Acylhydrazones as Reversible Covalent Crosslinkers for Self-Healing Polymers

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The utilization of dynamic covalent and noncovalent bonds in polymeric materials offers the possibility to regenerate mechanical damage, inflicted on the material, and is therefore of great interest in the field of self-healing materials. For the design of a new class of self-healing materials, methacrylate containing copolymers with acylhydrazones as reversible covalent crosslinkers are utilized. The self-healing polymer networks are obtained by a bulk polymerization of an acylhydrazone crosslinker and commercially available methacrylates as comonomers to fine-tune the T_g of the systems. The influence of the amount of acylhydrazone crosslinker and the self-healing behavior of the polymers is studied in detail. Furthermore, the basic healing mechanism and the corresponding mechanical properties are analyzed.

1. Introduction

Self-healing materials have become an important scientific and economic topic due to their ability to recover local mechanical damage and, therefore, to improve the reliability of these materials. Thereby, particularly polymers gained much attention, due to the large variety of different healing mechanisms available compared to other classes of materials (e.g., metals, ceramics). However, conventional polymers do not feature this healing ability unless external healing agents are encapsulated or specific functional groups are introduced into the polymeric material.[1–3] For this purpose, the incorporation of reversible covalent bonds (e.g., based on the Diels–Alder,[4–6] hetero-Diels–Alder[7] reaction or disulfides)[8,9] or weaker noncovalent bonds (e.g., hydrogen bonding,[10–12] ionic interactions,[13] or metal-ligand-interactions)[14–17] into the polymeric matrix offer the possibility to achieve an intrinsic self-healing behavior.

The incorporation of acylhydrazones into polymeric materials to promote self-healing can be related to the constitutional dynamic chemistry (CDC).[18] Herein, the acylhydrazone functionality enables both the supramolecular as well as the molecular linkage due to the dynamic character of the imino bond and the hydrogen bonding through the amide moiety. In previous studies, Lehn and co-workers investigated the reversibility of acylhydrazones in solution. For this purpose, the authors synthesized dynamic covalent polyacylhydrazones, so called dynamers, by polycondensation of dihydrazides with dicarbonyl compounds and demonstrated the monomer exchange reactions. This process could be achieved in response to external stimuli and, thus, it is possible to change the physical properties of these polymers in a controlled fashion.[19,20] Furthermore, Lehn and co-workers synthesized a rubber-like self-healing polymer by polycondensation of a siloxane-based dialdehyde and a bisacylhydrazone. The prepared polymer film was cut into two pieces and was completely healed within a few hours by bringing together the two cut surfaces followed by gentle pressing of the overlapped surfaces. This process occurred at room temperature without any additional pressure or load.[21]

Deng et al. synthesized covalent crosslinked polymer gels based on acylhydrazone bonds and examined their dynamic behavior. These gels displayed self-healing properties based on the reversibility of the acylhydrazone bond. The self-healing process already occurred after simply putting the cracked gel plates together without using any external stimulus at room temperature.[22] This basic concept could be improved later by the synthesis of a polymer hydrogel based on acylhydrazone as well as disulfide bonds. The recovery of mechanical damage was possible due to the exchange reaction of either an acylhydrazone

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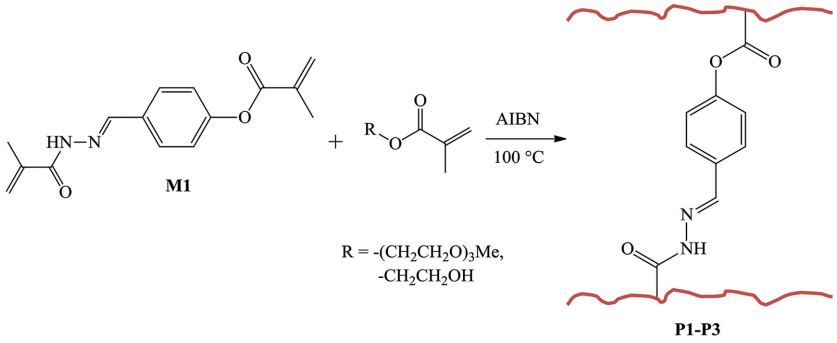
or a disulfide unit. Also in this case the self-healing process occurred autonomously without any external intervention.[22,23]

However, the self-healing of covalently crosslinked polymers based on acylhydrazone bonds (i.e., linear polymers with reversible crosslinker) has, to the best of our knowledge, not been reported so far. For this purpose, an acylhydrazone functionalized with two polymerizable groups was designed and this compound was utilized for the copolymerization with different commercially available methacrylates in bulk to create a polymer film. The resulting materials were investigated regarding a potential self-healing behavior and the self-healing mechanism was studied in detail. Finally, the thermal and mechanical properties were investigated by different methods.



