# Photo-crosslinking and reductive decrosslinking of polymethacrylate-based copolymers containing 1,2-dithiolane rings

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This study first describes a straightforward approach for the preparation of polymethacrylatebased networks containing variable amounts of lipoates. For this purpose, butyl methacrylate and a 1,2-dithiolane derivative of hydroxymethylmethacrylate (HEMA) are copolymerized in different ratios by free radical polymerization with the formation of linear network precursors. After optimizing the copolymerization conditions, the UV-induced crosslinking behavior has been studied. The latter is possible because of the presence of 1,2-dithiolane moieties, which can be photolytically cleaved and recombined upon UV-irradiation. The obtained networks are analyzed in terms of swelling degree, gel fraction and rheological behavior. Then, network decrosslinking has been achieved by immersing the networks in a reducing environment. Finally, successful preliminary coating experiments are conducted, demonstrating the potential applicability of the studied materials.

### **1. Introduction**

Polymethacrylates are among the most widely used polymers, showing good mechanical properties, high transparency, great weathering resistance and ease of processing.<sup>1</sup> Typical applications range from transparent glass substitutes to electronics and adhesives. A large share of the polymethacrylate market is reserved for coating materials.<sup>2</sup> Nonetheless, since they belong to the class of thermoplastics polymers, they exhibit limited creep sensitivity and poor solvent resistance.<sup>3</sup> By introducing reversible crosslinks into the material, higher dimensional and chemical stability and increased mechanical properties could be obtained while still keeping the (re)processability.<sup>4,5</sup>

In general, disulfides are a class of covalent bonds that have a relatively large bonding energy, yet they are also susceptible towards different exchange reactions. These can be triggered thermally,<sup>6–8</sup> by irradiation,<sup>9</sup> ultrasound,<sup>10</sup> treatment with bases<sup>6,11</sup> or redox reagents.<sup>12</sup> Dynamically crosslinked polymeric materials containing linear disulfide bonds have received much attention over the past decades,<sup>6–8,13,14</sup> while only recently strained cyclic disulfides and more particularly 1,2-dithiolanes gained more attention. Materials containing these 1,2-dithiolane moieties have the advantage of undergoing faster exchange reactions<sup>12</sup> in much milder conditions.<sup>15–18</sup>

Amongst the class of 1,2-dithiolanes, lipoic acid (LA) is probably the best known. This naturally occurring molecule plays a prominent role in the metabolism of animals and plants, for example as a cofactor in the acetylation of coenzyme A.<sup>16,19,20</sup> Endo and co-workers studied the thermally triggered radical copolymerization of lipoamide (the amide derivative of lipoic acid) with various vinyl monomers and established a reactivity order.<sup>21</sup> They demonstrated that lipoamide could readily be copolymerized with acrylates. However, when methacrylates were added as comonomer, no incorporation of the lipoamide was observed. Tsarevsky and co-workers used this reactivity order to obtain partially degradable polymer networks by radically triggering 2-acryloyloxy-ethyl lipoate (a monomer with two types of radically polymerizable groups) (**Figure 1**).<sup>22</sup>

Recently, Sangermano and Pezenna used lipoic acid and isosorbide diallyl together with a photo-initiator (Darocure 1173) to synthesize fully biobased UV-cured thiol-ene coatings.<sup>23</sup> However, early work by Calvin and co-workers mentioned the polymerization of lipoic acid using UV irradiation without the need of any photo-initiator.<sup>16</sup> Sumerlin and co-workers employed this interesting feature to prepare photocurable hydrogels.<sup>24,25</sup> They synthesized various acrylate functionalized 1,2-dithiolanes after which an aza-Michael reaction was conducted to afford telechelic hydrogel network precursors. These precursors were then crosslinked by irradiation with UV-light ( $\lambda = 365$  nm). Pivotal in their work is the self-assembly behavior) of the precursor in water.<sup>11,24,26</sup>

Recently, this photo-curing behavior was achieved in a bulk application. Dynamically crosslinked bottlebrush elastomers were synthesized from lipoic acid end-functionalized PDMS by Alaniz and Bates and co-workers.<sup>27</sup> Amino functionalized PDMS (~6-8% molar ratio of amine units) was recently modified with lipoic acid by Feringa and co-workers.<sup>28</sup> After irradiation, crosslinked materials that could be applied as adhesive material were formed.

