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## Urethane polythioether self-crosslinking resins

Benjamin Hendriks, Otto van den Berg, Filip E. Du Prez\*

Polymer Chemistry Research group, Centre of Macromolecular Chemistry (CMaC), Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Krijgslaan, 281, S4-bis, B-9000, Ghent, Belgium



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### ABSTRACT

A straightforward methodology for the synthesis of polythioether resins and resulting coatings was elaborated. The resins were produced *via* radical stepwise polyaddition of functional bisalkene and bithiol monomers to yield self-crosslinkable polythioethers, which can be formulated as one-component systems. The thermal curing of these self-crosslinking resins is enabled by the presence of both hydroxyl and blocked isocyanate moieties, thereby resulting in the formation of a urethane polythioether network. Furthermore, the presence of the thioether functions offered the opportunity to alter thermal and mechanical properties by oxidation into sulfide or sulfone linkages, resulting in polysulfoxide and -sulfone containing coatings. Thiol-ene chemistry in combination with blocked isocyanate chemistry provides a new platform for functional urethane- and sulfide-containing coatings, which can be tailored to a wide variety of applications.

### 1. Introduction

The radical addition of a thiol to a carbon-carbon double bond was described for the first time by Posner in 1905 [1]. However, this chemistry has not attracted much attention, despite some efforts to revive its use in academic and industrial sectors since the 70's [2–8]. Only recently, thiol-ene chemistry regained interest in polymer synthesis as a result of its tolerance to many different reaction conditions and solvents, the defined reaction products, the facile synthetic protocols and the commercial availability of the precursors. Now, thiol-ene chemistry is recognized as an efficient approach for the formation of linear and crosslinked polymer systems, detailed in several recent reviews [9–13]. For example, thiol-ene has been exploited for the synthesis of biobased or partly biobased polymers [14,15], for the synthesis of complex structures, such as dendrimers [16], hyperbranched polymers [17] sequence defined polymers [18,19] or for the development of photo-responsive networks [20,21]. The photoinduced addition of thiols across unsaturated C=C double bonds follows a free radical mechanism, where in the first step thiyl radicals are generated by hydrogen abstraction from a thiol monomer. Addition of this thiyl radical to a carbon double bond yields an adduct containing a carbon-centered radical, which can subsequently abstract another proton (chain transfer) to form the final addition product or terminate *via* radical-radical coupling. Radical thiol-ene reactions combine the advantages of uniform polymer network formation, rapid cross-linking, delayed gelation, reduced shrinkage and insensitivity to oxygen,

compared to network formation by traditional free-radical systems such as acrylates. The advantages of thiol-ene have led to an actively growing interest for this chemistry in the field of coatings in the last 15 years [22]. However, thiol-ene coatings have received less attention in the industrial sector due to some drawbacks.

One limitation that often arises from the presence of flexible thioether linkages in materials obtained *via* thiol-ene or thiol-Michael chemistry is their low glass transition temperature ( $T_g$ ), resulting in rubbery materials at room temperature. This prevents thiol-ene networks to be used in applications where mechanically and thermally robust networks are required. In optical applications, for example, a high surface hardness and high scratch resistance, while maintaining optical transparency and high refractive index (RI), are needed [23,24]. Some approaches have been undertaken to overcome those limitations, such as low hardness and toughness. Podgórski et al. [25] recently developed high modulus networks based on a mixture of thiol-ene and thiol-Michael formulations, but these still comprise drawbacks such as low functional group conversions and crosslinking-induced shrinkage as a result of the presence of acrylate monomers. Another approach to improve the properties of thiol-ene polymer networks is to incorporate sulfone monomers, which have shown to increase the  $T_g$  [26]. However, the incorporation of sulfone monomers *via* thiol-ene chemistry is limited to few compounds and its effect on material properties is always evaluated in networks containing both thioethers and sulfones. To circumvent this limitation, Podgórski and coworkers investigated the oxidation of thioether networks using various oxidation conditions to

\* Corresponding author.

E-mail address: [filip.duprez@ugent.be](mailto:filip.duprez@ugent.be) (F.E. Du Prez).

yield polysulfone-based materials with enhanced mechanical properties, which they compared to non-oxidized networks [27]. However, in every case, the lack of control in oxidation resulted in complete oxidation to sulfones and long reaction times. In addition, because of overoxidation, the effect of sulfoxides and partial oxidation could not be investigated.

Polyurethane coatings, on the other hand, are already used in many industrial applications including transportation, wood flooring, plastics and coil coatings. Their excellent properties such as high gloss, good chemical resistance and physical properties are the result of strong hydrogen bonds. Polyurethane coatings are created by the reaction between a polyol and a di- or polyisocyanate. Owing to the high reactivity of isocyanates towards water, alcohols or amines, these compounds need to be formulated separately or should be blocked to yield a bench-stable compound. A blocked isocyanate is an isocyanate that has been protected by reaction with a blocking agent, typically an active hydrogen compound [28]. Upon heating, the isocyanate is liberated and it can subsequently react with a nucleophile such as an alcohol or an amine to form a thermally more stable urethane or urea bond; respectively [29]. The relative stability of the blocked isocyanates towards moisture and other nucleophiles decreases the toxicity, whilst increasing the shelf life of the isocyanate reagent. Hence, the development of blocked isocyanates has cleared the way for more environmentally friendly and safer polyurethane synthesis and these compounds are widely adopted in industry, as evidenced by the number of patents and publications highlighting their use [28,30–35].