Scheme 1. Schematic representation of the synthesis of acylhydrazone crosslinked copolymers.

2. Results and Discussions

For the design of new self-healing materials based on acylhydrazone crosslinked polymers the acylhydrazone monomer (**M1**) containing two polymerizable groups was synthesized. For this purpose, a condensation reaction of 4-formylphenyl methacrylate (**1**) with methacryloyl hydrazide (**2**) was performed (Supporting Information, Scheme S1). This reaction proceeded smoothly at room temperature by adding magnesium sulfate to the reaction mixture to bind the released water. In order to perform a bulk polymerization, a good solubility of the crosslinker monomer **M1** in the comonomers is required. Therefore, solubility tests were performed and it could be shown that the acylhydrazone crosslinker monomer **M1** displayed a good solubility in polar methacrylates, like 2-hydroxyethyl methacrylate and triethylene glycol methylether methacrylate (up to 5 mol%); however, a rather low solubility was observed in nonpolar alkyl methacrylates (e.g., lauryl methacrylate).

In the next step, **M1** was copolymerized with triethylene glycol methylether methacrylate (TEGMEMA), 2-hydroxyethyl methacrylate (HEMA), and a 50:50 mixture of both (HEMA and TEGMEMA) using a free radical polymerization process (**Scheme 1**). The utilization of different methacrylates as comonomer offers the possibility to adjust the flexibility of the polymer backbone and, therefore, the glass transition temperature (T_g). Thereby, the polymer copolymerized with TEGMEMA revealed the lowest T_g (–33 °C) and the one with HEMA the highest one (101 °C). Based on the fact that only 5 mol% of acylhydrazone are soluble in TEGMEMA and 10 mol% in HEMA, a copolymer with a 50:50 polymer mixture of TEGMEMA and HEMA was synthesized, too. By this approach, a relatively low T_g (45 °C) could be obtained. Moreover, 5 to 10 mol% of acylhydrazone were incorporated into the polymer network to investigate the influence of the acylhydrazone content with regard to the self-healing properties.

The differential scanning calorimetry (DSC) curves feature glass transition temperatures in the range of –33 to 101 °C depending on the used comonomer (Supporting Information, Figure S1). The thermal properties of the crosslinked copolymers are summarized in **Table 1**. All materials are thermally stable up to 200 °C.

Furthermore, the effect of annealing in relation to the self-healing behavior was investigated for the crosslinked polymer **P2** by dynamic-mechanical thermal analysis (DMTA). For this purpose, two polymer films were synthesized. One polymer film was annealed for 7 d at 100 °C and the other one was used without further thermal treatment. The results of the DMTA measurements are depicted in **Figures 1** and **2**. For both polymer films the storage modulus (G′) is higher than the loss modulus (G″). As a consequence, the elastic deformation behavior predominates over the viscous behavior and this leads to some stiffness of the polymer films. The polymer film, which was not annealed, displayed a T_g of 48 °C while the T_g of the annealed one raised to 70 °C, presumably due to a rearrangement of the polymer network combined with the (re) formation of hydrogen bonds. Moreover, the maximum of the tan δ curve of the annealed sample is slightly higher than the sample which was used without additional thermal treatment. Thus, the rigidity increased by annealing the sample.

Furthermore, the frequency and time dependency for the annealed polymer film were investigated. The storage and the loss modulus stayed nearly constant by varying the frequency (in the 1 to 40 Hz range) as depicted in Supporting Information, Figure S2. The measurement of the storage and loss modulus over time also featured no significant changes (Supporting Information, Figure S3). For the conditions examined, the polymer film revealed no creep elongation.

In order to obtain polymer films, the polymerizations were performed in bulk in a special glass or Teflon mold. Afterwards, the resulting polymer films **P1** to **P3** were investigated for their potential self-healing behavior. For this purpose, damage was introduced into the material by cutting them with a scalpel. The

Table 1. Composition and thermal properties of the crosslinked copolymers.

