

Oxime crosslinked polymer networks: Is every reversible covalent bond suitable to create self-healing polymers?

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ABSTRACT: The incorporation of reversible covalent bonds into polymeric materials offers the possibility to generate polymers with self-healing ability. For this purpose, three new oxime crosslinkers are synthesized and crosslinked by the copolymerization with different commercially available methacrylates via a photo-polymerization process. These crosslinked materials are investigated regarding a potential self-healing behavior. Moreover, the influence of different additives (polymerizable acids, photo acids, and acid developers) to enable self-healing is studied in detail. Thereby, the limit of self-healing based on reversible covalent bonds is reached in these materials. Due to the high stability of the oxime bonds in bulk materials no exchange reactions as well as no self-healing behavior could be observed. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44168.

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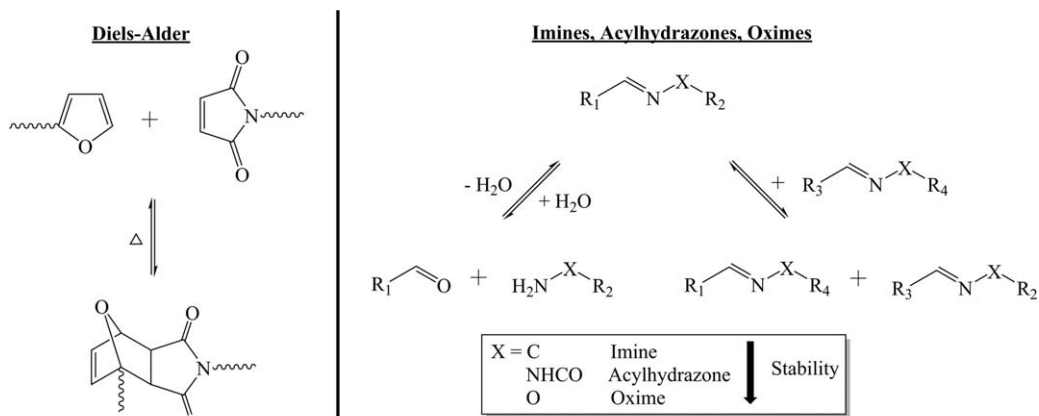
INTRODUCTION

Self-healing polymers are an important class of materials, which nowadays gained more and more attention. The introduction of self-healing capabilities into polymeric materials improves the security, lifetime as well as the reliability of such materials.^{1–3} One opportunity to design intrinsic self-healing polymers is the incorporation of reversible covalent bonds⁴ (based e.g., on the Diels-Alder^{5–7} or hetero Diels-Alder^{8,9} reaction, disulfides,^{10–12} acylhydrazones,^{13–15} and imines¹⁶) or weaker noncovalent bonds¹⁷ (e.g., hydrogen bonding,^{18,19} ionic interactions,^{20–22} or metal-ligand-interactions^{23–26}) into the polymeric matrix. Depending on the kind of reversible moiety, the resulting polymer properties as well as the conditions required for the self-healing process can be tuned. In this context, oxime bonds represent further interesting reversible groups for the incorporation into polymeric materials.^{27,28} Likewise, the structurally related acylhydrazones and imines, the oxime bond is well described as an acid labile linkage, which is highly reversible and dynamic. However, compared to acylhydrazones and imines, the oxime bond exhibits an improved stability followed by acylhydrazones and finally the weakest ones, the imines.²⁹ Consequently, rather stable polymeric materials can be fabricated, which are far less prone to undesired cleavage (e.g., hydrolysis) of the reversible moiety. The utilization of oximes (as well as acylhydrazones and

imines) offers the possibility to heal the induced damage by two different pathways. One option is the addition/elimination of water, which will result in the oxime cleavage with subsequent reformation under elimination of water. The second possibility is based on exchange reactions between two functional moieties (Scheme 1). In comparison the self-healing process of a Diels-Alder based polymer occurs on heating to a certain temperature resulting in the retro-Diels-Alder reaction (Scheme 1). Consequently, this addition reaction features distinct differences in comparison to the condensation reaction of oximes. Up to now, the reversibility of oxime bonds was only studied in solution or in gels (mainly hydrogels).^{28,30} Sumerlin and coworkers prepared some core-crosslinked star polymers via self-assembly based on an oxime network structure.³¹ Thereby, the authors could demonstrate the reversible nature of the bond by the addition of additional alkoxyamines or carbonyl compounds, which lead to a dissociation of the network due to competitive exchange reactions (at low pH values). This basic concept was further utilized for the synthesis of self-healing hydrogels.³² Due to the reversible nature of the oxime bond, these gels displayed a reversible gel-to-sol transition under acidic conditions and at ambient temperature in the presence of an excess of monofunctional alkoxyamine. This mechanism could also be utilized for the autonomous healing of such a system.

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Scheme 1. Schematic representation of self-healing mechanisms based on the Diels-Alder reaction (addition, left) and imines, acylhydrazones and oximes (condensation, right).

However, the reversibility of oxime bonds in the solid state has not been investigated so far. Herein, we report the synthesis of three different oxime crosslinkers (one aromatic and two aliphatic ones) and the copolymerization with different methacrylates in the bulk to fabricate oxime crosslinked polymer films. Their potential for self-healing applications as well as their mechanical properties were studied in detail. Furthermore, different additives were utilized in order to promote the desired self-healing behavior.