Herein we report the synthesis and extensive characterization of thiol-ene based self-crosslinking resins, which can be formulated as one-component systems. These resins are subsequently cured to create urethane-based polythioether coatings, which combine the advantages of both urethane and thioether moieties. First, a systematic screening of different functional thiol-ene monomers with varying cross-link densities was conducted. Then, the resulting coatings were evaluated by thermal and mechanical analyses and by standardized tests for adhesion, flexibility, pencil hardness, refractive index and chemical resistance. Finally, the resins and resulting coatings were modified by controlled oxidation through chemical incorporation of additives to further expand the scope of possible applications.

## 2. Materials and methods

### 2.1. Materials

Butyl acetate (99.5%), chloroform (99.8%), 2,2-dimethoxy-2-phenylacetophenone (99%, DMPA), *N,N*-dimethylacetamide (DMA, 99%), 1-dodecanol (99%), ethyl acetate (99.7%) and propylene glycol monomethyl ether acetate (PGMEA, 99.5%) were purchased from Sigma-Aldrich. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 35 wt% in  $\text{H}_2\text{O}$ ) and sodium hydroxide (97%) were purchased from Acros Organics. Acetic acid (99.8%, Fiers), 2-butanone (99.5%, Fluka Analytical), hydrochloric acid (36%, Chem Lab), and all previously mentioned substances were used as received without further purification. The synthesis of all monomers (*i.e.* compounds  $\text{A}_{1-3}$ , B and C, see Fig. 1) can be found in the supporting information.

### 2.2. Methods

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 or a Bruker Avance II 500 spectrometer at room temperature. Fourier Transform infrared spectroscopy (FT-IR) spectra were collected using a Perkin-Elmer Spectrum1000 FTIR infrared spectrometer with a diamond ATR probe. Online FT-IR measurements were performed on a ReactIR 4000 instrument from Mettler Toledo with the use of a silicon probe (SiComp, optical range  $4400\text{--}650\text{ cm}^{-1}$ ). Resins were produced using an UV LED setup containing  $3 \times 3\text{ W}$  LEDs with a wavelength range of  $370\text{--}380\text{ nm}$ . The UV light is focused using

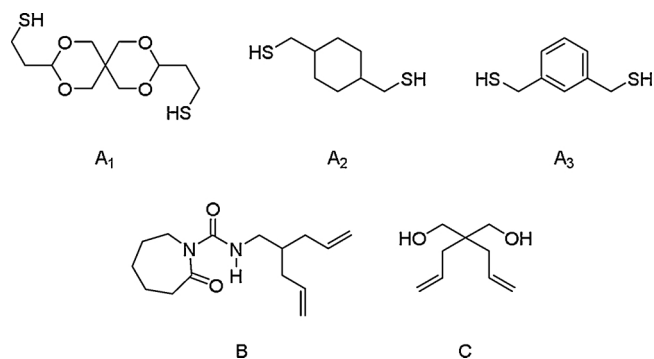


Fig. 1. Monomers prepared for the formation of polythioether self-crosslinking polymer resins.

$15^\circ$  lenses. Homogenous coating formulations with additives and solvents were obtained using a Speedmixer DAC 150.1 FVZ at 1500 rpm. Gelation time was determined on an Anton-Paar Physica MCR 302 rheometer in shear geometry with a plate diameter of 25 mm applying a shear strain of 0.5% with a frequency of 1 Hz. The gelation time was taken as the crossover of loss ( $G''$ ) and storage moduli ( $G'$ ). Thermogravimetric analyses (TGA) were performed with a Mettler Toledo TGA/SDTA851e instrument under air or nitrogen atmosphere at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$  from  $25^\circ\text{C}$  to  $800^\circ\text{C}$ . Differential scanning calorimetry (DSC) analyses were performed with a Mettler Toledo instrument 1/700 under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . The tensile test was run at a speed of  $10\text{ mm}\cdot\text{min}^{-1}$ . Polymer films were tested at room temperature and 40% relative humidity according to the following methods: ASTM D3363-00 Standard Test Methods for Measuring for Film Hardness by Pencil Test, ASTM D5402 Standard Practice for assessing the solvent resistance of organic coatings using solvent rubs, ASTM D3359 Standard Test Methods for measuring adhesion by tape test with an adhesion scale 0B (poor adhesion) to 5B (complete adhesion). Bend tests were performed manually by bending the steel panels using a bench vise according to ASTM D4145. Refractive indices and Abbe number were determined on a digital Abbe refractometer AR2008 from Krüss with a built-in light source of 589 nm. The refractometer was calibrated in full compliance with ASTM D1218 requirements. Transparency and Haze D65/10 of polymer films on microscope glass slides were measured by UltraScan VIS Hunterlab.

### 2.3. Synthesis of polythioethers as self-crosslinking resins

A glass vial was loaded with a solution of xylene dithiol  $\text{A}_3$  (4 g, 23.5 mmol), *N*-(2-Allylpent-4-en-1-yl)-2-oxoazepane-1-carboxamide **B** (3.11 g, 11.75 mmol) and 2,2-diallylpropane-1,3-diol **C** (1.84 g, 11.75 mmol) in 0.9 mL butyl acetate (10 wt%). To this solution 1 mol% of DMPA (60.2 mg, 0.235 mmol) was added, and the resulting mixture was subsequently flushed with argon for 5 min. Finally, the solution was irradiated with UV ( $370\text{--}380\text{ nm}$ ) for 45 min.