Crosslinked polymer	Acylhydrazone monomer	Comonomer	Acylhydrazone content	Glass transition temperature (T_g)	Decomposition temperature (T_d)
P1	**M1**	TEGMEMA	5 mol%	–33 °C	289 °C
P2	**M1**	TEGMEMA HEMA	10 mol%	45 °C	303 °C
P3	**M1**	HEMA	10 mol%	101 °C	321 °C

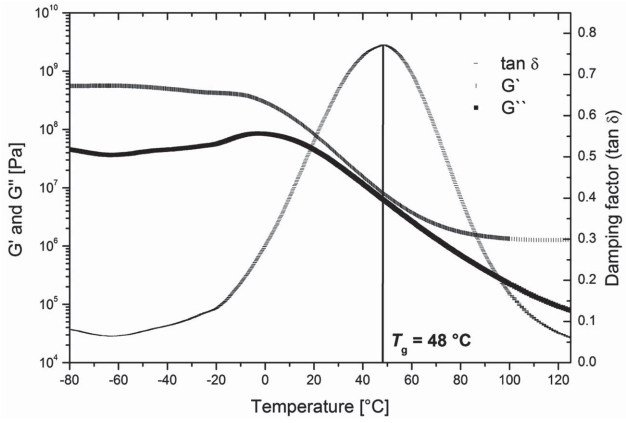


Figure 1. DMTA measurement: –80 °C to 125 °C of the polymer film **P2**.

resulting damaged materials were heated to a certain temperature to induce sufficient mobility for the self-healing process. This process was monitored with an optical microscope.

The first self-healing experiments were performed with the crosslinked copolymer **P1**, based on TEGMEMA as comonomer and an acylhydrazone content of 5 mol%. This polymer film displayed no self-healing properties. In contrast, the crack became even larger upon heating to 100 °C. This behavior may be attributed to a kind of shape memory effect.[24–26] The polymerization leads to shrinkage, which induces stress within the polymer film. The stress is released when a scratch is inflicted on the polymer film and, therefore, the scratch becomes larger upon thermal treatment. To overcome this behavior, polymer films were annealed before the self-healing studies were carried out. This should allow a reduction of the stress within the polymer films. Nevertheless, polymer film **P1** displayed no self-healing effect even after annealing for 5 d at 100 °C due to the rather low acylhydrazone content. The self-healing experiments for the crosslinked polymer **P2**, based on a 50:50 mixture of TEGMEMA and HEMA as comonomers and an acylhydrazone content of 10 mol%, are depicted in **Figure 3** (Supporting Information, Figure S4). This polymer film was again annealed for 5 d at 100 °C before scratches were inflicted. This composition was able to heal scratches up to one centimeter length.

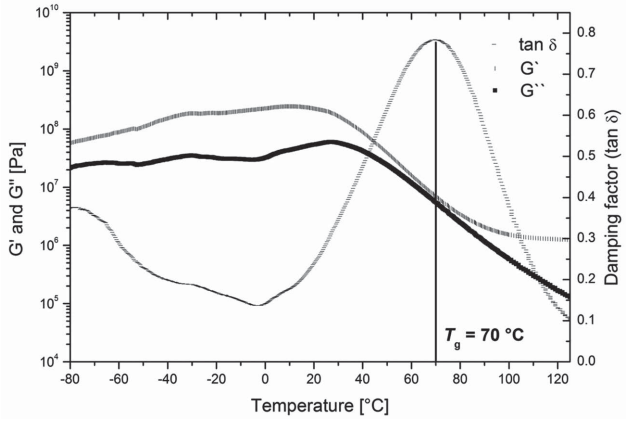


Figure 2. DMTA measurement: –80 °C to 125 °C of the annealed polymer film **P2**.

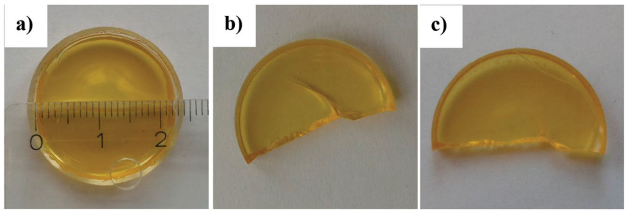


Figure 3. Self-healing study of crosslinked polymer **P2**: a) Annealed polymer film, b) scratch before heating, and c) healed scratch after heating for 64 h at 100 °C.