In this work, we first demonstrate a straightforward strategy for the synthesis of methacrylate based copolymers with pendant 1,2-dithiolane moieties. Three copolymers with different compositions were selected and their crosslinking was examined by irradiation with UV light ( $\lambda = 365$  nm) (

Figure 1). Then, decrosslinking of the obtained materials is investigated by reducing the disulfide bonds and the formation of the precursor copolymer. Finally, using these 1,2-

dithiolane functionalized polymethacrylates, a method to coat glass and metal surfaces will be described.



**Figure 1**. Comparison of the presented work with earlier reported works. Tsarevsky and coworkers combined acrylates with 1,2-dithiolanes, obtaining a partially degradable polymer network.<sup>22</sup> Sumerlin and co-workers incorporated a 1,2-dithiolane as hydrophobic unit on a PEG precursor.<sup>24</sup> Assembling these structures in water and irradiating with UV delivered adaptable hydrogels. Feringa and co-workers decorated amino functionalized PDMS with lipoic acid.<sup>28</sup> Crosslinked networks were obtained by UV irradiation in bulk. This work highlights the copolymerization of a 1,2-dithiolane methacrylate with butyl methacrylate (BMA) and subsequent UV curing and chemical recycling.

#### 2. Results and Discussion

#### 2.1. Synthesis of linear copolymers as network precursors

Following the reactivity order established by Endo and co-workers,<sup>21</sup> a methacrylate functionalized 1,2-dithiolane was considered as suitable comonomer. Thus, the carboxylic acid group in lipoic acid was used in an EDC coupling with hydroxyethylmethacrylate (HEMA) to deliver the 1,2-dithiolane containing methacrylate, further referred to as HEMA-LA.

With this 1,2-dithiolane monomer in hand, initial radical copolymerization trials were conducted. To ensure chain mobility in combination with the incorporation of enough 1,2-

dithiolane, a molecular weight of 20kDa was aimed at. First, similar conditions as in the work by Tsarevsky and co-workers<sup>22</sup> were tested (*i.e.* equimolar amounts of MMA and HEMA-LA, 3 hours at 70°C in DMAc). However, this yielded a copolymer with a M<sub>n</sub> of 20 kDa and a high dispersity (Đ) of 5.68. Moreover, after purification and drying, an insoluble crosslinked material was obtained, most probably due to a radical thiol-ene reaction between a methacrylate and a sulfur based radical originating from an opened 1,2-dithiolane. This crosslinking was also observed for the HEMA-LA as it forms gels if kept at room temperature for several weeks.<sup>29</sup> As this premature crosslinking is undesired, we optimized the polymerization conditions by lowering the HEMA-LA feed (to a maximum of 20 mol%) and adding a transfer agent (dodecanethiol, DT). In addition, 2-MeTHF was used as solvent to ease the purification and butyl methacrylate (BMA) was chosen as comonomer in order to tune the glass transition temperature  $(T_g)$  of the final copolymer, which will be a crucial parameter for the curing behavior. Ring opening of the 1,2-dithiolane and subsequent branching of the polymer structures would be observed in a shift to a lower retention time and increase in dispersity.<sup>30</sup> Therefore SEC analysis of the polymerization mixture containing a 9:1 BMA:HEMA-LA feed ratio was carried out and revealed a relative constant low dispersity up to 3 hours of polymerization time (see Figure S1, Figure S2 and Table S1). However, increasing the polymerization time resulted in a deviation of M<sub>n</sub> from the predicted value and an increase in D. These results demonstrated sufficient stability of the 1,2-dithiolane ring up to 3 hours for the reported experimental conditions. We used the optimized conditions for the synthesis of a series of poly(butyl methacrylate)-based copolymers with 5, 10 and 20 % dithiolane content (p(BMA-5LA), p(BMA-10LA) and p(BMA-20LA)) (Figure 2 A). The copolymers were analyzed by <sup>1</sup>H-NMR (Figure 2 B), SEC (Figure 2 C) and UV-Vis (Figure 2 D). A characteristic peak originating from the lipoate groups is visible in the region comprised between 3.5 to 3.65 ppm in the proton NMR spectrum. We could quantify the 1,2-dithiolane content by comparing the integral of this lipoate signal to the signal of the butyl side chains (around 3.9 ppm) using benzonitrile as an internal standard (see Table S2). The experimentally obtained values for the 1,2-dithiolane content are in close resemblance to the theoretically calculated ones from the feed ratio (Table 1). Additionally, the results found by NMR were confirmed by those found through UV-Vis analysis (after calibration using lipoic acid, see Figure S3 and Table S3). SEC showed broader peaks and a decrease in Mn values when increasing the HEMA-LA content, most likely because of branching via a radical thiol-ene reaction for which the chance is higher with increasing 1,2-dithiolane concentration.



