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# Cyclic Acetals as Expanding Monomers to Reduce Shrinkage

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Abstract: Polarity-reversal catalysts (PRCs) for hydrogen-atom transfer reactions have been known in radical chemistry for more than 60 years but are rarely described and utilized in the field of photopolymerization up to now. Herein, we present the use of thiols in a unique dual function as thiol-ene click reagents and as polarityreversal catalyst (PRC) for the radical-mediated redox rearrangements of benzylidene acetals. During the rearrangement reaction, cyclic benzylidene acetals are transformed into benzoate esters leading to a significant volumetric expansion to reduce thermoset shrinkage. We were able to show that this expansion on a molecular level reduces shrinkage and polymerization stress but does not significantly affect the (thermo-)mechanical properties of the cross-linked networks. One of the key advantages of this process lies in its simplicity. No additives like sensitizers or combinations of different initiators (radical and cationic) are needed. Furthermore, the same light source can be used for both the polymerization reaction and expansion through rearrangement. Additionally, the applied photoinitiator enables spatial and temporal control of the polymerization; thus, the developed system can be an excellent platform for additive manufacturing processes.

#### Introduction

Shrinkage stress in polymers may lead to the formation of microcracks, warping, or low surface quality and ultimately has a negative impact on the mechanical properties. Volumetric shrinkage and shrinkage stress are caused by distance changes between atoms during polymerization. In the uncured liquid state, the distance between monomers equals the Van-der-Waals contact distance of 3.4 Å. When a covalent bond is formed during polymerization, this distance is reduced to about 1.5 Å. The resulting net distance change of about -1.9 Å leads to volumetric shrinkage. Upon reaching the gelation point, the dynamic nature of polymer chains is terminated; hence further volumetric shrinkage induces mechanical stress in the polymer network. Thus, the development of strategies to reduce or eliminate shrinkage and polymerization stress in polymer networks has gained increased attention in recent decades.<sup>[11]</sup> The addition of fillers or addition-fragmentation chain transfer agents (AFCTs)<sup>[1c, 2]</sup> are typical examples of such strategies. Another solution to reduce shrinkage is the application of expanding monomers like spiroorthoesters (SOEs)<sup>[3]</sup>, acetals<sup>[4]</sup>, or the use of thiol-ene<sup>[5]</sup> based resins.

Known for over 100 years<sup>[6]</sup>, thiol-ene reactions are widely employed in polymer and material science for polymer synthesis and functionalization.<sup>[7]</sup> The main driving factor for the success of thiol-ene chemistry is the "click" character of the reaction.<sup>[8]</sup> Thiolene "click" reactions proceed with high selectivity, high yields, and fast reaction rates. In addition to the click principles, a uniform cross-linked density combined with the aforementioned low polymerization stress and low shrinkage are key advantages of thiol-ene coupling reactions.<sup>[9]</sup> The low polymerization stress is enhanced by the delayed gelation point of thiol-ene reactions resulting from the step-growth polymerization mechanism.

Polarity-reversal catalysts (PRC) for hydrogen-atom abstraction reactions have been known in radical chemistry for over 60 years.<sup>[10]</sup> Mostly utilized in the field of synthetic organic chemistry, the application of PRCs in the field of polymer chemistry is still underdeveloped. The basic principle of PRCs for hydrogen abstraction reactions is to replace a single-step abstraction, unfavorable due to polar effects, with a two-step process. In this two-step process, the radicals and substrates have matched polarities. For example, an electrophilic radical species, like a thiyl radical, abstracts hydrogen much more effectively from electron-rich C-H bonds than electron-deficient ones from similar bond strength.<sup>[11]</sup>

Building on our recent development of photopolymerizable precursors based on acetal moieties,<sup>[12]</sup> we were inspired by literature by Roberts *et al*.<sup>[11, 13]</sup> and Patton *et al*.<sup>[14]</sup> that used thiols

as PRC for radical-mediated redox rearrangements of benzylidene acetals. During the rearrangement reaction, cyclic benzylidene acetals are transformed into benzoate esters leading to a significant volumetric expansion. We postulated that the potential ring-opening of cyclic acetals during polymerization might lead to further reduced shrinkage and polymerization stress in thiol-ene polymer networks (see Scheme 1).