Consequently, at least 10 mol% of acylhydrazone is required to obtain self-healing properties.

Moreover, the HEMA based copolymer (**P3**) was investigated and the healing process at 125 °C is displayed in Supporting Information, Figure S5. This crosslinked copolymer was able to heal only smaller scratches due to the high T_g (length: 500 µm; width: 15 µm).

In order to quantify the self-healing behavior in more detail, scratch testing experiments with an in situ heater and a profilometer were performed for polymers **P2** and **P3**. For this purpose, polymer films were prepared on aluminum plates and annealed for 5 d at 100 °C. At first, a representative profile of each polymer coating along a 5 mm scratch length was recorded. Due to the fact that the samples were glassy at room temperature, resulting in brittle fracture and delamination of the coating, the samples were heated to 50 °C and held isothermally at this temperature for at least 2 h prior to testing. Scratches with a total length of 5 mm were produced using a progressive load from 0.03 to 30 N along the length of the scratch. Based on these experiments, a load of 20 N was found to be sufficient to create a scratch that just penetrated the polymer completely to reach the metal substrate. This approach enables a clear microscopic analysis of the scratched area after healing. Since polymeric samples exhibit an elastic recovery after scratching, a second measurement at a minimal load of 0.03 N was performed along the scratch to determine the elastic recovery. The difference between the penetration depth (Pd) and the residual depth (Rd, after elastic recovery) normalized to the penetration depth indicates the fractional elastic recovery of each sample. The sample was then heated for 24 h to 100 and 150 °C, respectively, to study the healing process. Subsequently, the samples were allowed to cool to 50 °C for additional 2 h followed by a profile scan of the surface. The results of these measurements are depicted in **Figures 4** and **5**. The post-healing profile scan follows the original profile of the undamaged sample very closely, thus indicating a high extent of recovery.

In case of polymer **P3**, the scratch penetrated into the aluminum substrate, but the scratch volume was entirely filled by the healing processes as shown by the in situ microscopy studies displayed in **Figure 6**. The required time for the healing process is longer than for the previously described acyhydrazone systems.[21,22] However, these systems were rubber-like materials and gels, respectively. In contrast, the herein investigated polymeric materials are crosslinked polymer films. The healing time is comparable to other crosslinked methacrylate systems, e.g., metallopolymers.[14]

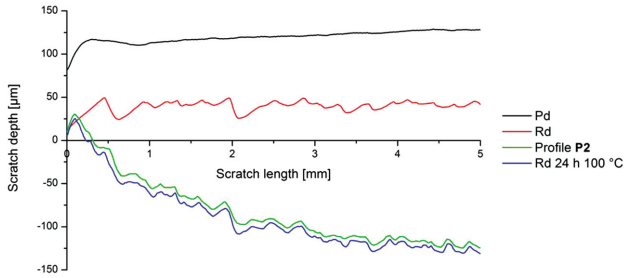


Figure 4. Healing recovery of the polymer **P2** after 24 h at 100 °C (negative values for sample height indicate sample thickness; positive values indicate scratch depth).

In order to obtain information about the self-healing mechanism, a temperature depending Fourier transform infrared (FT-IR) measurement was performed for the crosslinked polymer **P2** (**Figure 7**). To identify the corresponding signals of the acylhydrazone, a model compound **M2** (Supporting Information, Scheme S2) and a polymer mixture **P4** (HEMA/TEGMEMA 50:50) without any amount of crosslinker were synthesized. FT-IR measurements were recorded for both compounds and the resulting spectra were overlaid (Supporting Information, Figure S6). The assignment of the characteristic peaks is provided in Supporting Information, Table S1, e.g., the N-H vibration of the model acylhydrazone **M2** at 3700 cm^{-1}.