### 2.4. Oxidation to polysulfoxide and polysulfone

The self-crosslinking resin (2 g, 4.68 mmol) was dissolved in chloroform (19 mL) and next  $\text{H}_2\text{O}_2$  (2.3 mL, 23.4 mmol) and acetic acid (1.33 mL, 23.4 mol) were added. The resulting biphasic system was stirred vigorously for 2 h. Overoxidation to polysulfone was achieved by additionally heating this mixture for 2 h at  $65^\circ\text{C}$ .

In the case of polysulfoxide, the aqueous and organic layer were separated. Next, chloroform was evaporated until  $\sim 2\text{ mL}$ . The polymer was precipitated three times in 20 mL cold methanol. After filtration, the polymer was dried overnight under reduced pressure at  $40^\circ\text{C}$ .

For the polysulfone resin, the organic layer was evaporated *in vacuo*.

Next, the polymer was dissolved in DMA and precipitated three times in cold acetone. After filtration, the polymer was dried overnight under reduced pressure at 40 °C.

### 2.5. Preparation of formulations with self-crosslinking resins

Either the resin was synthesized in presence of a suitable solvent or the resin was formulated with a solvent and additives after UV-polymerization. Therefore, the resin was dissolved in solvent (10 wt%) and possible additives were added. For the chemical modification to an UV-active coating, 0.1 wt% of a fluorescent dye was added to the resin. The resulting mixture was placed in a plastic cup and mixed using the speed mixer at 1500 rpm until a homogenous solution/dispersion was obtained.

### 2.6. Coating application and thermal curing

Stainless steel Q-panels were manually cleaned before application. Cleaning of the panels involved degreasing with soap, washing with tap water and butanone and polishing with paper cloth. The coating solutions were then applied onto the substrate with an Erichsen Quadruple Film Applicator Model 360 200  $\mu\text{m}$ . Subsequently, the coated substrates were cured in a convection oven for 45 min at 170 °C. In addition to coatings on steel substrates, free films were also prepared to check free film properties such as gel content, glass transition temperature, degradation temperature and tensile strength. These free films were obtained by applying the resin in a coated aluminum pan followed by a 90-minute cure at 170 °C.

## 3. Results and discussion

### 3.1. Synthesis of a self-crosslinking polymer resin using thiol-ene chemistry

First, suitable thiol-ene reaction partners, aiming for high  $T_g$  coatings, were prepared (Fig. 1). For this, three different cyclic dithiols ( $A_1$ ,  $A_2$ ,  $A_3$ ) were synthesized (Supporting Information, section 2.1). In parallel, two dienes (**B** and **C**), which contain the necessary functional groups needed for the cross-linking reaction, were produced. The caprolactam blocked isocyanate-containing diene (**B**) was synthesized in 4 steps from ethyl cyanoacetate with caprolactam as a blocking agent (Supporting Information, section 2.2), while the complementary hydroxyl diene (**C**) was obtained via a two-step procedure from dimethyl malonate (Supporting Information, section 2.3). To evaluate the effect of crosslink density, the molar ratio of hydroxyl group: blocked isocyanate (OH:BI) was varied from 1:1 to 2:1. A decrease in the ratio of OH:BI is expected to produce polymers with increased rigidity due to higher crosslink density.

After the synthesis of bithiol and bisalkene monomers, self-crosslinking resins were prepared using photoinduced radical thiol-ene polymerization. All monomers and the photoinitiator DMPA were dissolved in 10 wt% of butyl acetate (green solvent). Next, the polymerization was initiated by UV-irradiation using UV LED with a wavelength range between 370 nm and 380 nm. The conditions for the UV-polymerization were optimized by varying the content of the photoinitiator and UV-intensity. Furthermore, online FT-IR was used to estimate the required polymerization time and calculate thiol-ene conversion. The change in peak area of the R-SH absorbance occurring at  $\sim 2570\text{ cm}^{-1}$  and alkene functional group located at  $3076\text{ cm}^{-1}$  was normalized against the individual spectra with respect to the characteristic band of the ester carbonyl group of butyl acetate centered at  $\sim 1730\text{ cm}^{-1}$  (Fig. 2). Thiol-ene conversions were calculated using the ratio of the current peak area to the original peak area prior to the reactions. With resin production in mind, a trade-off was made between enhanced reaction rate and increased initiator-induced yellow discoloration of the resulting mixture. It was found that 1 mol% of DMPA resulted in fast thiol-ene polymerization with 95% conversion in 45 min

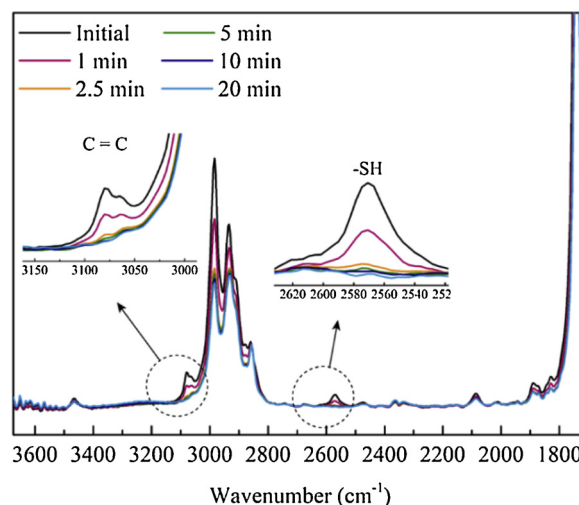


Fig. 2. Changes observed in the online FT-IR spectra over selected times for the photoreaction of a stoichiometric thiol-ene mixture.

without noticeable coating discoloration.