Scheme 1. The mechanistic cycle of the thiol-ene step growth reaction is shown on the left-hand side. The ene moiety is an allyl ether. Thus, no or only minor homopolymerization is occurring, and a clean step growth mechanism can be assumed. In the propagation step, the addition of a thiyl radical to the double bond is depicted. Next, the hydrogen abstraction is shown, creating a new thiyl radical to close the cycle. The first step on the right-hand side is the hydrogen abstraction by the thiyl radical. An electrophilic radical species, like a thiyl radical, abstracts hydrogen effectively from the electron-rich C-H bond of the cyclic benzylidene acetal. In the next step, the  $\beta$ -scission takes place. The  $\beta$ -scission is a redox rearrangement of the cyclic benzylidene acetal to a benzoate ester. After the rearrangement reaction, the hydrogen abstraction by the thiol takes place, creating a new electrophilic thiyl radical. This electrophilic thiyl radical can again abstract the hydrogen from the electron-rich C-H bond of the cyclic benzylidene acetal to close the cycle. Overall, the thiol promotes the transfer of a hydrogen atom between two nucleophilic carbon-centered radicals.<sup>[14]</sup>

This study presents the combination of low shrinkage thiol-ene resins with radical-mediated redox-rearrangement of cyclic benzylidene acetals to alkyl benzoate esters, catalyzed by thiols to reduce further or eliminate shrinkage. The function of a thiol in this system is to act as a protic polarity-reversal catalyst.<sup>[11, 15]</sup> The thiol promotes the overall transfer of a hydrogen atom between two nucleophilic carbon-centered radicals. The key advantage of this process lies in its simplicity. In contrast to AFCTs and SOEs, no additives like sensitizers or combinations of different initiators (radical and cationic) are needed. Furthermore, the process enables using the same light source for both the polymerization reaction and expansion through rearrangement. We demonstrate that the expansion on a molecular level reduces shrinkage and polymerization stress but does not significantly affect the (thermo-)mechanical properties of the cross-linked network. The applied photoinitiator enables spatial and temporal control of the polymerization; thus, the developed system can be an excellent platform for additive manufacturing processes.

#### **Results and Discussion**

#### **Monomer Design and Synthesis**

Envisioning the structure of **BAA** and **BAM**, we got inspired by a study by Roberts *et al.*<sup>[13a]</sup> investigating the redox rearrangement of monocyclic benzylidene acetals to benzoate esters. Structures comparable to **BAA** and **BAM** showed redox rearrangements with high conversion rates. We hypothesized that to reduce shrinkage, bicyclic benzylidene acetals may be more effective compared to monocyclic benzylidene acetals. Two cyclic acetal rings may be opened *via* redox rearrangement, resulting in an increased expansion during polymerization to counteract the volumetric shrinkage (see Scheme 2).

For the reference system, we chose a monomer recently reported by Patton *et al.*<sup>[18]</sup>. In the case of the bicyclic ketal **BAK** the abstractable hydrogen is exchanged for a methyl group. Hence, the hydrogen abstraction, which is a crucial step for the redox rearrangement, is not possible (see Scheme 2).

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### BAA BAM റ BAK $\cap$ HS SH HO OH ΗÓ CH<sub>3</sub> HS SH Darocur<sup>®</sup> 1173 Ô PYR 0 PETMP

Scheme 2. Chemical structure of the bicyclic benzylidene acetal and ketal monomers BAA (1,4-bis(4-((allyloxy)methyl)-1,3-dioxolan-2-yl)benzene), BAM (1,4-bis(4-((allyloxy)methyl)-4,-methyl)-1,3-dioxolan-2-yl)benzene) and BAK (1,4-bis(4-((allyloxy)methyl)-1,3-dioxolan-2-yl)benzene). Chemical structure of the photoinitiator Darocur® 1173 (D1173), the stabilizer PYR (pyrogallol) and PETMP (pentaerythritol tetrakis(3-mercaptopropionate)).

