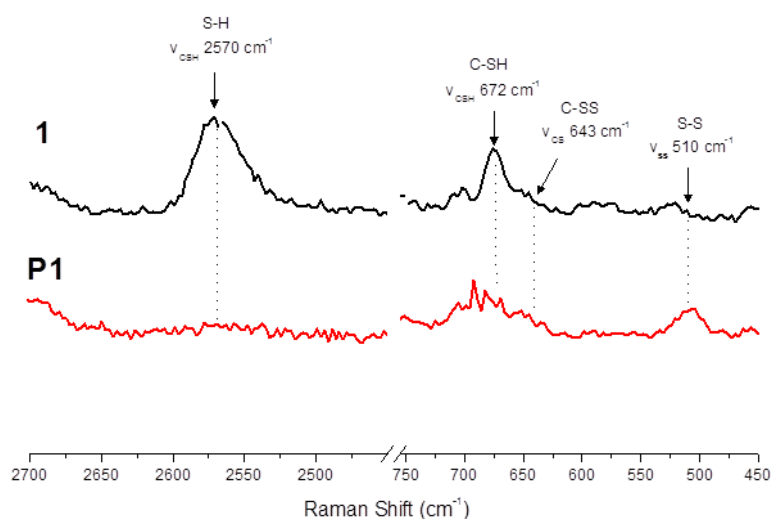


Figure S4. Raman spectra of thiol oligomer **1** and disulfide polymer **P1**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm², UV exposure time = 2.3 s

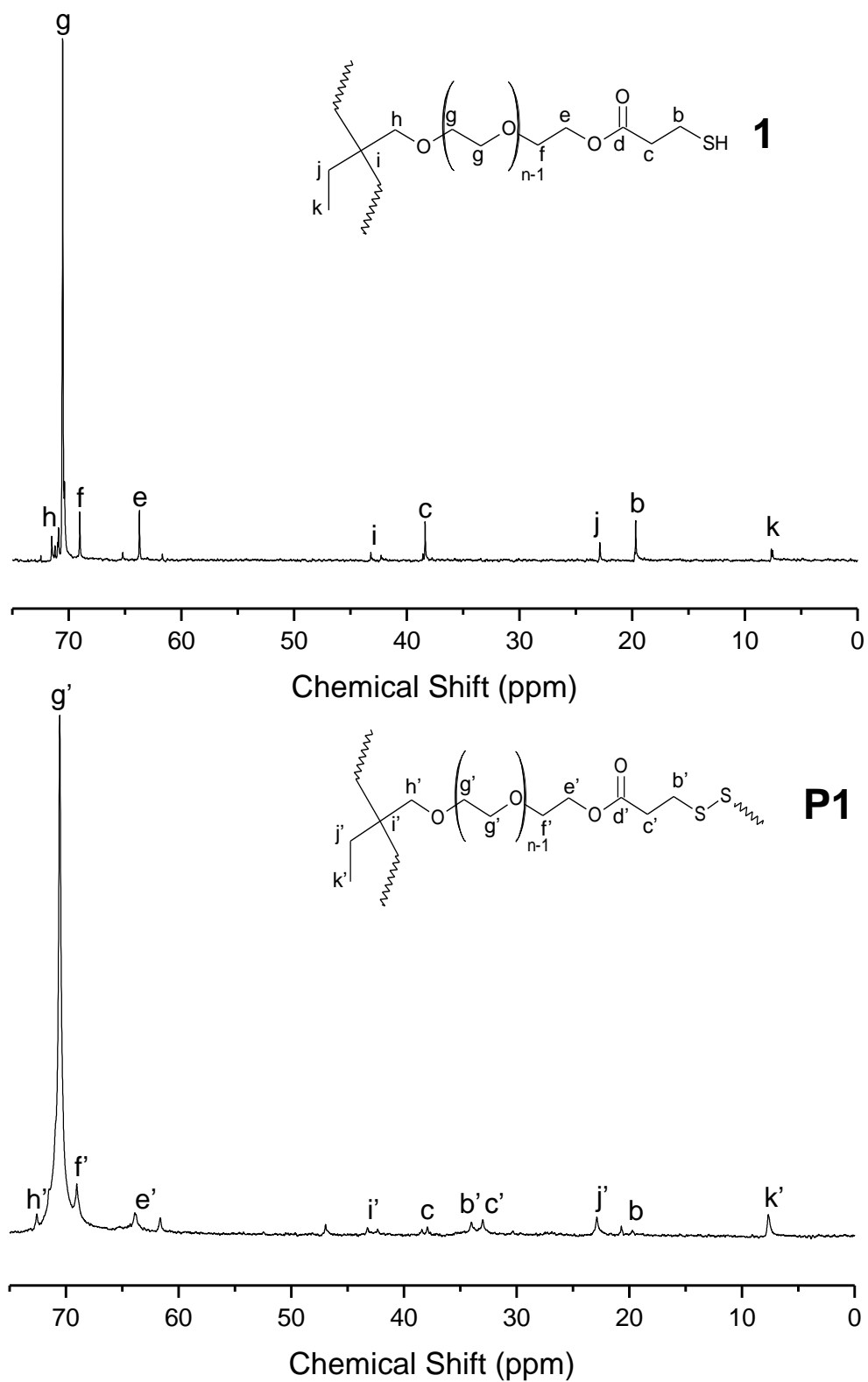


Figure S5. ^{13}C NMR spectra of oligomer **1** and polymer **P1**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm^2 , UV exposure time = 2.3 s