**Figure 2**. (A) Free radical copolymerization of BMA and HEMA-LA with different 1,2dithiolane content, using the optimized conditions (*i.e.* AIBN as initiator and DT as transfer agent in 2-MeTHF at 70 °C for 3 hours). (B) Stacked <sup>1</sup>H-NMR spectra of the copolymers in deuterated chloroform with benzonitrile as standard (region 7.4-7.75). Quantification of the 1,2dithiolane content can be calculated from the integration between 3.5 and 3.65 ppm compared to the integral of the CH<sub>2</sub>-O present in the butyl side chains. (C) SEC traces of the copolymers in THF. (D) UV-Vis spectra of the copolymers in 2-MeTHF indicating the absorption region of 1,2-dithiolanes (330 nm).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were conducted to investigate the thermal properties of the polymeric network precursors. All copolymers have a 5% degradation temperature in a range of 290 to 310 °C (**Figure S4**). DSC analysis revealed  $T_g$  values ranging from 6 °C to 23 °C (see **Table 1** and **Figure S5**), with lower values for copolymers consisting of a higher fraction of HEMA-LA as a result of the longer side chains.

Copolymer	Copolymer composition [BMA:HEMA-LA] (mol%) <sup>a)</sup>	Copolymer composition [BMA:HEMA-LA] (mol%) <sup>b)</sup>	M <sub>n</sub> (kDa) <sup>c)</sup>	Ð <sup>c)</sup>	T <sub>g</sub> (°C)
p(BMA-5LA)	94:6	94.6:5.4	21.0	1.36	23
p(BMA-10LA)	90:10	90.4:9.6	19.3	1.52	15
p(BMA-20LA)	82:18	85.9:14.1	17.0	1.63	6

Table 1. Overview of the copolymer analyses by <sup>1</sup>H-NMR, SEC, UV-Vis and DSC.

<sup>a)</sup>Calculated by <sup>1</sup>H-NMR using benzonitrile as standard; <sup>b)</sup>Calculated from values obtained by UV-Vis spectroscopy; <sup>c)</sup>Obtained from size exclusion chromatography in THF using PS standards.

#### 2.2. Crosslinking of the copolymers

After preparing the functionalized polymethacrylate copolymers, different stimuli were tested to initiate crosslinking. Since lipoic acid is known to polymerize above its melting temperature (60-62 °C) as a result of a homolytic cleavage of the 1,2-dithiolane ring and subsequent formation of a disulfide bond,<sup>31–35</sup> crosslinking was attempted by heating in bulk for 1 hour at 70°C. However, gelation did not occur, even after heating to 140 °C for 1 hour. Recently, this observation was confirmed by Bates *et al.* using PDMS functionalized with lipoic acid.<sup>27</sup> To better understand this unexpected result, a monomer mimic (*i.e.* ethyllipoate (EtLA), the ethyl ester of lipoic acid) was synthesized. Remarkably, also in this example no polymerization through disulfide formation between 1,2-dithiolane groups was observed upon heating. A close literature review showed that the thermal ring opening of 1,2-ditholanes has only been reported for assembled structures, in which dithiolanes reside in the hydrophobic regions.<sup>11,24,26</sup>

Photolytical ring-opening was already reported in early and more recent works.<sup>16,24,36,37</sup> For this reason, the photopolymerization of the monomer mimic EtLA (1 mg/mL in THF) upon UV irradiation ( $\lambda = 365$  nm) was attempted. Analysis of the reaction mixture at regular time intervals revealed a relatively fast decrease in the characteristic dithiolane absorption band around 330 nm (**Figure 3** B). Similarly to the results of Mishra *et al.* an additional strong absorbance around 300 nm was observed. Feringa and co-workers assigned this peak to the presence of oligomeric species.<sup>28</sup> Moreover, an additional absorption band around 254 nm corresponding to linear disulfides was also present<sup>38</sup> and a clear increase of the molecular weight was observed by SEC (**Figure 3** C).