EXPERIMENTAL

All used chemicals were purchased from Aldrich, ABCR, TCI, and were used without further purification. Poly(ethylene glycol) methyl ether methacrylate, butyl methacrylate, 2-hydroxyethyl methacrylate, and lauryl methacrylate were passed over a short aluminum oxide plug. The solvents were dried over calcium chloride (chloroform, dichloromethane, triethylamine), sodium/benzophenone (toluene), and over active mole sieves (DMF). Chromatographic separation was performed with silica gel 60 from Merck.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 400 (400 MHz), a Bruker AC 300 (300 MHz), and a Bruker AC 250 (250 MHz) at 298 K. Chemical shifts are reported in parts per million (ppm, δ scale) relative to the residual signal of the solvent. Coupling constants are given in Hz.

Elemental analysis was carried out using a Vario EL III (Elementar) elemental analyzer.

The thermogravimetric analysis (TGA) was carried under nitrogen using a Netzsch TG 209 F1 and DSC was measured on a Netzsch DSC 204 F1 Phoenix instrument under a nitrogen atmosphere with a heating rate of 10 and 20 K min^{-1} .

Photopolymerization was carried out with the help of light curing chamber (Kulzer Dentacolor XS; Excitation from 320 to 520 nm; Intensity 250 mW/cm^2).

The self-healing behavior was studied with the help of an optical microscope by cutting the crosslinked films resulting in scratches on the micrometer scale and afterwards heating to a defined temperature (mostly 100 $^\circ\text{C}$) for several hours.

Tensile tests were performed on a standard tensile machine (Z020, Zwick/Roell) at room temperature with a testing speed of one millimeter per minute. The samples were prepared according to the DIN ISO 527-3 (total length: 115 mm; overall width: 25 mm). The gauge length was 25 mm with a width of 5 mm and a thickness of 1 mm.

Swelling experiments were performed with crosslinked polymers **P13** and **P21**. For this purpose, samples with 2 cm length, 1.5 cm width, and a thickness of 1 mm were prepared. The samples were placed into a 1 M solution of benzaldehyde in chloroform and allowed to swell for 48 hours. The weight of the polymer samples was determined before and after the swelling process.

Exchange reaction tests were performed with crosslinked polymers **P13** and **P21**. For this purpose, the polymers were placed into a lockable container filled with a 1 M solution of benzaldehyde in chloroform. The samples were heated to 100 $^\circ\text{C}$ in the drying oven for 21 hours to allow exchange reactions to take place.

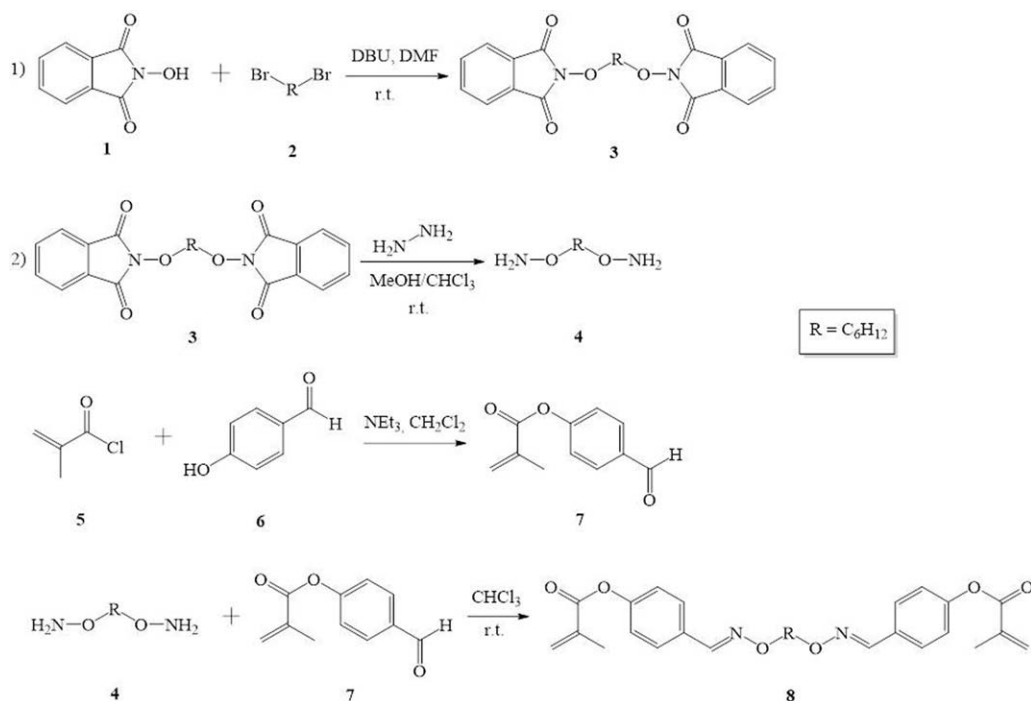
Synthesis of the Oxime Crosslinkers

Oxime I (8). A 0.82 g *O,O'*-Diaminohexandiol (5.53 mmol) and 3.16 g 4-formylphenyl methacrylate (16.60 mmol) were dissolved in 60 mL chloroform. Magnesium sulfate was added to the solution in order to bind the water resulting from the condensation reaction. The reaction mixture was stirred for seven days at room temperature. After that, the magnesium sulfate was filtered off and the solvent was removed. The crude product was purified by washing with methanol.