In the case of **BAM**, we hypothesized that the methyl group is stabilizing the radical formed in the  $\beta$ -scission. A more stable tertiary radical is formed, which might shift the equilibrium of the  $\beta$ -scission from the cyclic to the open form (see Scheme 3). This shift in the equilibrium might accelerate the reaction rate of the  $\beta$ -scission for **BAM** and the overall reaction rate. As mentioned above, the bicyclic ketal **BAK** cannot undergo the crucial step of hydrogen abstraction necessary for the redox rearrangement, as the abstractable hydrogen has been replaced with a methyl group.



Scheme 3. Proposed chemical equilibrium of BAA and BAM in the  $\beta$ -scission reaction step. BAK cannot undergo the crucial step of hydrogen abstraction necessary for the redox rearrangement, as the abstractable hydrogen has been replaced with a methyl group.

**BAA** and **BAK** were synthesized *via* an acid-catalyzed condensation reaction starting from terephthalaldehyde or 1,4-

diacetylbenzene, respectively. Terephthalaldehyde was selected as a low-cost and commonly used difunctional aldehyde in organic synthesis. 3-Allyloxy-1,2-propanediol was chosen to introduce both, the acetal or ketal moiety and the photopolymerizable ene-group in one step. In the case of **BAM**, the corresponding diol 3-(allyloxy)-2-methylpropane-1,2-diol was not commercially available, but could be synthesized in a simple two-step procedure. A subsequent acid-catalyzed condensation reaction with terephthalaldehyde yielded the final product. Acceptable monomer yields were obtained for all monomers after purification (**BAA**: 50% of theoretical yield; **BAM**: 59% of theoretical yield; **BAK**: this work 44% of theoretical yield, literature<sup>[18]</sup> 38% of theoretical yield).

The photopolymerizable allyl ether groups show no or only minor homopolymerization and lead to a clean thiol-ene step-growth reaction. The pure thiol-ene step-growth mechanism should further reduce shrinkage.

A thorough literature search for **BAA** and **BAM** as photopolymerizable precursors for acetal-containing monomers yielded no results. The structure and purity of **BAA**, **BAM** and **BAK** were elucidated and confirmed by <sup>1</sup>H-, <sup>13</sup>C-NMR, HRMS, and HPLC. In the NMR experiments, multiple peaks were observed for some carbons in case of all monomers. This can be explained by the formation of stereoisomeric products during the synthesis.

#### **Preparation of Formulations**

Commercially available pentaerythritol tetrakis(3mercaptopropionate) (**PETMP**) was used as a tetrafunctional thiol, yielding highly crosslinked polymer networks. **PETMP** was used in a 1:1.1 double bond ratio (DB ratio) with one double bond parts

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### of the monomer BAK, BAA, or BAM to 1.1 parts of thiol moieties. This ratio is in the following described as 110 double bond percent (DB%). According to the literature $^{\left[13a,\ 13c,\ 15,\ 19\right]}$ an excess of 10 DB% of thiol is optimal to promote the redox rearrangement of cyclic benzylidene acetals to benzoate esters. As described in the introduction, the thiol-ene click reaction proceed with high selectivity and high double bond conversions from up to 99%. The 10 DB% excess of free thiol moieties can act as PRCs to enable the redox rearrangement. Darocur® 1173 (D1173) was used as a photoinitiator for all

formulations, as it provided promising results in literature for the redox rearrangement of cyclic benzylidene acetals.[14] Furthermore, D1173 is a liquid photoinitiator and thus convenient to dissolve in viscous formulations. Pyrogallol (PYR, 0.1 wt-%) was added as an efficient literature-known stabilizer for thiol-ene formulations to increase the storage stability.<sup>[17]</sup>

#### **Volumetric Shrinkage Measurements**

The volumetric shrinkage upon curing was calculated from the densities of both, the monomers, and the obtained DMTA specimens. The density of the monomers was obtained via a 1 mL pycnometer, and the density of the polymers was measured via the Archimedes principle (buoyancy of a material in fluid). Both are inexpensive and straightforward methods to evaluate volumetric changes by measuring density variations of a sample before and after polymerization. The buoyancy method has the advantage of being independent of the size or geometry of specimens. In addition, buoyancy is the only method for measuring polymerization shrinkage, having published standards for execution in ISO 17304.<sup>[1a, 20]</sup>