### 3.2. Coating formulation

The preparation of homogenous thin films without visible defects required systematic optimization of the solvent mixture used for film application. Indeed, solvents play an important role in solvent-borne coatings by affecting the formulation viscosity, the rate of drying and film leveling. Inappropriate solvent choice can lead to poor wetting of the formulation on the substrate and on additives, and can lead to film defects, such as pinholes, bubbles and craters.

Poor film properties were observed for resins formulated without solvent. Applying the resin uniformly at room temperature was difficult due to the resulting high viscosity (250–300 Pa s at 25 °C). In addition, the viscosity dropped significantly upon heating (20 Pa.s at 75 °C), which lead to separated covered areas on the substrate as a result of the resin's high surface tension. Good results were obtained when using butyl acetate or propylene glycol methyl ether acetate as solvent. Both solvents evaporate slowly and appear to provide suitable wetting of the resins on the stainless-steel substrate (Fig. S1, Supporting Information).

### 3.3. Thermal cure of self-crosslinking resins

The deblocking reaction of the caprolactam blocked isocyanate at different temperatures was followed using  $^1\text{H-NMR}$  to get more information regarding the deblocking rate as well as to establish the curing conditions for the synthesized coating resins. For the evaluation of the deblocking kinetics, the caprolactam blocked isocyanate was mixed with a high boiling point alcohol (*i.e.* 1-dodecanol) in bulk and heated for several hours at a given temperature. At distinct time intervals, samples were taken and analyzed using  $^1\text{H-NMR}$ . Next, the fraction of blocked isocyanate was plotted as a function of reaction time with reaction half times ranging from half an hour at 160 °C to less than 10 min at 200 °C (Fig. 3). From this model study on low molecular weight compounds, an activation energy of *ca.* 89  $\text{kJ}\cdot\text{mol}^{-1}$  was calculated for the crosslinking reaction (*i.e.* deblocking-urethane formation) using the Arrhenius equation.

Next, self-crosslinking resins containing the caprolactam blocked isocyanate were heated in the estimated deblocking temperature range ( $> 160\text{ °C}$ ) and storage ( $G'$ ) and loss ( $G''$ ) moduli were followed as a function of the reaction time. (Fig. 4) The gelation time was determined at the crossover point ( $G' = G''$ ) [36,37]. Since there is no conventional method in determining the time needed for full cure, this time was chosen at the point where the difference in storage moduli between two

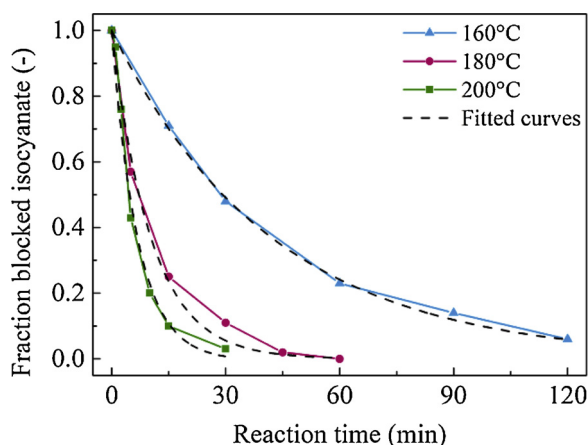


Fig. 3. Decrease of the fraction of blocked isocyanate as a function of time during the reaction of the caprolactam blocked isocyanate (B) with 1-dodecanol at different temperatures.

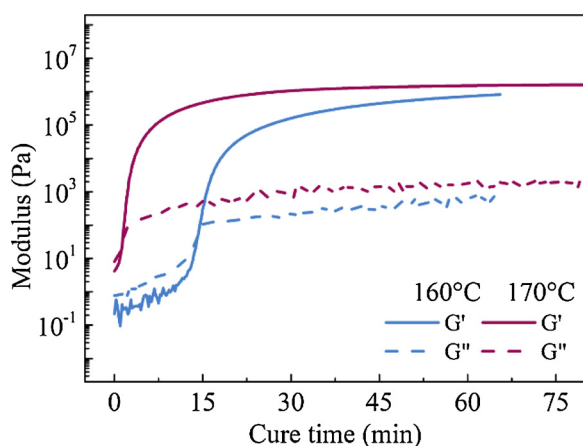


Fig. 4. Determination of the gelation time and the time needed for full cross-linking at 160 and 170 °C.

consecutive measuring points is less than 0.5%. With an increase in temperature from 160 °C to 170 °C, the resins show a decrease in gelation time from 14 to 1.5 min and in full cure time from 65 to 35 min, respectively. As a result, the self-crosslinking resins were heated for 45 min at 170 °C to ensure complete cure.