Yield: 1.95 g of a colorless solid, 72%

^1H NMR (300 MHz, CDCl_3): δ = 8.08 (s, 2H, CH=N), 7.62 (d, J = 9 Hz, 4H, Ar-H), 7.15 (d, J = 9 Hz, 4H, Ar-H), 6.36 (s, 2H, =CH₂), 5.78 (s, 2H, =CH₂), 4.19 (t, J = 7.5 Hz, 4H, -OCH₂), 2.08 (s, 6H, -CH₃), 1.76 (m, 4H, -CH₂), 1.48 (m, 4H, -CH₂) ppm.

^{13}C NMR (300 MHz, CDCl_3): δ = 165.6, 151.9, 147.3, 135.7, 130.1, 128.0, 127.5, 122.0, 74.3, 29.1, 25.8, 18.4 ppm.



Scheme 2. Schematic representation of the synthesis of the new oxime crosslinker **8**.

Elemental analysis. $C_{28}H_{32}N_2O_6$ calcd: C 68.28% H 6.55% N 5.69%

(492.57) found: C 68.25% H 6.51% N 5.82%

Oxime II (12)

A 1.00 g *O, O'*-Diaminopropanediol dihydrochloride (5.59 mmol) and 2.85 g 5-methacryloyl-1-pentantol (16.76 mmol) were dissolved in 60 mL methanol. The reaction mixture was stirred for two days at room temperature. The solvent was removed and, finally, the crude product was purified by column chromatography (silica, chloroform/ethyl acetate 20:1).

Yield: 1.63 g of a colorless liquid/oil, 71%

¹H NMR (300 MHz, $CDCl_3$): δ = 6.09 (s, 2H, =CH₂), 5.55 (s, 2H, =CH₂), 4.00–4.21 (m, 8H, –OCH₂), 2.40 (t, J = 7.5 Hz, 1H, –CH₂), 2.25 (t, J = 7.5 Hz, 3H, –CH₂), 1.80–2.00 (m, 18H, –CH₂, –CH₃) ppm. (*cis* and *trans* isomers)

¹³C NMR (300 MHz, $CDCl_3$): δ = 167.4, 156.9, 156.3, 136.3, 125.4, 70.3, 64.3, 64.1, 32.6, 29.0, 26.1, 25.4, 24.9, 20.1, 18.3, 14.2 ppm. (*cis* and *trans* isomers)

Elemental analysis. $C_{21}H_{34}N_2O_6$ calcd: C 61.44% H 8.35% N 6.82%

(410.51) found: C 61.20% H 8.36% N 6.54%

Oxime III (13)

A 0.50 g *O, O'*-Diaminohexandiol (3.37 mmol) and 1.72 g 5-methacryloyl-1-pentantol (10.12 mmol) were dissolved in 40 mL chloroform. The reaction mixture was stirred for four days at room temperature. The solvent was removed and, finally, the crude product was purified by column chromatography (silica, chloroform/ethyl acetate 20:1).

Yield: 1.40 g of a colorless liquid/oil, 92%

¹H NMR (300 MHz, $CDCl_3$): δ = 6.03 (s, 2H, =CH₂), 5.49 (s, 2H, =CH₂), 4.02–4.16 (m, 4H, –OCH₂), 3.85–4.00 (m, 4H, –OCH₂), 2.34 (t, J = 9 Hz, 1H, –CH₂), 2.19 (t, J = 7.5 Hz, 3H, –CH₂), 1.74–1.91 (m, 16H, –CH₂, –CH₃), 1.49–1.62 (m, 4H, –CH₂), 1.25–1.38 (m, 4H, –CH₂) ppm. (*cis* and *trans* isomers)

¹³C NMR (300 MHz, $CDCl_3$): δ = 167.4, 167.3, 156.6, 156.0, 136.4, 125.4, 73.4, 73.3, 64.3, 64.1, 32.6, 29.1, 29.0, 26.1, 25.9, 25.5, 24.9, 20.1, 18.3, 14.2 ppm. (*cis* and *trans* isomers)

Elemental analysis. $C_{21}H_{34}N_2O_6$ calcd: C 63.69% H 8.91% N 6.19%

(410.51) found: C 63.54% H 8.77% N 6.23%

RESULTS AND DISCUSSION

For the design of new oxime crosslinked polymers, a novel monomer (**8**) was synthesized (Scheme 2). For this purpose, di- (*N*-phthalimidooxy)hexane (**3**) was prepared by the reaction of

Table I. Composition of the Crosslinked Polymers P1 to P4 Utilizing Oxime Monomer **8** as Crosslinker and the Corresponding Thermal Properties

Crosslinked polymer	Oxime content [mol %]	Comonomer(s)	T_g [°C]	T_d [°C]
P1	10	PEGMEMA/BMA 1:3	–42	244
P2	5	PEGMEMA/BMA 1:3	–36	297
P3	7	PEGMEMA/BMA 1:3	–31	263
P4	12	PEGMEMA/BMA 1:3	–20	297

Table II. Composition of the Crosslinked Polymers P5 to P13 Utilizing 10 mol % of the Oxime Monomer **8** as Crosslinker and the Corresponding Thermal Properties