The reference system containing BAK exhibited polymerization shrinkage of 6.20 vol%, which is in the range of comparable step growth thiol-ene systems.<sup>[3b, 5a, 21]</sup> In the case of BAA and BAM, the volumetric shrinkage was reduced to 3.23 vol% and 3.40 vol%, respectively. This corresponds to an overall shrinkage reduction of 48% for BAA and 45% for BAM, in comparison to the BAK reference system. In the case of BAA and BAM, two factors may contribute to this significant reduction in volumetric shrinkage. One is that the cleavage of two covalent bonds results in the opening of two cyclic acetals and ultimately leads to a large volumetric expansion. The other is that the expanding monomers BAA and BAM are not used as an additive but as one of the two main components of the formulation. Consequently, the influence BAA and BAM have on the shrinkage of the polymer is significant.

Table 1. Monomer  $(\rho_{\text{monomer}})$  and polymer  $(\rho_{\text{polymer}})$  densities for BAK, BAA, and **BAM** and the calculated volumetric polymerization shrinkage  $(\Delta V_p)$ . The measuring error for the pycnometer measurements ( $\rho_{monomer}$ ) is given with  $\pm$  0.001. The highest standard deviation determined for  $\rho_{polymer}$  is  $\pm$  0.002 (all measurements were done in triplicates). The standard deviation for the volumetric polymerization shrinkage  $(\Delta V_p)$  was calculated according to the principles of propagating uncertainty through the mathematical operations of multiplication and division (for detailed information see SI page 9 and 10).

Monomer	ρ <sub>monomer</sub> ∕g ml⁻¹	ρ <sub>polymer</sub> /g ml⁻¹	$\Delta V_p$ / vol%	
BAK	1.140	1.215	6.20 ± 0.12	
BAA	1.147	1.185	$3.23 \pm 0.06$	
BAM	1.141	1.181	3.40 ± 0.06	

#### Monitoring of the Curing Reaction and Shrinkage Force

Real time FTNIR-photorheology was used to examine the photoreactivity and material properties of BAA, BAK, and BAM formulations during the polymerization process (see Table 2, and Scheme 5, page 5). Through photorheology studies combined with real-time Fourier-transform near infrared spectroscopy measurements, the material's modulus can be obtained with the corresponding double-bond conversion. This method allows to link mechanical data with chemical information and enables a rational assessment of the photopolymerization process. More details about the setup and the measurements can be found in literature.<sup>[16]</sup> A more detailed investigation of the kinetics of the ßscission rearrangement reaction and its yields can be found in the supporting information, page 10-14.

The influence of the different benzylidene acetal and ketal structures on the double bond conversion, reaction speed, and shrinkage stress were evaluated. The time to reach the gel point  $(t_{qel})$ , which is characterized by the intersection of the storage (G) and loss modulus (G'), and the time until 95% of the final double bond conversion (DBCfinal) is reached (t95) are characteristic values to determine the reaction speed of a monomeric system. BAA and BAM need, compared to BAK, a significantly longer time to reach  $t_{gel}$  and  $t_{95}$ . We hypothesized that the reaction rate of the  $\beta$ -scission is lower in comparison to the reaction rate of the free radical polymerization (See Scheme 1. in the introduction, and Scheme 4). In the first step of the β-scission, the central hydrogen of the cyclic acetal moiety is abstracted. The resulting radical is a primary benzylic radical, which is relatively stable due to the resonance effect. This stability might decelerate the rearrangement reaction to the non-cyclic ester form and trap the formed radical. Thus, the overall reaction rate of the polymerization reaction is decelerated in the case of BAA and BAM, and both monomers are less reactive in comparison to BAK.

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Scheme 4. Proposed mechanism of the  $\beta$ -scission. Highlighted in the orange dotted box are the stable tertiary radicals prior to the  $\beta$ -scission. These stable intermediates might slow down the redox rearrangement reaction.