In the temperature dependent FT-IR spectra no significant changes can be observed with respect to the characteristic peaks of the model acylhydrazone **M2** and the polymer mixture **P4** (TEGMEMA/HEMA) in the range of 35 to 110 °C. Consequently, no cleavage of the acylhydrazones by water (from the environment) occurred. Thus, the healing mechanism is presumably based on the exchange reaction of two acylhydrazones.[19,21]

In order to further investigate the self-healing mechanism on a molecular level, solid state NMR experiments were performed for the crosslinked polymer **P2**. At first, a ^{1}H MAS-NMR of **P2** at room temperature was performed using fast magic angle spinning (MAS) (**Figure 8**). After that, the sample was heated to 70 °C and was measured again (Figure 8). The spinning rate of the rotor was reduced from 15 to 12 kHz to guarantee a stable spinning. The resulting overlaid spectra (Figure 8) depict clearly changes. At 70 °C the signals appear sharp and with very small line thicknesses compared to the one at room temperature. Thus, the material has passed the glass transition temperature

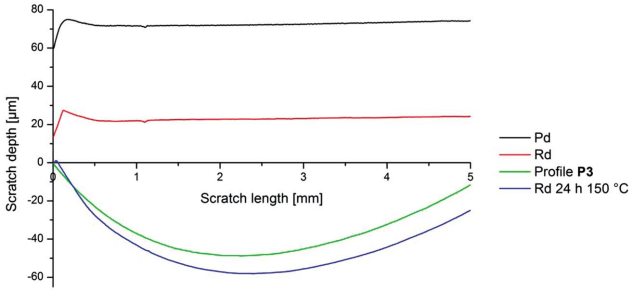


Figure 5. Healing recovery of the polymer **P3** after 24 h at 150 °C (negative values for sample height indicate the sample thickness; positive values indicate the scratch depth).

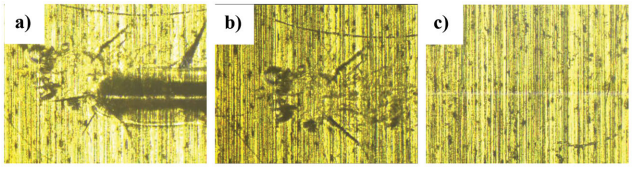


Figure 6. Scratch healing for polymer **P3**: a) Scratch caused by the indenter tip, b) disappearance of the scratch after being held at 150 °C for 24 h, and c) complete scratch recovery.

(T_g (**P2**) = 45 °C), which results in a higher flexibility. After cooling to room temperature again, another ^{1}H MAS-NMR was performed and the resulting overlaid spectra are depicted in **Figure 9**. The line thickness of the start spectrum is smaller than the one after the sample was heated at 70 °C and the signal intensities switched slightly. Consequently, the order of the sample before heating to 70 °C is presumably higher than after cooling again. Furthermore, the effect of a higher rotation frequency, which also results in sharper signals, can be seen in Figure 9. Besides the ^{1}H MAS-NMR experiments also ^{13}C CP-MAS-NMR spectra were recorded using cross polarization (CP) technique to enhance the sensitivity of the ^{13}C nucleus (Supporting Information, Figures S7 and S8). Thereby, the sample was measured at room temperature before heating, at 70 °C and after cooling. With regard to the first overlaid spectra (Supporting Information, Figure S7) some changes in the signal intensities can be seen, which were caused by the increased flexibility of the polymer network that affect the efficiency of magnetization transfer of cross polarization (Hartmann–Hahn matching). The second experiment, which is depicted in Supporting Information, Figure S8, shows that at room temperature no significant changes could be obtained in the ^{13}C CP-MAS-NMR before and after heating the sample. In summary, the solid NMR experiments demonstrate that there are no significant changes on the molecular structure during heating the sample to 70 °C. These findings support the hypothesis that the healing mechanism is based on the exchange reaction of two acylhydrazones moieties.

The general concept of the proposed self-healing mechanism is depicted in **Figure 10**. After the infliction of damage, water could potentially interact with the damaged surfaces. This could lead to the cleavage of a small fraction of acylhydrazone moieties resulting in free aldehydes and hydrazides. However, neither the solid state NMR nor the IR measurements provide any information for a cleavage of the reversible crosslinker. Additionally, acylhydrazones can undergo a reversible metathesis reaction resulting in an exchange of two acylhydrazone moieties.[19,20] Consequently, this process provides the required mobility for the self-healing at elevated temperatures. After cooling, the network is immobilized again.