### 3.4. Coating properties

Typical thiol-ene polymers and resulting coatings have flexible thioether linkages, leading to low glass transition temperatures ( $T_g$ ) that limit their application in coatings for which high hardness is a technical requirement. The  $T_g$  of the coatings was determined by Differential Scanning Calorimetry (DSC). The effect of structure rigidity, crosslink density and plasticizers were assessed by varying the monomer composition. First, the effect of structure rigidity was evaluated by systematically changing the chemical structure of dithiol (Table 1, entry 1-3). As expected, by changing the aliphatic dithiols  $A_1$  and  $A_2$  to the aromatic  $A_3$ , the  $T_g$  increases slightly (22 °C and 26 °C to 28 °C). Next, the molar ratio of hydroxyl groups vs. blocked isocyanates was changed to see the effect of crosslink density on  $T_g$  (entry 3-5). Indeed, a higher  $T_g$  is observed by varying the molar ratio of OH:BI from 2:1 to 1:1. Finally, the sample thickness also indirectly affected the  $T_g$  (entry 3-8), as observed by the large  $T_g$  changes obtained for all samples. This might be ascribed to either the incomplete curing of the thicker samples or the presence of plasticizers, such as residual solvent or blocking agents. Overall, the  $T_g$  of the non-oxidized urethane

Table 1

DSC and TGA analysis of the UTE polymer films prepared by thiol-ene chemistry. Both analyses were performed with a heating rate of 10 °C.min<sup>-1</sup> under nitrogen flow.  $T_g$ ,  $T_{5\%}$  and  $T_{max}$  were determined from the corresponding analysis curves. All samples with \* have a film thickness greater than 1 mm.

Entry	Dithiol	Ratio [OH]:[BI]	$T_g$ (°C)	$T_{5\%}$ (°C)	$T_{max}$ (°C)
1	$A_1$	2:1	26	302	368
2	$A_2$	2:1	22	273	379
3	$A_3$	2:1	28	291	385
4	$A_3$	1.5:1	42	289	357
5	$A_3$	1:1	45	279	354
6*	$A_3$	2:1	11	276	368
7*	$A_3$	1.5:1	17	277	351
8*	$A_3$	1:1	21	276	357

polythioether (UTE) coatings varies between 22 °C to 45 °C. The  $T_g$  of the UTE coatings depends on the combined effect of the structure rigidity and the hydrogen bonding formed by the urethane crosslinks. Thermogravimetric analysis (TGA) of all samples indicated a 5% mass loss at temperatures ( $T_{5\%}$ ) ranging between 270 °C and 320 °C. The temperature for the maximum mass loss rate ( $T_{max}$ ) was found to be in the range of 350 °C to 385 °C. As the thermal stability values ( $T_{5\%}$  and  $T_{max}$ ) are quite similar, it is fair to say that all synthesized urethane polythioether coatings exhibit good thermal stability under inert atmosphere, independent of the used monomer composition. From the thermal analysis results, a standard coating composition consisting of  $A_3$ , B and C, was chosen.

Next, stress-strain curves were measured for this composition to give an indication of the mechanical properties, such as ductility, toughness and mechanical strength of the urethane polythioethers (Fig. 5). As expected, the increase in young modulus with the decrease of the molar ratio (OH:BI) is related to a higher crosslink density. Networks crosslinked using a molar ratio OH:BI of 2 showed the highest ductility with a strain at break over 100%. A combination of both stiffness and ductility was observed for networks prepared using a molar ratio of 1.5, which resulted in materials with a high toughness.

Refractive indices (RI) and Abbe numbers were determined with an Abbe refractometer according to ASTM D1218 requirements. High refractive index values of around 1.59 are obtained for all compositions (Table 1). However, these values are lower compared to other thiol-ene materials due to the presence of many refractive index decreasing atoms such as oxygen and nitrogen. Nonetheless, these coatings exhibit RI-values that are similar to the highest values observed for polymeric systems. Next, refractive indices were used to calculate the corresponding Abbe numbers, ranging from 24.5 to 25.5, which are in the range of the lowest values for polymeric systems. For these materials,

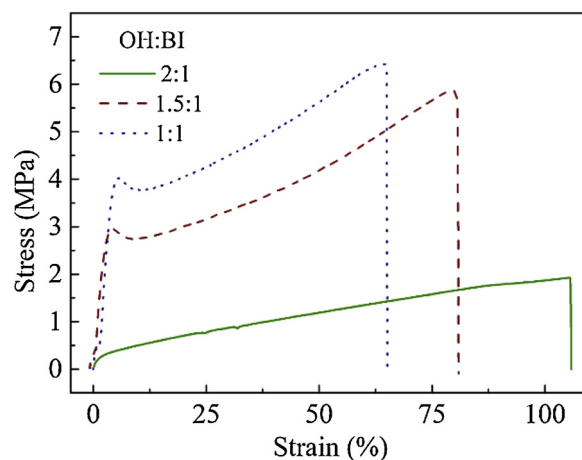


Fig. 5. Stress-strain curves for urethane polythioether networks with different crosslink densities.

the low Abbe number might be in part attributed to the fact that xylene dithiol is an aromatic species with an optical absorption in the near-UV range. The RI measured at 589 nm, which is used for the determination of the Abbe number, might be too close to the absorption and hence its value will increase, thereby reducing the Abbe number [38]. Besides the high refractive index values, the prepared polymer films exhibited high optical transparency and low haze, which were measured under ambient conditions and D65 illumination. The polymer films prepared here show a high average transparency of  $89.3 \pm 0.09\%$  and a low haze of  $1.35 \pm 0.38\%$ , which makes them in principle suitable for optical applications.