The simultaneously measured NIR spectra allow calculating the double bond conversion (DBC) from the reduction of the peak area of the allyl ether double bond signal ( $6090 - 6175 \text{ cm}^{-1}$ ). By comparing the integral before irradiation with the integral at the gel point and at the end of the curing process, the DBC at the gel point (*DBC*<sub>gel</sub>), as well as the final (*DBC*<sub>final</sub>), can be calculated.

The  $DBC_{gel}$  and  $DBC_{final}$  for all three monomers are in similar ranges of 75%-78% and 97%-99%, respectively. These comparatively high  $DBC_{gel}$  and  $DBC_{final}$  values are typically reported for thiol-ene step growth reactions.<sup>[7a]</sup> A high double bond conversion at  $(DBC_{gel})$  is advantageous because upon gelation, the photopolymerization progresses with increased shrinkage stress. This increased shrinkage is caused by the restricted mobility in the solid state and the simultaneous decrease in the interatomic distance due to the formation of covalent bonds. Consequently, a similar  $DBC_{gel}$  for all three monomers is crucial to be able to conclude that a difference in the reduction of shrinkage stress and volumetric shrinkage is not caused by a delay of the gel point, as it would be the case with *e.g.* chain transfer reagents. The volumetric shrinkage of formulations has been shown to be proportional to the degree of the double bond conversion.<sup>[22]</sup> Thus, it is important to compare the shrinkage of different formulations at an equal double bond conversion. Due to the same  $DBC_{final}$  of all three monomers (99%), the final shrinkage force and volumetric shrinkage of all three monomers can be compared directly.

During polymerization, the normal force applied at the top plate of the rheometer to maintain a constant gap distance is recorded. The measured force counteracts the volume contraction (under constant strain) of a resin; thus, the corresponding shrinkage stress can be determined. Due to the gelation and subsequent volumetric shrinkage of the forming polymer network, the measuring plate is pulled downwards, resulting in an increasing negative normal force measured by the rheometer.<sup>[16]</sup> The occurring shrinkage is indicated by this increasing normal force. The highest normal force and thus the highest shrinkage was measured in the case of **BAK** (-15.8 N). Both monomers, **BAA**, and **BAM**, reach a lower normal force of -4.9 N and -4.6 N, respectively. This corresponds to an overall shrinkage force reduction of 69% for **BAA** and 71% for **BAM**, in comparison to the **BAK** reference system.

The measured reduction of the normal force in the case of **BAA** and **BAM** is around 20% higher when compared to the reduction of the volumetric shrinkage. The results of both analytical methods show a significant reduction in the shrinkage force and the volumetric shrinkage in the case of **BAA** and **BAM**.

It can be concluded that the expansion of the monomers **BAA** and **BAM** to counteract the shrinkage has no significant influence on the stiffness of the material. The shrinkage stress of the material can be reduced without a negative impact on the material's properties.

Furthermore, a similar storage modulus and, thus a comparable stiffness of the material is necessary to be able to compare the normal forces, which are indicating the shrinkage. If the storage modulus of two materials is different, an equal volumetric shrinkage will result in different shrinkage forces pulling down the measuring plate.

Table 2. Summary of real time FTNIR-photorheology measurement data of BAA, BAM, and BAK monomers (in formulations with 110 DB% PETMP, 10 wt-%
D1173, 0.1 wt-% PYR, cured with 100 mW cm <sup>-2</sup> , λ = 320-500 nm). The depicted parameters are: time until gelation t <sub>gel</sub> , time until 95% of double bond conversion is
reached t <sub>95</sub> , double bond conversion at gel point DBC(gel), final double bond conversion DBC(final), final normal force F <sub>N(final)</sub> , and final storage modulus G '(final).