Crosslinked polymer	Comonomer(s)	Aldehyde monomer 7 [mol %]	Photo acid (PA)	Acid (A)	Acid developer (AD)	T_g [°C]	T_d [°C]
P5	PEGMEMA/BMA 1:3	10	—	—	—	-34	283
P6	PEGMEMA/BMA 1:3	10	—	AI	—	-27	300
P7	PEGMEMA/BMA 1:3	10	PAI	—	—	-27	251
P8	PEGMEMA/BMA 1:3	10	PAII	—	—	-27	306
P9	PEGMEMA/BMA 1:3 + 1 droplet HEMA	10	PAIII	—	—	-20	268
P10	PEGMEMA/BMA 1:3 + 1 droplet HEMA	10	PAIV	—	—	-20	302
P11	PEGMEMA/BMA 1:3	10	—	—	ADI	-34	277
P12	PEGMEMA/BMA 1:3	10	—	—	ADII	-34	266
P13	PEGMEMA/BMA 1:3	10	—	AII	—	-29	310

N-hydroxyphthalimid with 1,6-dibromohexane.³³ In the next step, di-(*N*-phthalimidoxy)hexane (**3**) was treated with hydrazine monohydrate resulting in *O,O'*-diaminohexandiol (**4**).³⁴ Furthermore, 4-hydroxy benzaldehyde (**6**) was esterified with methacryloyl chloride (**5**) to introduce a polymerizable group.^{13,35} The prepared monomer, 4-formylphenyl methacrylate (**8**), was finally reacted with the previously synthesized *O,O'*-diaminohexandiol (**4**) resulting in the aromatic oxime crosslinker **8**.

For the preparation of the oxime crosslinked polymers (**P1** to **P13**) with a potential self-healing behavior, the aromatic oxime crosslinker **8** was copolymerized with a mixture of poly(ethylene glycol) methyl ether methacrylate (PEGMEMA) ($M_n = 500$ g/mol) and butyl methacrylate (BMA) in the ratio 1:3 (Tables I and II). This ratio was chosen in order to obtain a relatively low glass transition temperature as well as a good solubility of the crosslinker. For this purpose, different amounts (5, 7, 10, and 12 mol %) of the oxime crosslinker **8** were chosen and the reaction was carried out in bulk in a special Teflon mould to obtain a polymer film for subsequent self-healing experiments. The polymerizations were performed via a photo-polymerization process using a photo cube ("Kulzer") and benzoin methyl ether

as initiator. A general schematic representation of the crosslinking process is depicted in Scheme 3.

After that, the obtained polymer films (Figure 1) were treated like the self-healing acylhydrazone polymers, that is, annealed overnight at 100 °C in the drying oven before a potential self-healing behavior was investigated.¹³

Furthermore, the thermal properties of the crosslinked polymers were analyzed by differential scanning calorimetry (DSC) and TGA. The composition of the crosslinked polymers (**P1** to **P13**) and the corresponding thermal properties are summarized in Tables I and II. All glass transition temperatures were in the range of -20 to -42 °C (as measured by DSC) and the polymers were stable up to 250 °C (investigated by TGA). The DSC and TGA of the crosslinked polymer **P13** is shown exemplary in the Supporting Information (Figures S13 and S14). These thermal properties are comparable to other self-healing polymethacrylate networks (e.g., Diels-Alder, metallopolymers) investigated prior by us.^{5,23,24}

In order to investigate a potential self-healing behavior, the polymer films were scratched by the utilization of a scalpel

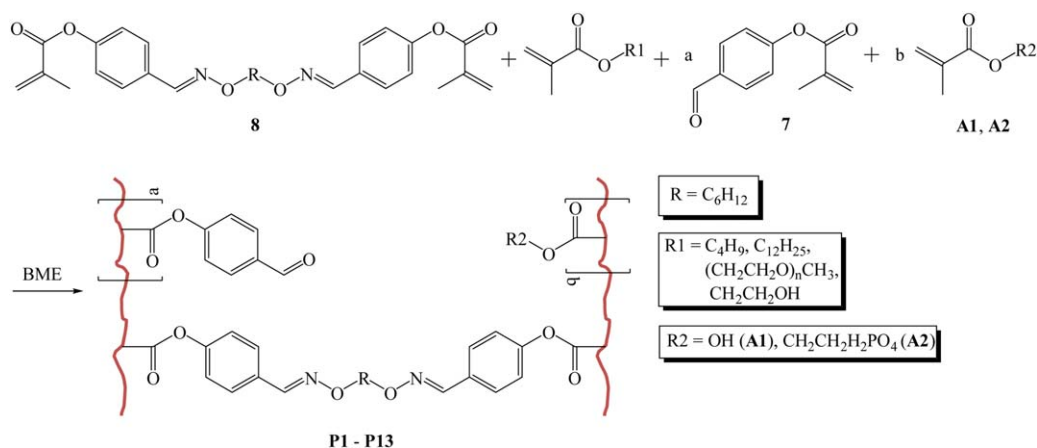
**Scheme 3.** Schematic representation of the crosslinking of oxime crosslinker **8**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 1. Polymer films of PI obtained via photo-polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