**Figure 3.** Photochemical polymerization of 1,2-dithiolanes. (A) Reaction scheme for the polymerization of 1 mg/mL EtLA in THF using 365 nm light. (B) UV-Vis spectra of the reaction mixture sampled at regular time intervals. (C) SEC traces of aliquots from the polymerization mixture.

Following these promising results on the monomer mimic, photochemical crosslinking of the copolymers was investigated.<sup>39,40</sup> The copolymers were dissolved in 2-MeTHF to yield a pale yellow solution. After irradiation for 10 minutes, the yellow color disappeared, and the formation of a gel was observed. Other solvents (CHCl<sub>3</sub>, BuOAc and PGMEA) were also investigated to check the influence of solvent evaporation during curing. PGMEA performed similar as 2-MeTHF while the solution in chloroform only showed an increase in viscosity (no gel formation). After 20 minutes of irradiation in butyl acetate only a pink colored solution was obtained indicating the presence of sulfur based radicals (**Figure S6**).<sup>16</sup>

Pendant thiols originating from a ring opened 1,2-dithiolane could possibly give a dynamic character to the materials *via* thiol-disulfide exchange.<sup>11,24</sup> Therefore, to assess the presence of potential free or pending thiol groups, an Ellman's essay was performed. For this, a gel formed in 2-MeTHF was swollen in a dithionitrobenzoic acid solution after which UV-Vis analysis was carried out on the supernatant. No increase in absorption around 412 nm was observed, indicating the absence of free thiols and the exclusive formation of linear disulfides (**Figure S7**).<sup>41,42</sup>

### 2.3. Photo-rheological investigation

The photocuring of the solutions was further examined by isothermal photo-rheology at 30 °C. The copolymers were dissolved in degassed 2-MeTHF to obtain samples at 20 wt%. A time sweep experiment was performed, whereby the sample was first equilibrated during a period of 5 minutes of darkness after which the UV light was switched on. Next, after an induction period of approximately 35 s, a clear increase in storage modulus (G') could be observed indicating film curing (**Figure S8**). As solvent evaporation during the experiment could not be neglected and could have an influence on the curing, the same experiment was repeated with 20 wt% PGMEA (bp: 146.4 °C) solutions (**Figure 4**).



**Figure 4**. Time sweep experiment of 20 wt% p(BMA-xLA) solutions in PGMEA at 30 °C, highlighting a fast curing behavior ( $\bullet = G', x = G''$ ).

Since the network precursors have  $T_{gs}$  below room temperature (**Table 1**), bulk curing of thin films (maximal 200  $\mu$ m) was attempted. Since the increase in  $T_{g}$  during the photocuring process could vitrify the sample, time sweep experiments were conducted at 30, 50 and 70 °C. At higher

temperatures, the polymer chains have an increased mobility, which could increase the crosslinking rate.



**Figure 5**. Time sweep experiments on thin film bulk p(BMA-xLA) at different temperatures (A: 30 °C; B: 50 °C; C: 70 °C), highlighting a change in curing behavior ( $\bullet = G', x = G''$ ).

Within 20 minutes of irradiation, fully cured bulk materials were obtained for almost all compositions at every temperature (**Figure 5**). Yet, at 30 and 50 °C p(BMA-5LA) did not crosslink as observed from the absence of crossover between storage and loss modulus (G").

As expected, the crossover shifts to shorter irradiation times with increasing temperature (*e.g.* for p(BMA-20LA) 405 s at 30 °C, 210 s at 50 °C and 50 s at 70 °C). Interestingly, a clear change in color from yellow to pinkish to colorless could also be observed during bulk irradiation (**Figure S9**).