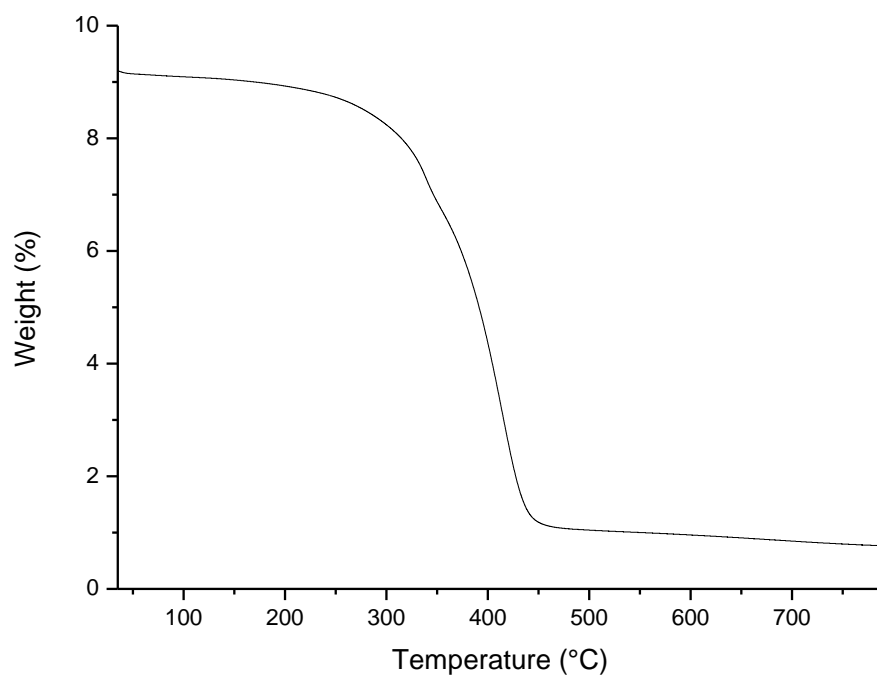


Figure S6. TGA thermogram of **P1**. Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm², UV exposure time = 2.3 s

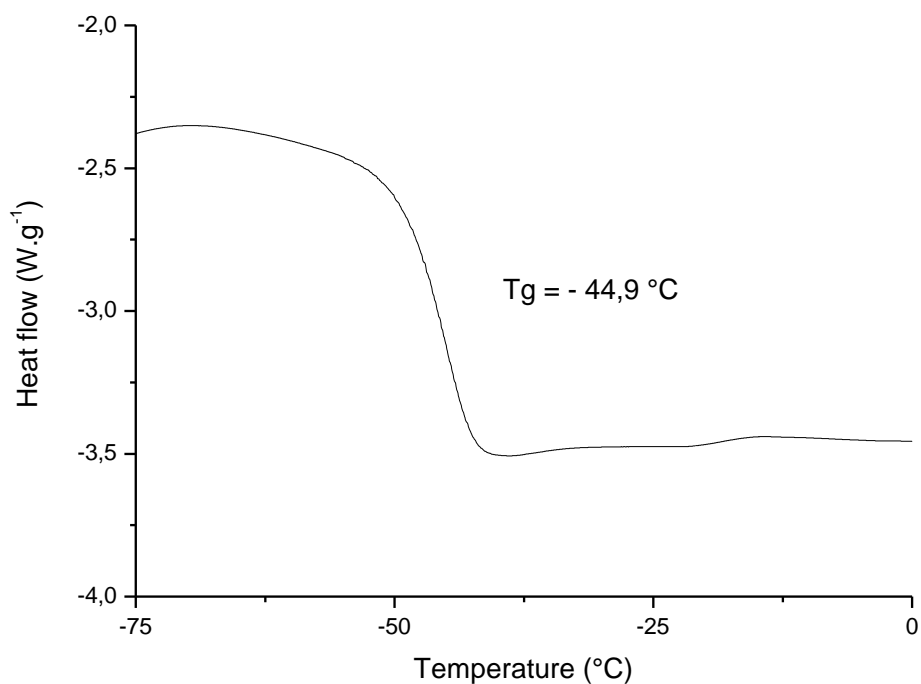


Figure S7. DSC thermogram of **P1** (Heating ramp of 10 °C/min). Irradiation conditions: 10 passes under UV conveyor, total light dose = 13.5 J/cm², UV exposure time = 2.3 s.