Coating hardness was evaluated according to ASTM D3363 pencil hardness scale with a soft to hard range from 6B to 6H (and with:  $1B < HB < 1H$ , in terms of hardness). A clear trend of increased hardness with a decrease in the molar ratio OH:BI from 2 to 1 was observed (Table S1). Lower OH:BI ratios result in a higher crosslink density and a higher  $T_g$ , and consequently in an improved hardness.

The adhesion of the urethane polythioether coatings to stainless steel panels was evaluated according to the standard cross-cut adhesion method B, ASTM D3359. All polymer films exhibited excellent adhesion to steel under ambient conditions (Table S1). In addition, plastic substrates (polystyrene and silicone), glass substrates and various metal substrates (aluminum and zinc alloys) could be coated without adhesion issues. The wide range of possible substrates (from hydrophobic to hydrophilic), to which the polymer films adhere, might be attributed to the combination of a hydrophobic backbone with hydrophilic side chains and crosslinks. Reduced adhesion of polymer films to steel was observed when immersing the coated panels in water (3B4B). In addition, the coatings exhibited poor adhesion (0B) after immersion in boiling water. Therefore, the water uptake of the prepared polymer networks was determined in cold and hot water, 20 °C and 100 °C respectively. Network samples were weighed, immersed in water and the swelling degree (% water uptake) was evaluated after 24 h. The urethane polythioether networks hardly swell in cold water with a maximum water uptake of 1% (Table S2). Surprisingly, immersion in boiling water resulted in a slight negative swelling degree, i.e. 1%–2.5% shrinkage. In addition, the samples had become opaque. After drying in the vacuum oven, the networks became transparent again. The shrinkage can be attributed to the dissolution of caprolactam, which is released upon deblocking and subsequent curing of the resin, in boiling water. The same conclusion can be made by observing the gel content. The lower the molar ratio OH:BI, the more blocked isocyanates are present relative to hydroxyl groups. Therefore, more caprolactam is released. The change in transparency might then be explained by the deposition of caprolactam on or near the surface of the networks after immersion in hot water for 24 h. Since no Soxhlet extraction was performed to remove the caprolactam, the latter remained on the surface of the network, which results in a seemingly opaque material. By drying the samples in an oven, the concentrated caprolactam at the surface was solubilized again by the bulk of the network, resulting in a transparent material. The mass loss and resulting shrinkage of the coatings might also explain the reason why they delaminate easily in boiling water.

To test the flexible nature of urethane polythioether coatings, coated steel panels were submitted to a bend test according to ASTM D4145. Multiple 180° bends of the coated materials were made, and the amount of cracking produced at each bend was visually determined. Ratings were classified from 0 T, 1 T, 2 T, etc., where 0 T is the first and thus harshest 180° bend. All coatings exhibited excellent flexibility as no cracks could be observed for the severe 0 T bend (Table S1). The extreme flexibility of these clear coats can be attributed to the flexible thioether linkages and the homogeneity of the polymer networks.

The film integrity of the coatings was evaluated by the double rub method (ASTM D4752), using methyl ethyl ketone (MEK) and xylene as solvents. Furthermore, the chemical resistance properties of the coatings were evaluated by dipping the coated panels in 5% HCl (v/v) and 5% NaOH (w/v) for 24 h respectively. After performing the chemical

resistance, solvent resistance and hydrolytic stability tests, the coated panels were again evaluated for degree of adhesion and inspected visually for any blisters and cracks. The urethane polythioether coatings showed excellent resistance to acid (5% HCl) and base (5% NaOH) without appearance of defects such as blistering or loss of gloss of the polymer film. In addition, the solvent resistance of the coatings was evaluated by solvent rub testing, which showed no effects on the physical properties, such as loss of gloss or thickness of the films, even after 200 cycles for both xylene and MEK.

Finally, contact angle measurements were performed on standard UTE coatings (Table S1). Surprisingly, an increase in contact angle from 76° to 84° is observed for coatings with increased OH:BI molar ratio, suggesting that mainly the number of polar crosslinks determines the surface wettability.

### 3.5. Post-modification

#### 3.5.1. Selective oxidation to sulfoxide or sulfone

The oxidation of sulfides into sulfones is generally performed with the sole purpose of fully converting all thioethers to sulfones, thus no control over oxidation is needed. Oxidation of polymers containing thioethers to sulfones results in an increase in thermal and mechanical properties. For coatings, this implies a change in properties such as increased  $T_g$ , Young modulus and surface hardness. However, this also results in a loss of flexibility and in some cases optical properties, due to the increased chance of obtaining small crystalline domains. Therefore, it might be desirable to tune the properties according to a specific use or application and thus interesting to determine the effect of partial oxidation on polymer and coating properties. Therefore, an oxidation model study was performed on polymer level. For these oxidation experiments, the self-crosslinking resins were dissolved in chloroform (0.25 M). The amount of sulfur in the resin was determined using the following equation:

$$\text{mol S} = \frac{M_p}{M_{RU}} * f \quad (1)$$

in which mol S represents the amount of sulfur (S) for a given amount of polymer,  $M_p$  is the mass of the polymer,  $M_{RU}$  is the average molar mass of the repeating unit in the polymer chain and  $f$  is the functionality of the RU (number of thioethers in one repeating unit). For 1 g of self-crosslinking resin consisting of B:C:A<sub>3</sub> (1:1:2) (Fig. 6), the average molar mass of the repeating unit is  $761 \text{ g} \cdot \text{mol}^{-1}$ , the functionality is 4 and the amount of S is  $5.2 \times 10^{-3} \text{ mol}$ . The average mass of the repeating unit is an estimation as it assumes similar reactivity of both dienes.