After crosslinking, the thermal properties of the obtained networks were analyzed. TGA showed similar results as for the precursor copolymers (**Figure S10** and **Table S4**). However, a clear increase in glass transition was observed in all cases caused by the crosslinking reaction, with the largest increase detected for p(BMA-20LA) (**Figure S11**, **Figure S12** and **Figure S13**). This could be rationalized by the fact that there is a higher fraction of 1,2-dithiolane in this copolymer, eventually resulting in a higher crosslink density and thus higher G' values (**Figure 5**).

The gel fraction and swelling degree in ethyl acetate were determined for all the networks, the values are summarized in **Table 2**. All networks behave similar in terms of gel fraction and swelling degree.

Table 2. Gel fractions	and swelling degree	of the different cor	polvmer network	s in ethvl acetate.

Copolymer	Gel fraction (%)	Swelling degree (%)
p(BMA-5LA)	<b>88</b> ±3	<b>487</b> ±128
p(BMA-10LA)	<b>86</b> ±1	<b>864</b> ±20
p(BMA-20LA)	<b>81</b> ±3	<b>693</b> ±50

#### 2.4. Decrosslinking by reduction

Given the dynamic nature of the disulfide crosslinks in the materials, we envisioned that decrosslinking could be achieved in a reducing environment. To do so, the network obtained from p(BMA-10LA) was swollen in THF with 10 equivalents of sodium borohydride, relative to the amount of dithiolane in the precursor. After 2 days, a clear solution was obtained because of dissolution of the network, indicating a successful decrosslinking. SEC analysis was carried out on an aliquot of the solution and compared to the network precursor (**Figure 6**). A slightly broader peak (D = 1.5 for the initial p(BMA-10LA) versus D = 1.7 for the reduced network) is observed. The M<sub>n</sub> after reduction is slightly lower compared to the pristine precursor copolymer (17.6 versus 19.3 kDa). This could be attributed to a change in polarity as the precursor

copolymers contain rather hydrophobic 1,2-dithiolane rings, whereas the reduced networks contain more polar thiol groups, leading to different interactions during SEC-analysis.



**Figure 6**. Overlay of the SEC traces of p(BMA-10LA) and the reduced network from the same copolymers, showing almost identical results.

#### **2.5. Coating application**

After studying the different curing conditions, the obtained films were evaluated for their potential applicability as protective coating for different substrates. For this purpose, copolymer solutions in PGMEA were applied on a glass substrate using a Elcometer 3540/6 four-sided film applicator to create a film of uniform thickness (150  $\mu$ m) Then crosslinking was induced by UV irradiation for 30 min, after which a clear and highly transparent film was obtained. When 2-MeTHF was used as solvent, tiny defects could be observed (**Figure S14**), most likely because of the higher evaporation rate of 2-MeTHF. The flexibility of the coating was investigated by coating a metallic plate after which several bends were applied according to ASTM D4145. Multiple 180° bends of the coated steel panels were made using a bench vise and the amount of cracking produced at each bend was visually determined. No visual cracks could be observed, even for the severe 0T bend (**Figure S15**), thus demonstrating the excellent flexibility of the film. This analysis should be considered as a first evaluation of coating properties.

#### 3. Conclusion

In summary, polymethacrylates with variable amounts of pendant 1,2-dithiolane groups originating from lipoic acid were synthesized in an easy and straightforward way. The copolymerization procedure was optimized, eventually yielding copolymers with intact 1,2-

dithiolane moieties. The composition of the obtained copolymers was in close resemblance to the feed ratio. By making use of the photophysical properties of the strained 1,2-dithiolanes, crosslinking was achieved in minutes, both in solution as well as in bulk. Because of the redox reactivity of the disulfides in the polymer networks, decrosslinking was possible *via* the introduction of reducing agents, yielding a polymer with similar properties as the network precursors. The materials presented in this work demonstrated their potential applicability as polymeric coatings owing to their high transparency and flexibility.