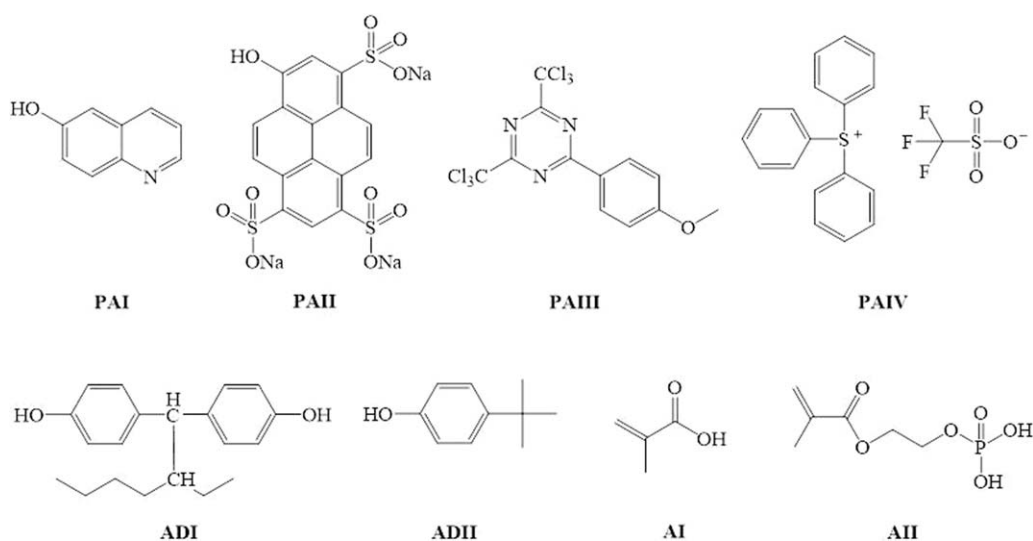
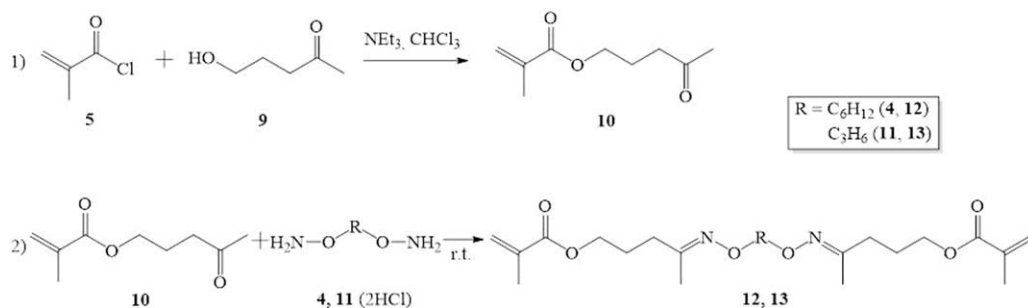


Figure 2. Additives to promote a potential self-healing behavior. From left to right: 6-Hydroxyquinoline (PAI), 8-hydroxypyrene-1,3,6-trisulfonic acid trisodium salt (PAII), 2-(4-methoxyphenyl)-4,6-bis(trichloromethyl)-1,3,5-triazine (PAIII), triphenylsulfonium triflate (PAIV), 4,4'-(2-ethylhexylidene)diphenol (ADI), 4-tert-butylphenol (ADII), methacrylic acid (AI), 2-methacryloyloxyethyl dihydrogen phosphate (AII).

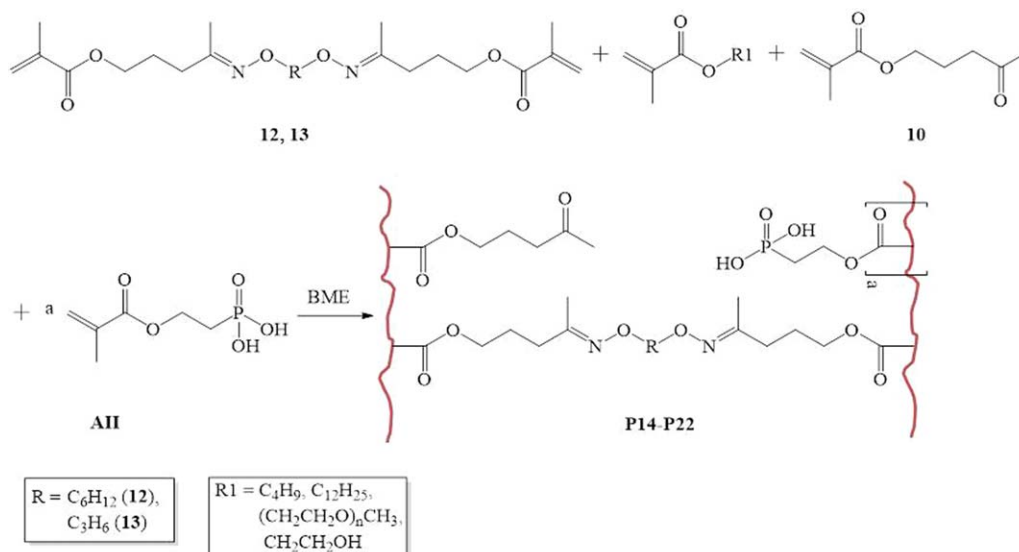
(scratches on the micrometer scale). Afterwards, the damaged polymer films were heated to a certain temperature for several hours to induce sufficient mobility for the self-healing process. This process was monitored by an optical microscope.

The first self-healing experiments were performed with the crosslinked polymer **P1** with an oxime content of 10 mol %. Heating the scratched polymer up to 100 °C for more than 5

days displayed no self-healing behavior and also further heating to 150 °C did not affect the scratch. Moreover, the influence of water steam as well as acidic atmosphere (acetic acid) on the damage was investigated (on heating the film at 100 °C). In literature, the oxime bond is well described as an acid labile linkage.²⁸ However, also this treatment did not result in a self-healing effect. Hereafter, the influence of different oxime



Scheme 4. Schematic representation of the synthesis of the aliphatic oxime crosslinkers **12** and **13**.