To the dissolved resin, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and acetic acid (AcOH) were added, which resulted in the formation of the strongly oxidizing peracetic acid. The reaction mixture was stirred vigorously to increase the surface contact area between the aqueous and organic layer. At certain time intervals samples were taken, characterized via <sup>1</sup>H-NMR and the formation of oxidized products was plotted as a function of the reaction time (Fig. 7). The oxidation of thioethers at

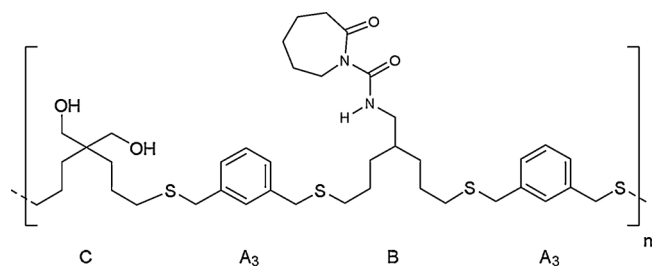
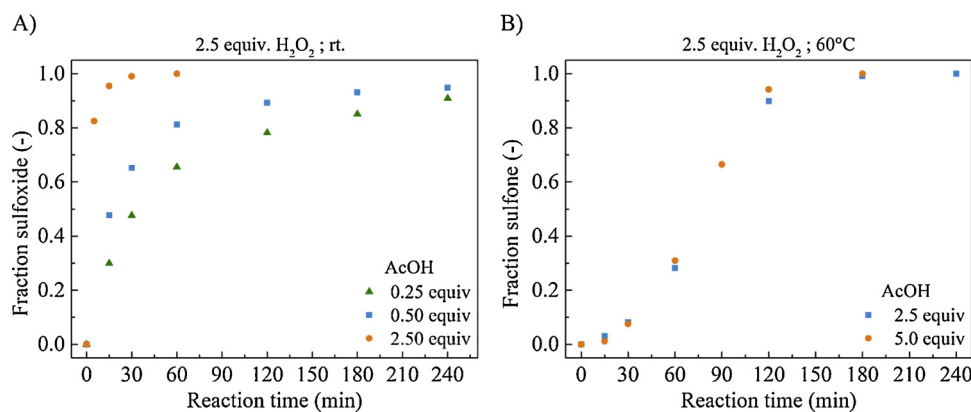


Fig. 6. General structure of the polymer comprising one molecule of the diene diol (C), one of the blocked isocyanate diene (B) and two molecules of dithiol (A<sub>3</sub>), as repeating unit.



**Fig. 7.** Oxidation of thioether moieties present in the self-crosslinking resin as a function of reaction time. **A)** Influence of acetic acid proportion on the oxidation rate of thioether to sulfoxide at room temperature. **B)** Oxidation of the formed sulfoxide to sulfone at 60 °C for different amount of acetic acid. All oxidation experiments were performed using 2.5 equiv.  $\text{H}_2\text{O}_2$  relative to the number of sulfur atoms present in the polymer.

room temperature, within a reasonable time frame, solely results in the formation of sulfoxides with the oxidation rate increasing with higher concentration of acetic acid and with 85% conversion reached after 5 min using 2.5:2.5  $\text{H}_2\text{O}_2$ :AcOH. The oxidation of sulfoxides to sulfones occurred only upon heating the dissolved polymer resin under peracetic acid conditions, with a near complete conversion obtained after 3 h. As such, it is possible to fine tune the extent of oxidation and thus have a good control over coating properties.

### 3.5.2. Coating properties of oxidized resins

Similar to the evaluation of non-oxidized samples, the coating properties of the oxidized urethane polythioether films were evaluated to compare them to non-oxidized samples. TGA measurements indicated a reduced thermal stability of the oxidized samples with 5% weight loss reached between 180 °C and 235 °C vs 290 °C for the neat urethane polythioether (See **Table S1, entry 3** and Fig. S2 in the supporting information). This reduced thermal stability was also observed by Wudl et al. [39] Neither the polysulfoxide nor -sulfone containing coatings showed any crystallinity in DSC analyses (Fig. S3, supporting information). The higher  $T_g$  values observed for materials with sulfones and sulfoxides are in agreement with the assumed limited flexibility and mobility of the rigid polymer chains compared to regular thioether moieties. The  $T_g$  increases from ~28 °C for the neat urethane polythioether (See **Table S1, entry 3**) to 60 °C and 125 °C for complete oxidation to sulfoxide ( $\text{SOX}_{100}$ ) and sulfone ( $\text{SX}_{100}$ ) respectively. Because of the increase in  $T_g$ , coatings produced from oxidized resins showed an increase in pencil hardness with a hardness of 5H for completely oxidized samples. Depending on the extent of oxidation and thus the ratio of sulfoxide and sulfone, the hardness varied between 1H and 5H. Unsurprisingly, the increase in  $T_g$  resulted in a loss of flexibility but only for the higher extent of oxidation ( $\text{SX}_{100}$ ). Additionally, oxidized coatings still exhibited excellent adhesion to many substrates, such as steel, aluminum, glass and polystyrene. Moreover, the refractive indices of oxidized samples were somewhat lower than non-oxidized versions but still in the high range of refractive indices ( $\text{RI} \sim 1.57$ ). Finally, and as expected, the static contact angle of treated samples drops significantly when the thioether resins are oxidized because of the more hydrophilic nature of sulfoxide and sulfone groups.