Networks	t_/s	t / min	DBC / %	DBC / %	F / N <sub>N(final)</sub>	G' / kPa
BAK	1.2	2.1	75	99	-15.8	363.7
BAA	525	78.2	75	99	-4.9	366.8
BAM	917	88.1	78	99	-4.6	375.8



Scheme 5. Results of photorheological analysis of formulations containing BAK, BAA, and BAM (Formulations with 110 DB% PETMP, 10 wt-% D1173, 0.1 wt-% PYR, cured with 100 mW cm<sup>-2</sup>,  $\lambda$  = 320-500 nm, 25°C): (a) Double bond conversion and normal force over time obtained from photorheology measurements. The double bond conversion is depicted using dotted lines: ••• BAK, BAA, and BAM. The half-filled triangles represent the normal force:  $\triangle$  BAA  $\triangle$  BAK  $\triangle$  BAM. (irradiation with light starts at 0 s). (b) Normal force exerted by the formulation onto the measuring plate during photorheology measurements. BAK, BAA, and BAM. (c) The final normal force exerted by the respective polymer networks BAK, BAA, and BAM onto the measuring plate during photorheology measurements. All measurements were conducted in triplicates; the standard deviation is indicated in the diagram.

#### **Thermomechanical Characterization**

To characterize the thermomechanical properties of the cured polymer networks, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), nano-indentation measurements, and simultaneous thermal analysis (STA) were performed (see Table 3, and Scheme 6).

The viscoelastic properties of the photocured specimens were determined *via* DMTA. An important information acquired from this measurement is the glass transition temperature ( $T_g$ ), which can be derived from the maximum of the tan( $\delta$ ) plot. Moreover, the storage modulus at the glassy state  $G'_{(-80^\circ\text{C})}$  can be determined and gives information about the mechanical properties of the polymer. The storage modulus at the rubbery plateau  $G'_{(-65^\circ\text{C})}$  provides an indication for the cross-link density. The tan( $\delta$ ) and the full width at half maximum (fwhm) of the tan( $\delta$ ) curve correlate with the homogeneity of the polymer network.<sup>[23]</sup>

The  $T_g$  of all samples is near-identical (5°C - 8°C). In addition, the storage modulus at the glassy state  $G'_{(-80^\circ\text{C})}$  for all samples is in a comparable range of 2620 MPa – 2770 MPa. Thus, no considerable softening can be observed in the case of **BAA** and

**BAM**, although more flexible ester groups are introduced to the network through the rearrangement reaction.

The storage moduli at the rubbery plateau  $G'_{(65^{\circ}C)}$  are also comparable for all networks, reaching from 6.4 MPa to 7.3 MPa, suggesting similar cross-linking densities.

The shapes of the  $tan(\delta)$  curves are indicative for the formation of a homogeneous polymer network with a sharp single phasetransition. A narrow  $tan(\delta)$  distribution (<25°C at fwhm) were observed for all thermosets - characteristic for thiol-ene stepgrowth polymerizations leading to homogeneous polymer networks. A difference in the  $tan(\delta)$  and fwhm of  $tan(\delta)$  between the reference BAK in comparison with BAA and BAM is visible. A decrease of  $tan(\delta)$  and an increase of fwhm is observed in the case of BAA and BAM, indicating an increasing variability of the cross-link density leading to a less homogeneous network. The decrease in network homogeneity is likely to be caused by the rearrangement reaction. The  $T_g$  was also determined via DSC. In this case, the  $T_q$  is identified by a single second-order endotherm present in each thermogram. The  $T_g$  of all samples determined via DSC (-7°C - -3°C) are in comparable ranges, showing that no considerable influence on the thermomechanical properties can be observed in the case of **BAA** and **BAM**.

**Table 1.** Summary of DMTA measurement data of **BAA**, **BAM**, and **BAK** monomers (in formulations with 110 DB% **PETMP**, 10 wt-% **D1173**, 0.1 wt-% **PYR**, cured with 100 mW cm<sup>-2</sup>,  $\lambda = 320-500$  nm). The depicted parameters are: The glass transition temperature determined *via* DSC ( $T_{g:DSC}$ ). The  $T_{g:DSC}$  was identified by a single second-order endotherm present in each thermogram, the glass transition temperature ( $T_{g:DMTA}$ ), which was derived from the maximum of the tan( $\delta$ ) plot, storage modulus at the glassy state G' (-80°C), storage modulus at the rubbery plateau G' (65°C), the maximum of tan( $\delta$ ) and the full width half maximum (fwhm) of tan( $\delta$ ).