Scheme 5. Schematic representation of the crosslinking of oxime crosslinkers **12** and **13**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contents was explored. For this purpose, three new polymer films with an oxime content of 5 (**P2**), 7 (**P3**), and 12 mol % (**P4**) were synthesized. Thereby, the obtained polymer film with only 5 mol % was very soft and flexible while the one with 12 mol % was stiff and brittle. However, in all cases the induced scratches (via a scalpel) could not be removed upon heating to 100 °C for several hours.

Subsequently, other polymers (**P5** to **P13**) with an oxime (**8**) content of 10 mol % and a mixture of PEGMEMA and BMA (ratio 1:3) as comonomer were designed (Table II). This time also 10 mol % of the aldehyde monomer **7** (enabling transfer reactions as competitive reagent) as well as acid monomers (**AI** and **AII**), photo acids (**PAI-PAIV**), and acid developers (**ADI** and **ADII**) (providing protons) were intermixed to support a potential self-healing property (the exact compositions are given in the supporting information). However, all these additives, which are depicted in Figure 2, did not enable any self-healing behavior.

In literature, the aliphatic oximes are described to be less stable than the aromatic ones.²⁸ Consequently, the linker moiety was

exchanged. Thus, two new oxime linkers (**12** and **13**) were synthesized, which were both aliphatic (Scheme 4). 5-Hydroxy-2-pentanone (**9**) was esterified with methacryloyl chloride (**5**) and the obtained product was reacted with *O,O'*-diaminohexandiol (**4**) and *O,O'*-diaminopropanediol dihydrochloride (**11**), respectively, resulting in the aliphatic oximes **12** and **13**.

In order to obtain polymer films for additional studies, 10 mol % of the oxime crosslinkers (**12**, **13**) were copolymerized with different commercially available methacrylates (Scheme 5). Furthermore, 10 mol % of the ketone monomer **10** were incorporated to support the exchange reactions of the oximes. Finally, likewise to the previous crosslinked polymers, the influence of the very strong polymerizable acid (**AII**) as well as photo acids (**PAI-PAIV**) on a potential self-healing behavior was investigated (the exact compositions are given in the Supporting Information). The composition of the crosslinked polymers (**P14** to **P22**) and the corresponding thermal properties are summarized in Table III. All glass transition temperatures were in the range of -20 to -53 °C (DSC measurements) and the polymers were stable up to 230 °C (TGA investigations).

Table III. Composition of the Crosslinked Polymers P14 to P22 Utilizing 10 mol % of the Oxime Monomer **12** as Crosslinker and the Corresponding Thermal Properties

Crosslinked polymer	Comonomer(s)	Ketone monomer 10 [mol %]	Photo acid (PA)	Acid (A)	T_g [°C]	T_d [°C]
P14	PEGMEMA/BMA 1:3	10	—	—	-37	235
P15	BMA	10	—	—	34	254
P16	LMA	10	—	—	-53	226
P17	PEGMEMA/BMA 1:3	10	PAI	—	-28	245
P18	PEGMEMA/BMA 1:3	10	PAII	—	-26	262
P19	PEGMEMA/BMA 1:3 + 1 droplet HEMA	10	PAIII	—	-31	244
P20	PEGMEMA/BMA 1:3 + 1 droplet HEMA	10	PAIV	—	-22	258
P21	PEGMEMA/BMA 1:3	10	—	AII	-39	275
P22	PEGMEMA/BMA 1:3	10	—	AII	-31	244



Figure 3. Tensile test specimen of **P13**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Similar to the aromatic crosslinked polymers **P1** to **P13**, all aliphatic crosslinked oximes **P14** to **P22** did unfortunately not feature any self-healing behavior on heating to 100 °C for several hours.

The scratch healing experiments did not reveal any ability for self-healing of the fabricated polymer films. Therefore, also the mechanical properties of the polymers as well as tensile tests of “remended” samples were investigated. For this purpose, the polymers **P13**, **P21**, and **P22**, which are the most promising candidates for a potential self-healing, were utilized to produce bone-like test specimens (see Figure 3).

The obtained mechanical properties are summarized in Table IV. The polymers exhibit a relatively high elongation at break (ϵ_B) while the stress value (σ_{max}) is rather low. This behavior is similar to elastomers. However, the elongation at break is much too low for elastomeric materials. Thus, these crosslinked polymers feature a mixture of elastomeric and thermoplastic properties. Compared to **P21** and **P22**, the crosslinked polymer **P13** possesses an approximately three-times higher E-modulus and, thus, also a smaller value for the elongation at break was reached. This observation is due to the aromatic oxime crosslinker **8**, which is less flexible than the aliphatic ones. The stress-strain curve of the crosslinked polymer **P13** is exemplary depicted in Figure 4.

Moreover, the crosslinked polymers **P13**, **P21**, and **P22** were investigated with regard to a potential bulk healing ability. For this purpose, the broken specimen of the tensile test experiments were brought back into contact and placed for several hours at 100 °C in the drying oven. However, also this procedure did not result in a self-healing effect even so if the cut surfaces were pressed together with additional forces.