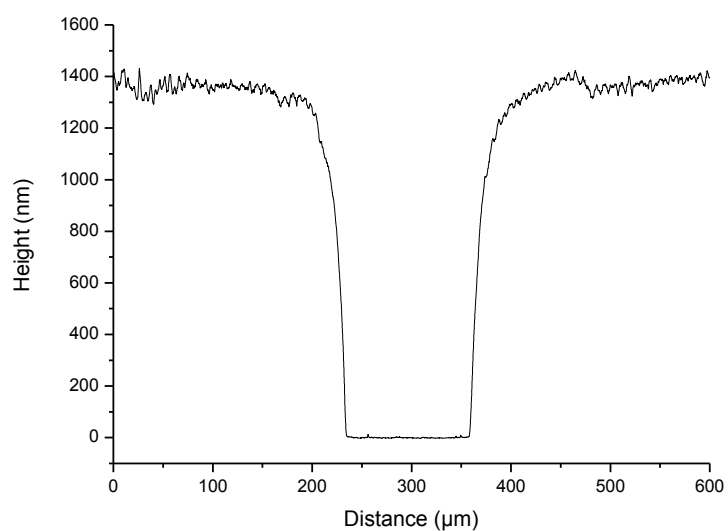


Figure S8. Height profile of photopatterned **P1** film. The measurements were performed with a profilometer (Dektak 150, Bruker).

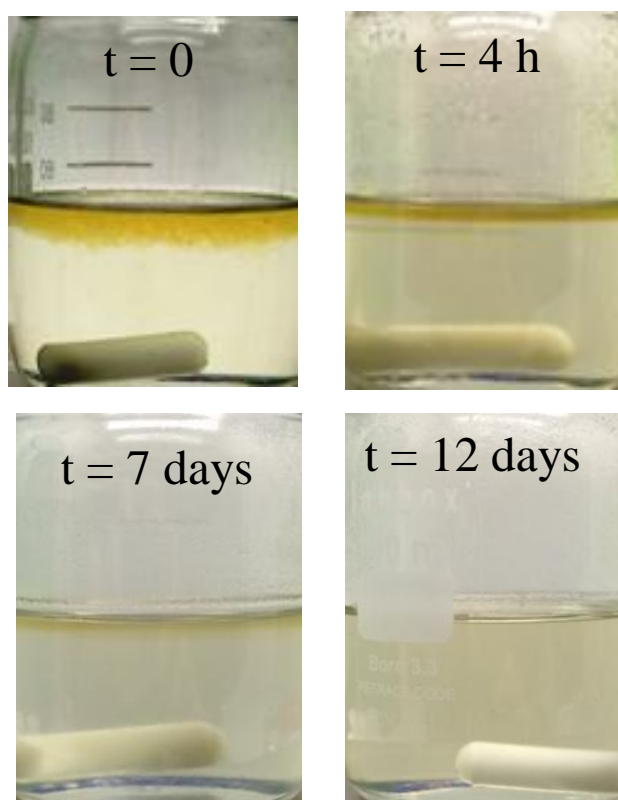


Figure S9. Pictures showing the reductive depolymerization of polymer **P1**. Reduction conditions: P1 with 8 eq of DTT and 0.75 eq of EtN₃ under stirring.

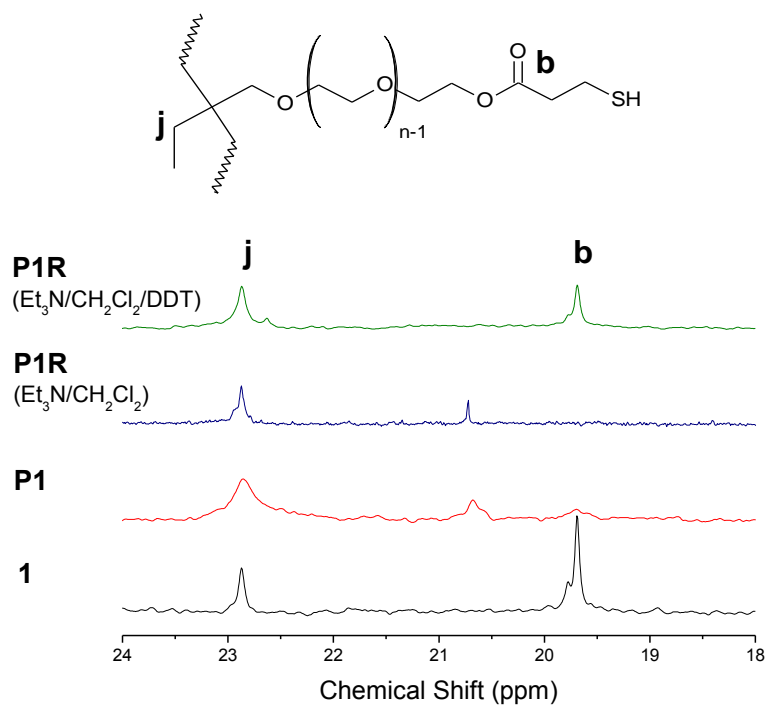


Figure S10. ^{13}C NMR spectra of thiol oligomer **1**, poly(disulfide) **P1**, and the latter polymer after reduction **P1R** with or without dithiothreitol (DTT).