3. Conclusion

Polymer films displaying a self-healing behavior were prepared by the copolymerization of an acylhydrazone, containing two polymerizable groups, with different methacrylate monomers by using a free radical polymerization process. The polymer film which contains less than 10 mol% of acylhydrazone

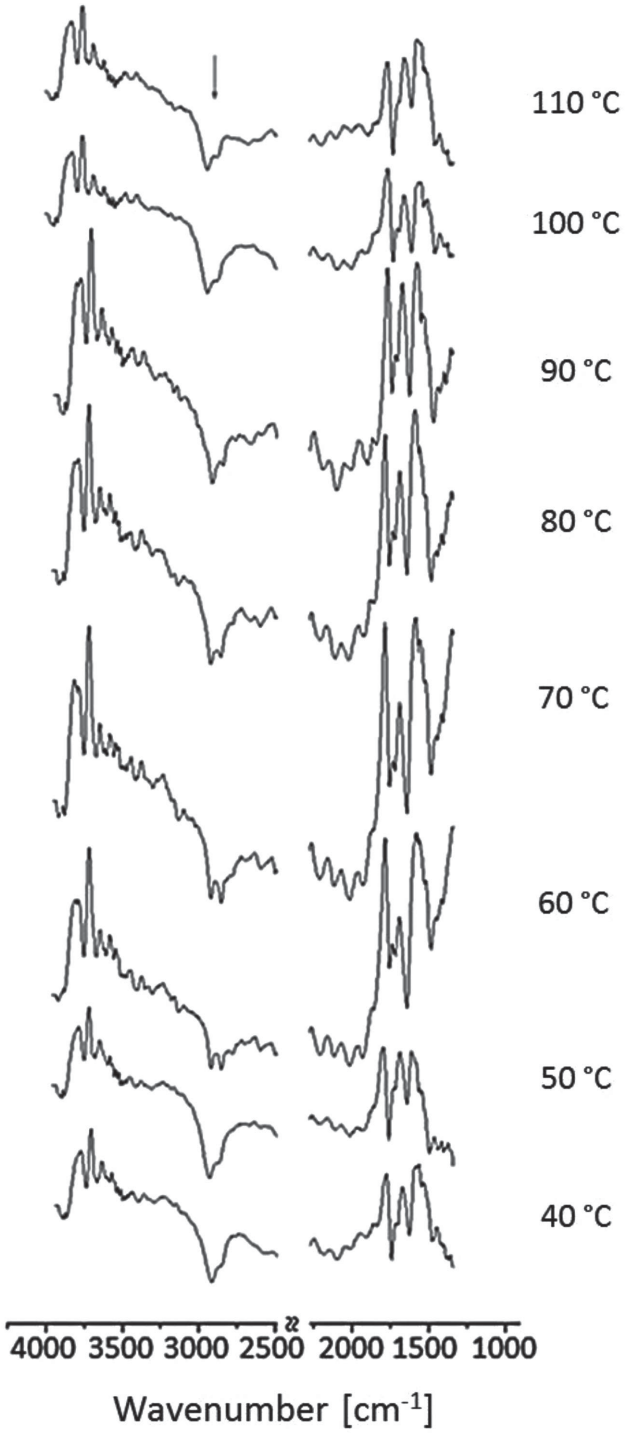


Figure 7. Temperature depending IR measurements of the crosslinked polymer **P2**.

displayed no self-healing properties. In contrast, polymers **P2** and **P3** with 10 mol% of crosslinker revealed a very good self-healing effect at elevated temperatures. These polymers were able to heal deep scratches up to one centimeter in length at temperatures around 125 °C. The FT-IR spectra as well as the solid state NMR experiments showed that the structure stays

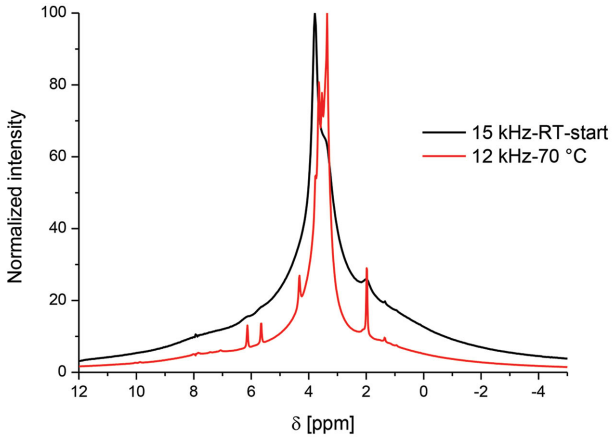


Figure 8. ^{1}H-MAS-NMR of **P2** at RT and at 70 °C.

the same upon heating and, thus, that exchange reactions are a possible explanation for the healing mechanism. In future, the self-healing properties could be further improved, e.g., the healing temperature could be tuned to the intended use temperature and the healing kinetics to the desired damage repair time by the utilization of alternative methacrylate monomers as well as other acylhydrazones.