Table IV. Mechanical Properties of the Crosslinked Polymers **P13**, **P21**, and **P22**

Crosslinked polymer	σ_{max} [MPa]	E-modulus [MPa]	ϵ_B [%]
P13	1.14	9.30	16.42
P21	0.38	2.00	20.40
P22	0.46	1.60	32.38

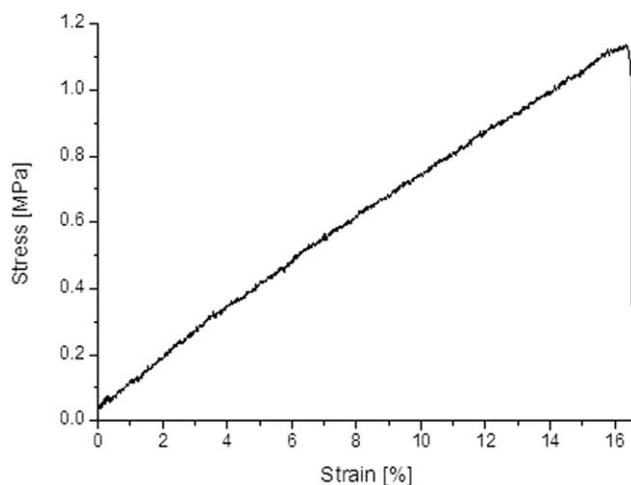


Figure 4. Stress-strain curve of the crosslinked polymer **P13**.

Furthermore, swelling experiments with the crosslinked polymers **P13** and **P21** were performed. For this purpose, a sample of each crosslinked polymer (2 cm length, 1.5 cm width, and a thickness of 1 mm) was placed into a 1 M solution of benzaldehyde in chloroform and allowed to swell for 48 hours. The weight of the polymer samples was determined before and after the swelling process and is summarized in Table V.

After the swelling process the crosslinked polymer **P13** featured a three times higher mass while the crosslinked polymer **P21** showed a 4.8 times mass increase. Thus, the crosslinked polymer **P21** with the aliphatic oxime crosslinker featured a lower crosslinking density compared to the one with the aromatic one **P13**.

Finally, the ability to undergo exchange reactions was investigated. Therefore, a sample of the crosslinked polymer **P13** and **P21**, respectively, was placed into a lockable container filled with a 1 M solution of benzaldehyde in chloroform. The samples were heated to 100 °C in the drying oven for 21 hours to enable exchange reactions with the competing benzaldehyde, which was applied in excess. If exchange reactions would take place the polymer should be dissolved after the heating process. However, the polymer remained insoluble and, consequently, no exchange reactions were present.

In summary, compared to imines and acylhydrazones, the stability of the oxime bond seems to be too high to obtain any self-healing property in a bulk material.²⁹ All additives, which are described in literature to support the reversibility of oximes (addition of acid monomers, photo acids, acid developers) as well as exchange reactions (addition of aldehyde/ketone monomer) were

Table V. Results of the Swelling Experiment with the Crosslinked Polymers **P13** and **P21**

Crosslinked polymer	Weight before swelling [g]	Weight after swelling [g]	Degree of swelling [%]
P13	0.225	0.670	300
P21	0.248	0.942	480

investigated and did not result in a self-healing polymer.³¹ Thus, the limit for self-healing in bulk materials seemed to be already reached by the utilization of the weaker acylhydrazone bonds. Thereby, small scratches (micrometer range) could be healed within 24 hours at 100 °C while larger scratches (up to 1 cm length) required already up to 64 hours.¹³ This observation reveals that already the acylhydrazone bond can be considered as a rather stable crosslinker. In contrast, imines are able to self-heal even at room temperature.¹⁶ As the oxime bond is described to be the one with the highest stability compared to imines and acylhydrazones, the reversibility/exchange did not/sufficiently occur in the fabricated solid materials.^{28,29}

CONCLUSIONS

A series of new oxime crosslinked polymers was synthesized and investigated with regard to a potential self-healing ability. For this purpose, three new oxime crosslinkers, one aromatic and two aliphatic ones, were synthesized and crosslinked by the copolymerization with different commercially available methyl methacrylates via a photo-polymerization process. Several additives were intermixed to promote the reversibility of the oximes as well as exchange reactions for example, carbonyl-containing monomers and different acids (acid monomers, photo acids, and acid developers). For all synthesized polymers, no self-healing behavior could be observed, due to the high stability of the oxime bonds. However, this kind of stability can also be beneficial for certain applications like highly stable coatings.

Can we learn anything for the design of self-healing materials? In contrast to reversible addition reactions (prime example the DA), exchange reactions within reversible polymers require lower stabilities of the corresponding reversible linker in order to obtain self-healing properties. The mobility generated within the network is not sufficient to close the scratches or to mend the cracked surfaces of the test specimen.