#### 4. Experimental

#### Materials

The 1- Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride salt (EDC, 98) was purchased from ABCR Chemicals/ Petroleum ether, 2-hydroxyethyl methacrylate (HEMA, 97%) and sodium borohydride (98%) were purchased from Acros Organics. N,N'dicyclohexylcarbodiimide (DCC, 99%) was bought from Alfa Aesar. Hydrochloric acid (36%) was purchased from Chem-Lab. Chloroform (CHCl<sub>3</sub>, 99.8%) and dichloromethane (DCM,  $\geq$ 99%) were obtained from Fischer Chemicals. 4-dimethylaminopyridine (DMAP, 99%) was purchased from Fluorochem. The basic aluminum oxide ( $\geq$  99%) was purchased from Honeywell. Dimethylacetamide (DMAc,  $\geq$  99%) was purchased from Merck. The DL- $\alpha$ -lipoic acid (99%) was purchased from Nanjin Gemsen International Co. Ltd., China. 2methyltetrathydrofuran ( $\geq$  99%) and sodium sulphate ( $\geq$ 99%) were purchased from Roth. Butyl acetate (BuOAc, >99.5%), butyl methacrylate (99%) dodecane thiol (≥98%), hydroquinone (≥99%), methyl methacrylate (99%) and propylene glycol monomethyl ether acetate (PGMEA,  $\geq$ 99.5%) were purchased from Sigma Aldrich. Azobisisobutyronitrile (AIBN,  $\geq$  99%) was purchased from Janssen Chimica and was recrystallized three times before use. The methacrylate monomers were passed through a short plug of basic alumina prior to polymerizations.

#### **Characterizations**

<sup>1</sup>H- and <sup>13</sup>C-NMR (Attached Proton Test, APT) were recorded on a Bruker Avance 300 or 400 MHz FT-NMR spectrometer in CDCl<sub>3</sub>. Size exclusion chromatography (SEC) analyses were performed on a Varian PLGPC50plus instrument using a refractive index detector, equipped with two PLgel 5µm MIXED-D columns at 40°C at a flow rate of 1 mL/min. Narrow

polystyrene standards were used for calibration and the samples were injected using a PL AS RT autosampler. Thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/SDTA 851 device under nitrogen atmosphere from 25 to 800 °C with a heating rate of 10°C/min and analysed with the STARe software from Mettler-Toledo. Differential Scanning Calorimetry (DSC) analyses were performed on a Mettler-Toledo 1/700 under nitrogen atmosphere with a heating rate of 10°C/min. Samples (3-10 mg) were loaded into aluminium sample pans, the thermograms were analysed using the STARe software from Mettler-Toledo and the glass transition temperatures were extracted from the second heating run as midpoint. Liquid chromatography-Mass Spectrometry (LC-MS) were performed on a reversed phase LC-MS Agilent Technologies 1100 series LC/MSD system equipped with a soft electrospray source (ESI-MS) and a diode array detector. Depending on the sample, a solvent gradient from 0-100 % or 75-100% acetonitrile in water was used. UV-Vis spectra were recorded on a Analytik Jena Specord 200 in quartz cuvettes with a thickness of 10 mm. Typically, samples were dissolved in 3 mL chloroform or THF and absorbance between 200 and 500 nm was recorded. Rheological tests were conducted on an Anton-Paar MCR 301 rheometer. The experiments were performed in parallel plate geometry using 8mm sample disks, a frequency of 1 Hz and a strain of 1%. For UV-curing experiments the lower plate assembly was replaced by a UV light guide accessory, equipped with a disposable acrylic plate and connected to a OmniCure S2000 Spot UV Curing system containing a 200 W Mercury vapor short arc lamp with a 365 nm filter.

#### Synthesis of the ethyl ester of lipoic acid (ethyllipoate, EtLA)

EtLA was synthesised following an adapted route from literature.<sup>43</sup> In short, DL- $\alpha$ -lipoic acid (5 g, 24.23 mmol) was dissolved in dichloromethane (30 mL) in a 250 mL round bottom flask equipped with a stirring bar. DMAP (0.296 g, 0.0024 mmol) was added together with 4.25 mL ethanol. The mixture was cooled in an ice bath and protected from the light. DCC (5 g, 24.23 mmol) was dissolved in 20 mL dichloromethane and added dropwise to the vigorously stirring solution. The mixture was stirred overnight after which the dicyclohexylurea was filtered off. The mixture was concentrated in vacuo and passed over a silica plug using 5 v% ethyl acetate (EtOAc) in hexane. Finally, the solvent was removed in vacuo to yield 3.49 g yellow oil (61.5%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 4.16 (q, 2H), 3.57 (q, 1H), 3.12 (m, 2H) 2.54 (m, 1H) 2.36 (t, 2H), 1.9 (m, 1H), 1.65 (m, 4H), 1.5 (m 2H), 1.21 (t, 3H) (**Figure S16**); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 173.17, 59.95, 56.01, 39.87, 38.14, 34.27, 33.78, 28.42, 24.36, 13.92. (**Figure S17**) and LCMS (ESI) m/z: [M+H]<sup>+</sup> for [C10H18O2S2]<sup>+</sup>; calculated: 235.074, found: 235.1