4. Experimental Section

Materials and Instrumentations: All used chemicals were purchased from Fluka, Aldrich, ABCR and were used without further purification. 2-Hydroxyethyl methacrylate and triethylene glycol methylether methacrylate were passed over a short aluminum oxide plug. The solvents were dried over calcium chloride (chloroform, dichloromethane, triethylamine). Chromatographic separation was performed with silica gel 60 from Merck. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 400 (400 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. Solid state NMR measurements were performed at 9.4 T on a Bruker Avance 400 spectrometer equipped with double-tuned probes capable of MAS (magic angle spinning). The samples

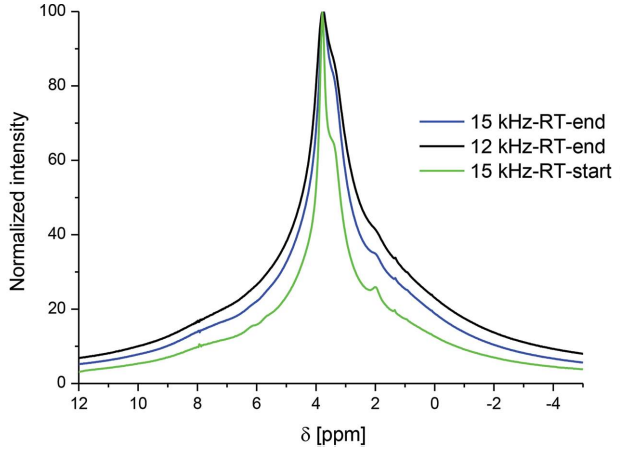


Figure 9. ^{1}H-MAS-NMR of **P2** before and after heating at 70 °C.

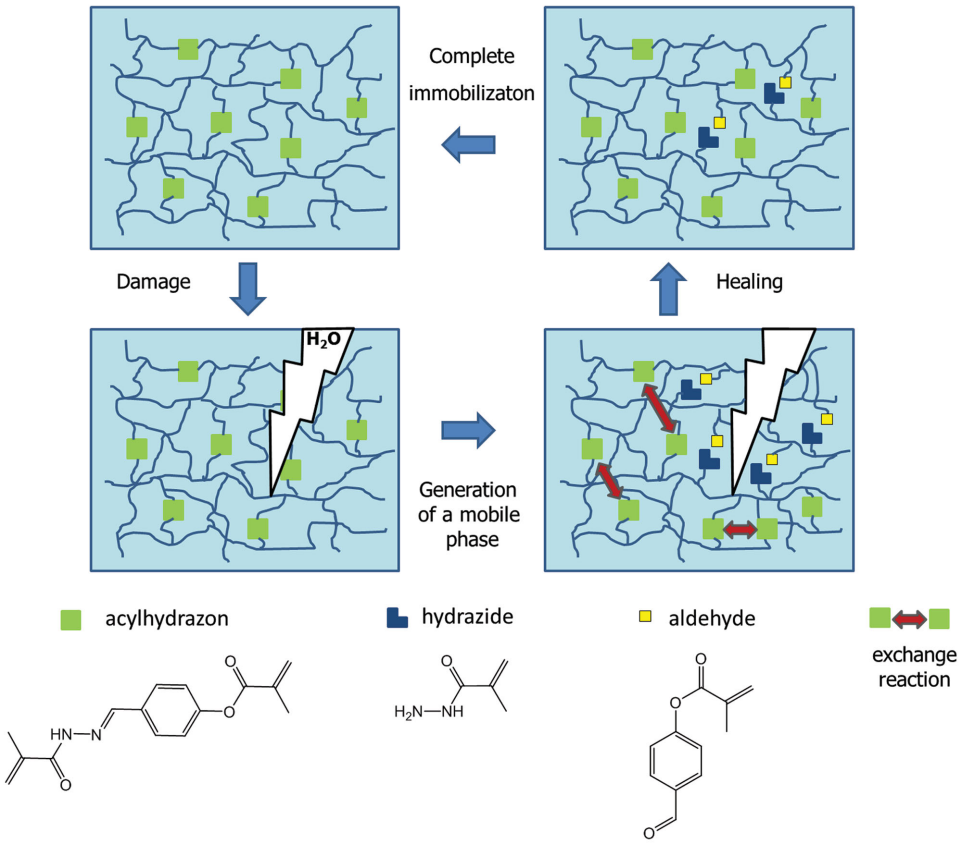


Figure 10. General concept of self-healing processes based on reversible acylhydrazones.