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REFERENCES

- Hager, M. D.; Greil, P.; Leyens, C.; van der Zwaag, S.; Schubert, U. S. *Adv. Mater.* **2010**, *22*, 5424.
- Zhang, M. Q.; Rong, M. Z. *Sci. China Chem.* **2012**, *55*, 648.
- Roy, N.; Bruchmann, B.; Lehn, J. M. *Chem. Soc. Rev.* **2015**, *44*, 3786.
- Kuhl, N.; Bode, S.; Hager, M. D.; Schubert, U. S. *Adv. Polym. Sci.* **2016**, DOI: 10.1007/1012_2015_1336.
- Kötteritzsch, J.; Stumpf, S.; Hoepfener, S.; Vitz, J.; Hager, M. D.; Schubert, U. S. *Macromol. Chem. Phys.* **2013**, *214*, 1636.
- Kötteritzsch, J.; Hager, M. D.; Schubert, U. S. *Polymer* **2015**, *69*, 321.
- Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nut, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698.
- Oehlenschlaeger, K. K.; Guimard, N. K.; Brandt, J.; Mueller, J. O.; Lin, C. Y.; Hilf, S.; Lederer, A.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. *Polym. Chem.* **2013**, *4*, 4348.
- Oehlenschlaeger, K. K.; Mueller, J. O.; Brandt, J.; Hilf, S.; Lederer, A.; Wilhelm, M.; Graf, R.; Coote, M. L.; Schmidt, F. G.; Barner-Kowollik, C. *Adv. Mater.* **2014**, *26*, 3561.
- Canadell, J.; Goossens, H.; Klumperman, B. *Macromolecules* **2011**, *44*, 2536.
- Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. *Adv. Mater.* **2012**, *24*, 3975.
- Lafont, U.; van Zeijl, H.; van der Zwaag, S. *ACS Appl. Mater. Interf.* **2012**, *4*, 6280.
- Kuhl, N.; Bode, S.; Bose, R. K.; Vitz, J.; Seifert, A.; Hoepfener, S.; Garcia, S. J.; Spange, S.; van der Zwaag, S.; Hager, M. D.; Schubert, U. S. *Adv. Funct. Mater.* **2015**, *25*, 3295.
- Deng, G.; Tang, C.; Li, F.; Jiang, H.; Chen, Y. *Macromolecules* **2010**, *43*, 1191.
- Deng, G.; Li, F.; Yu, H.; Liu, F.; Liu, C.; Sun, W.; Jiang, H.; Chen, Y. *ACS Macro Lett.* **2012**, *1*, 275.
- Lei, Z. Q.; Xie, P.; Rong, M. Z.; Zhang, M. Q. *J. Mater. Chem. A* **2015**, *3*, 19662.
- Herbst, F.; Döhler, D.; Michael, P.; Binder, W. H. *Macromol. Rapid Commun.* **2013**, *34*, 203.
- Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. *Nature* **2008**, *451*, 977.
- Herbst, F.; Seiffert, S.; Binder, W. H. *Polym. Chem.* **2012**, *3*, 3084.
- Kalista, S. J. Jr.; Ward, T. C. *J. R. Soc. Interf.* **2007**, *4*, 405.
- Kalista, S. J.; Pflug, J. R.; Varley, R. J. *Polym. Chem.* **2013**, *4*, 4910.
- Bose, R. K.; Hohlbein, N.; Garcia, S. J.; Schmidt, A. M.; van der Zwaag, S. *Phys. Chem. Chem. Phys.* **2015**, *17*, 1697.
- Bode, S.; Zedler, L.; Schacher, F. H.; Dietzek, B.; Schmitt, M.; Popp, J.; Hager, M. D.; Schubert, U. S. *Adv. Mater.* **2013**, *25*, 1634.
- Bode, S.; Bose, R. K.; Matthes, S.; Ehrhardt, M.; Seifert, A.; Schacher, F. H.; Paulus, R. M.; Stumpf, S.; Sandmann, B.; Vitz, J.; Winter, A.; Hoepfener, S.; Garcia, S. J.; Spange, S.; van der Zwaag, S.; Hager, M. D.; Schubert, U. S. *Polym. Chem.* **2013**, *4*, 4966.
- Burnworth, M.; Tang, L.; Kumpfer, J. R.; Duncan, A. J.; Beyer, F. L.; Fiore, G. L.; Rowan, S. J.; Weder, C. *Nature* **2011**, *472*, 334.
- Bode, S.; Enke, M.; Bose, R. K.; Schacher, F. H.; Garcia, S. J.; van der Zwaag, S.; Hager, M. D.; Schubert, U. S. *J. Mater. Chem. A* **2015**, *3*, 22145.
- Herrmann, A. *Org. Biomol. Chem.* **2009**, *7*, 3195.
- Polyakov, V. A.; Nelen, M. I.; Nazarpak-Kandlousy, N.; Ryabov, A. D.; Eliseev, A. V. *J. Phys. Org. Chem.* **1999**, *12*, 357.
- Kalia, J.; Raines, R. T. *Angew. Chem. Int. Ed.* **2008**, *47*, 7523.

30. Jin, Y.; Song, L.; Su, Y.; Zhu, L.; Pang, Y.; Qiu, F.; Tong, G.; Yan, D.; Zhu, B.; Zhu, X. *Biomacromolecules* **2011**, *12*, 3460.
31. Mukherjee, S.; Bapat, A. P.; Hill, M. R.; Sumerlin, B. S. *Polym. Chem.* **2014**, *5*, 6923.
32. Mukherjee, S.; Hill, M. R.; Sumerlin, B. S. *Soft Matter* **2015**, *11*, 6152.
33. Kim, J. N.; Kim, K. M.; Ryu, E. K. *Synth. Commun.* **1992**, *22*, 1427.
34. Petrassi, H. M.; Sharpless, K. B.; Kelly, J. W. *Org. Lett.* **2001**, *3*, 139.
35. Garcia-Acosta, B.; Garcia, F.; Garcia, J. M.; Martinez-Manez, R.; Sancenon, F.; San-Jose, N.; Soto, J. *Org. Lett.* **2007**, *9*, 2429.