Networks	T / °C	T / °C	Gʻ/ MPa	Gʻ/ MPa	tan(δ)	fwhm of tan(δ)
BAK	-7	6	2770	6.8	1.06	11.3
BAA	-5	5	2740	7.3	0.57	21.1
BAM	-3	8	2620	6.4	0.54	24.9



Scheme 6. (a) Storage modulus as a function of temperature obtained from DMTA measurements of the polymer samples ••• BAK, BAA, and BAM. Tan( $\delta$ ) as a function of temperature obtained from DMTA measurements of the polymer samples – - BAK, – - BAA, and – - BAM. All formulations were prepared with the corresponding monomer BAK, BAA, or BAM, 110 DB% PETMP, 10 wt% D1173, 0.1 wt-% PYR. The formulations were cured in a silicone mold (sticks, 5 × 2 × 40 mm<sup>3</sup>) with an Uvitron UV 1080 Flood Curing System with Uvitron Intelliray 600 halide lamps (600 W, measured intensity of 100 mW cm<sup>-2</sup> at the position of the samples, determined with an Ocean Optics USB 2000+ spectrometer, 320-580 nm). (b) Heat flow as a function of temperature obtained from DSC measurements of the polymer samples ••• BAK, BAA, or BAM, and BAM. The cured polymer formulations contained BAK, BAA, or BAM with 110 DB% PETMP, 10 wt-% D1173, 0.1 wt-% PYR, cured with 100 mW cm<sup>-2</sup>,  $\lambda$  = 320-500 nm. For each polymer sample, 15 mg was weighed into an aluminum pan, and the experimental temperature ranged from -90°C to 150°C with a 10 K min<sup>-1</sup> heating rate. The measurements were conducted under a nitrogen atmosphere.

Nano-indentation measurements at room temperature were carried out to evaluate the mechanical properties of the three different polymer networks containing **BAK**, **BAA**, and **BAM**. The hardness of **BAK** was found to be 2.2 MPa, which is in a comparable range with **BAA** (2.7 MPa) and **BAM** (2.4 MPa). The reduced modulus of **BAK**, **BAA**, and **BAM** was found to be 12.9 MPa, 14.5 MPa, and 13.5 MPa, respectively. These results indicate that no considerable influence caused by the redox rearrangement on the thermomechanical properties can be observed in the case of **BAA** and **BAM**.

To assess the thermal stability of the **BAK**, **BAA**, and **BAM** thermosets, simultaneous thermal analysis was carried out under nitrogen atmosphere. Scheme 7 depicts the thermal degradation profiles for each network type. A single mass loss transition was observed for all samples. **BAK** was found to exhibit high resistance to thermal degradation. The temperature at which 10% mass loss occurs ( $T_{d,10\%}$ ) was found to be 341°C (see Table 2). This mass loss behavior is typical for thioether-based networks and in accordance with the literature.<sup>[18]</sup>

**BAA** and **BAM** were found to exhibit similar mass loss behavior but with a lower onset degradation temperature compared to **BAK**. The thermal degradation of **BAA** and **BAM** is already starting at 267°C and 261°C, respectively. In the case of **BAK**, a complete degradation occurred with no significant char or residue remaining in the TGA pan. In the case of **BAA** and **BAM**, 13-14% residual mass was remaining in the TGA pan.

The heat flow diagram shows that **BAK** displays an endothermic peak at 375°C, while **BAA** and **BAM** exhibit an exothermic peak at 325°C (see Scheme 7). The exothermic peak observed in **BAA** and **BAM** thermograms may be attributed to the thermal-induced occurrence of the redox rearrangement. It is reasonable to assume that the redox rearrangement is not taking place with a complete conversion.

**Table 2.** Summary of simultaneous thermal analysis (STA) and nanoindentation measurement data of **BAA**, **BAM**, and **BAK** monomers (in formulations with 110 DB% **PETMP**, 10 wt-% **D1173**, 0.1 wt-% **PYR**, cured with 100 mW cm<sup>-2</sup>,  $\lambda = 320-500$  nm). The depicted parameters are temperature of 10% mass loss  $T_{d,10\%}$ , residual mass  $m_t$ , hardness H, and reduced modulus  $E_t$ .