Synthesis of 2-(methacryloyloxy)ethyl 5-(1,2-dithiolan-3-yl)pentanoate (HEMA-LA) DL- $\alpha$ -lipoic acid (20 g, 96.94 mmol), 2-hydroxyethylmethacrylate (12.62 g, 96.94 mmol) and 4-dimethylaminopyridine (1.18 g, 9.96 mmol) were dissolved in 200 mL dichloromethane and the flask was cooled in an ice bath. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride salt (27.87 g, 145.41 mmol) was added in portions under continuous stirring. The solution was stirred overnight while being protected from light. Then the obtained mixture was washed three times with 1N HCl (200 mL), three times with a saturated sodium bicarbonate solution (200 mL) and three times with brine (200 mL). The organic phase was dried over anhydrous magnesium sulfate, filtered and the solvent was removed in vacuo to yield a yellow oil (80%). The resulting compound was used without further purification. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.06 (s, 1H), 5.60 (s, 1H), 4.30 (s, 4H), 3.55 (m, 1H), 3.15 (m, 2H), 2.45 (m, 1H), 2.30 (t, 2H), 1.90 (s, 3H), 1.85 (m, 1H), 1.70 (m, 4H), 1.45 (m, 2H) (**Figure S18**); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>,  $\delta$ ): 173.21, 167.10, 135.94, 126.06, 62.2, 62.1, 56.31, 40.22, 38.50, 34.59, 33.88, 28.70, 24.60, 18.28, (**Figure S19**); LC-MS (ESI) m/z: [M+H<sub>2</sub>O]<sup>+</sup> for [C<sub>14</sub>H<sub>24</sub>O<sub>5</sub>S<sub>2</sub>]<sup>+</sup>; calculated: 336.45, found: 336.1

### Polymer synthesis

In a typical procedure, the methacrylate monomers (*i.e.* methyl methacrylate (MMA) or butyl methacrylate (BMA) together with the 1,2-dithiolane methacrylate) were dissolved in 2-MeTHF. AIBN (0.0025 eq with respect to the methacrylate monomers) and dodecane thiol (0.091 eq, with respect to the methacrylate monomers) were added and the solution was purged with nitrogen gas for 30 minutes. The polymerization was started by heating the mixture at 70 °C in an oil bath. After 3 hours, the reaction was stopped by cooling and opening the flask to the air. The copolymer was purified by precipitation in a tenfold excess of petroleum ether (three times), after which the polymer is dried overnight at ambient temperature. A typical <sup>1</sup>H-NMR spectrum is presented in **Figure S20**.

### Photo-crosslinking

The copolymer was dissolved in either 2-MeTHF,  $CHCl_3$  or PGMEA in an appropriate vial, after which the oxygen was removed by purging with argon for 15 minutes. The vials were put in a Primotec Metalight classic UV chamber equipped with 12 UV light bulbs ( $\lambda = 365$  nm) and irradiated for the specified time.

### Preparation of coating substrates

Metal and glass substrates were prepared by washing and degreasing them with detergent and subsequent thorough rinsing with water. Next, the substrates were rinsed three times with acetone and finally three times with isopropyl alcohol. Afterwards, they were dried using a clean cloth. Solutions of the copolymer were put on the surface and evenly coated using an Elcometer 3540/6 four-sided film applicator to create a film of uniform thickness (150  $\mu$ m).

### **Supporting Information**

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

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A methacrylate copolymer containing strained cyclic disulfides is synthesized and crosslinked in a fast way with UV-light. Transparent materials are obtained with potential application in coatings while full network disintegration could be accomplished under reducing conditions.

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# Photo-crosslinking and reductive decrosslinking of polymethacrylate-based copolymers containing 1,2-dithiolane rings

ToC figure (110 mm broad x 20 mm high)