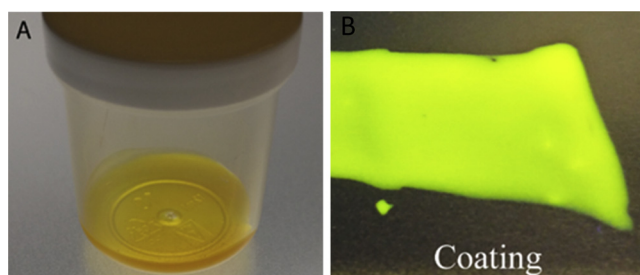
Although oxidation results in reduced thermal stability, flexibility and RI, it leads to a high increase in  $T_g$  and consequently in an increase in hardness (**Table S2**, supporting information). However, by limiting the extent of oxidation to a sulfoxide – sulfone ratio between complete sulfoxide or sulfone (in between  $\text{SOX}_{100}$  and  $\text{SX}_{100}$ ), an optimum balance in properties can be obtained without the disadvantages of complete sulfone oxidation. As a result, the resulting sulfoxide-sulfone-containing coatings or materials exhibit improved properties, which can be tuned accordingly.

### 3.5.3. Additives

To further demonstrate the ability for post-polymerization modification via chemical incorporation of an additive, self-crosslinking resins were formulated with a fluorescent dye. This particular dye, hydroxyl terminated nitrobenzodialzo (NBD–OH) (Fig. S4, supporting information), is known to yield an orange compound that is green fluorescent as well [40]. To ensure chemical incorporation and successful modification, the reaction kinetics between the caprolactam blocked isocyanate (**B**) and NBD–OH were evaluated with  $^1\text{H-NMR}$ , showing similar reactivity as with the diol diene (**C**) with a high conversion within 2 h at 160 °C. To produce the modified coating, a self-crosslinking resin with composition  $\text{A}_3\text{:B:C}$  (*vide supra*, Fig. 6) was mixed with 0.1 wt% of NBD–OH and cured for 90 min at 170 °C. As displayed in Fig. 8, the chemical modification yielded orange colored materials with a green fluorescence under 240 nm UV light. To prove that the fluorescent dye is in fact chemically incorporated and cannot leach out anymore, two urethane polythioether samples were swollen for 24 h in a solution of the dye dissolved in ethyl acetate. After immersion, both samples were orange colored, indicating physical incorporation of the dye (Fig. 8). Next, one of the samples was dried and subsequently heated at 170 °C for 90 min to react the dye with residual blocked isocyanates. After soxhlet extraction for 48 h with ethyl acetate, a difference between both substrates could be observed because of the leaching of the physisorbed dye (Fig. S5). Indeed, the substrate that had undergone an additional thermal treatment remained unchanged, clearly indicating homogenous chemisorption of the dye to the material.

## 4. Conclusion

New functional dithiol and diene monomers were synthesized for the development of self-crosslinking resins via UV-induced thiol-ene chemistry. The resulting self-crosslinking resins then served as



**Fig. 8.** Incorporation of a fluorescent dye into the self-crosslinking resins. **(A)** Resin and fluorescent dye formulation. **(B)** Application of the formulation and curing to yield an orange coating with green fluorescence (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

precursors for the production of urethane polythioether coatings via a simple heat treatment. The screening of the properties of these new urethane polythioether coatings has provided a base for the development of functional thioether coatings using thiol-ene chemistry. Coatings were evaluated according to standard ASTM tests for adhesion, flexibility, hardness and solvent resistance. Urethane thiol-ene based films exhibited excellent adhesion to various inorganic and organic substrates under ambient conditions and after immersion in water. Coatings with OH:BI ratio of 1 exhibited higher  $T_g$ , greater pencil hardness and higher Young moduli. The UTE coatings demonstrated maximum flexibility, which is characteristic for thiol-ene polymers. Moreover, the films exhibited high transparency of 89%, low haze (< 2%) and high refractive indices (around 1.58). In addition, self-crosslinking resins could be modified by oxidation or through the incorporation of functional molecules. Controlled oxidation allowed for the improvement of properties such as  $T_g$  and hardness without sacrificing the excellent adhesion, flexibility and optical clarity of these coatings. Based on these properties, urethane thiol-ene borne polymers and coatings are promising for a variety of coating applications, enabled by polymer backbone modification, additional side group functionalities and variable crosslink densities.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.porgcoat.2019.105215>.

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