Networks	T/°C	m / %	H / MPa	E / MPa
BAK	341	5	2.2	12.9
BAA	267	13	2.7	14.5
BAM	261	14	2.4	13.5



**Scheme 7.** Weight as a function of temperature obtained from STA measurements of the polymer samples •••BAK, •••BAA, and •••BAM. Heat flow as a function of temperature obtained from STA measurements of the polymer samples – •BAK, – •BAA, and – BAM. The cured polymer formulations contained **BAK**, **BAA**, or **BAM** with 110 DB% **PETMP**, 10 wt-% **D1173**, 0.1 wt-% **PYR**, cured with 100 mW cm<sup>-2</sup>,  $\lambda$  = 320-500 nm. The measurements were performed with a temperature ramp from 25°C to 600°C under an N<sub>2</sub> atmosphere (10 K min<sup>-1</sup>). All samples were accurately weighed into aluminum DSC pans (10.0 ± 1 mg) and measured at a constant gas flow rate (40 mL min<sup>-1</sup>). The mass loss and DSC signal were recorded.

Conclusion

RESEARCH ARTICLE

#### Reduced shrinkage in photopolymers is believed to have many positive effects, such as the enhancement of toughness. For the mechanical testing of photopolymers, samples are printed using a layer-by-layer assembly. High shrinkage can cause fractures originating from delamination, eventually leading to cracks within the material or on its surface, resulting in lower toughness.<sup>[25]</sup> In conclusion, this study represents the first application of thiols as PRCs in redox rearrangements of acetals to reduce shrinkage in polymers. Two literature unknown bicyclic benzylidene acetals and one bicyclic benzylidene ketal reference compound have been successfully synthesized and investigated with respect to the reactivity during radical photopolymerization and to the resulting materials' (thermo)mechanical properties. The study has shown that the volumetric shrinkage can be reduced in the range of 45-48% by using the benzylidene acetal-based monomers BAA and BAM instead of the reference compound BAK. A shrinkage stress reduction in the case of BAA and BAM of 69-71% was determined via the change of normal forces in photorheology studies. The thermomechanical properties of all and

cured polymer networks were determined via dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), nano-indentation measurements, simultaneous thermal analysis (STA). Overall, the results show that the redox rearrangement reaction of BAA and BAM significantly reduces shrinkage without negatively affecting the thermomechanical properties of the material.

Future research could focus on further optimizing the monomer structures to accelerate the redox rearrangement reaction of the acetals to benzoate esters. The synthesis of asymmetric acetals with electron-donating or electron-withdrawing groups in para position could be an interesting approach to promote the redox rearrangement. Ester-free thiols could be utilized to follow ester bonds formation via IR and determine the conversion of the rearrangement reaction. The trifunctional use of thiols as participants in the thiol-ene polymerization reactions, PRCs to reduce shrinkage, and photoinitiators<sup>[24]</sup> could further simplify the system.

Applications such as 3D printing usually require a more complex formulation consisting of different compounds like diluents, toughness enhancers, and Tg-modifiers. In such a system, bicyclic benzylidene acetal-type monomers like BAA and BAM could be used as one component to reduce shrinkage without compromising the material properties. With further optimization, thiols as PRCs in the redox rearrangement of acetals may be a promising system to reduce shrinkage for the 3D printing of photopolymers. Furthermore, this strategy could have the potential to be widely applied to reduce shrinkage in polymerization reactions, ultimately enhancing the performance of polymers.

#### Supporting Information

The authors have cited additional references within the Supporting Information.[26-31]

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Keywords: thiol-ene · shrinkage reduction · polarity-reversal catalysts • cyclic acetal • photopolymer

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#### Entry for the Table of Contents



The Van-der-Waals distance of a thiol and ene is depicted. After the thiol-ene reaction a thioether bond is formed resulting in a shorter interatomic distance. This shrinkage leads to stress in the polymer which can be reduced by radical-mediated redox-rearrangements catalyzed by thiols. A compact cyclic acetal extent to a longer linear ester. This volumetric expansion is counteracting the shrinkage resulting from the thiol-ene reaction.

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