were packed in 3.2 mm rotors made of zirconium oxide spinning at 15 and 12 kHz. ^{1}H-MAS-NMR was obtained with single pulse excitation (90° pulse, pulse length 2.4 µs) and a recycle delay of 6 s. ^{13}C-{^{1}H}-CP-MAS-NMR spectra were acquired using cross polarization (CP) technique with contact time of 3 ms to enhance the sensitivity, a recycle delay of 6 s and ^{1}H decoupling using a TPPM (two pulse phase modulation) pulse sequence. The spectra are referenced with respect to tetramethyl silane (TMS) using TTSS (tetrakis(trimethylsilyl)silane) as secondary standard (3.55 ppm for ^{13}C, 0.27 ppm for ^{1}H). The spectra were acquired at room temperature and at 70 °C with 11 342 to 38 309 scans. 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}. The FT-IR spectra were measured on a Bruker Tensor 37 utilizing a temperature controlled sample holder from Harrick (Demountable Liquid Cell TFC-M13–3). In such experiments, the flow operation mode was turned off. The sample was used in powder form and was pressed between two calcium fluoride windows. All measurements were carried out in transmission mode. All DMTA experiments were performed on a MCR 301 rheometer from Anton Paar using convection oven device CTD 450 which covers a broad temperature range. The test specimen was 12.5 mm × 28.5 mm × 4 mm which was polymerized in a special Teflon mold and mounted into the solid rectangular fixture (SRF) device for DMTA measurements in torsion. The instrument was operated by setting the sample gap at 15 mm and a frequency of 10 Hz with 0.1% strain. The sample was cooled to –80 °C and the measurement was conducted during the warm-up cycle to 125 °C. Furthermore, the frequency and time dependency was investigated by keeping the temperature constant at 25 °C. The frequency was varied from 0.1 to 100 Hz and the time dependency was measured at a constant frequency of 10 Hz. Moreover, the temperature dependency above 125 °C was investigated by heating the sample up to 220 °C (10 Hz, 0.1% strain). Micro-scratch testing (CSM micro-scratch tester) was performed to obtain accurate damage healing data. Using a 100 µm diameter Rockwell diamond tip, first a pre-scan at 0.03 N load was performed to gauge the profile of each coating and to subtract the coating inhomogeneity from the scratch depth measurements. Scratches with a total length of 5 mm were produced using a progressive load from 0.03 to 30 N along the length of the scratch. At 20 N load the indenter tip penetrated to the aluminum substrate, which allows a clear microscopic analysis of the scratched area after healing. Therefore, for the subsequent tests, a constant load of 20 N was selected. Scratches were performed at 50 °C in order to ensure that the polymer was near its glass transition to prevent brittle failure or delamination. A post scan with 0.03 N load along the same track as the original scratch was performed within 60 s of the completion of the high load scan to determine and quantify the elastic recovery of the scratch. Upon determination of the elastic recovery, the sample was heated at a rate of 50 °C min^{-1} to temperatures of 100 or 150 °C. This temperature was held for 24 h. Upon cooling to 50 °C a final scan of the scratch again using a load of 0.03 N was performed to determine scratch healing of the polymer. The synthesis of the acylhydrazone monomers are given in the Supporting Information.

General Procedure for the Polymerization: The desired amounts of the two monomers were mixed together. Azobis(isobutyronitril) (AIBN) was used as initiator. The ratio of [M] to [I] was always 200/1. The amounts of all reagents are summarized in **Table 2**. The reaction was performed in the drying oven at 100 °C overnight.

Table 2. Composition of the polymerization reactions.

Crosslinked polymer	Monomers	Ratio of the monomers [mmol]
P1	**M1**	0.22
	TEGMEMA	4.31
P2	**M1**	0.77
	TEGMEMA	3.84
	HEMA	3.84
P3	**M1**	0.77
	HEMA	7.68

Supporting Information

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

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