

# UV-Induced Cationic Ring-Opening Polymerization of 2-Oxazolines for Hot Lithography

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Cite This: *ACS Macro Lett.* 2020, 9, 546–551

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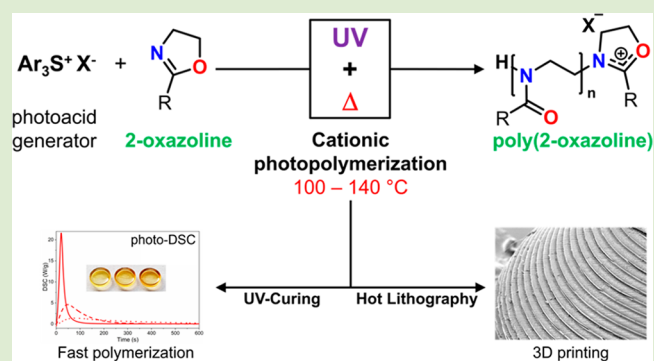
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**ABSTRACT:** The cationic ring-opening polymerization (CROP) of 2-oxazolines gives polymers with unique characteristics arising from its polyamide backbones and structural versatility. Up to now, poly(2-oxazoline)s were obtained by classical thermal polymerization methods not aiming for application in bulk curing of structural polymers. We introduce the cationic photopolymerization of 2-oxazolines at elevated temperatures for the direct UV-induced curing of materials with exclusive chemical and structural particularities. After efficient photoinitiation via onium salt photoacid generators (PAGs), the immanent low-rate propagation is crucially promoted by thermal energy input to the ring-opening reaction. In simultaneous thermal analysis (STA), photo-DSC, and (thermo)mechanical analyses we investigated the UV-induced CROP of 2-oxazolines in a temperature range of 100–140 °C and show the exceptional potential of the introduced photopolymers. Furthermore, we applied the photopolymerizable system in Hot Lithography, a stereolithography-based 3D printing technology at elevated temperatures.



Cationic ring-opening polymerization (CROP) represents a versatile class of chain-growth polymerization that gives polymers with exceptional mechanical, chemical, thermal, and electrical properties. Most characteristics arise from the beneficial structure–property relationship of heteroatom-containing polymer backbones, which are accessible by CROP in great variety.

Over the past decade, CROP of 2-oxazolines has been in the focus of interest for the structural versatility and polymer characteristics of poly(2-alkyl/aryl-2-oxazoline)s (PAOx), as well as the accessibility of copolymers by its living polymerization character.<sup>1–4</sup> Several reviews have exclusively focused on the potentials of this polymer class in the biomedical field, with the most prominent aim being to replace polyethylene glycol (PEG) in medicinal use for nonfouling and nonadhesive surfaces, biomedical analysis, protein and drug conjugation, and polymer-based drug delivery.<sup>5–12</sup> Most applications in structural materials are, yet, limited to functional poly(2-oxazoline) precursors that do not yield polymer networks via a cationic polymerization mechanism.<sup>2,5,13</sup>

Currently, the CROP of 2-oxazolines is initiated by the alkylation of the cyclic imino ether using strong electrophiles, such as methyl tosylates, nosylates, or triflates, in microwave-assisted preparation methods at 100–140 °C.<sup>14–16</sup> The low ring-strain of the 2-oxazoline moiety demands for substantial external energy input to reach efficient reactivity, where the initiator crucially determines the propagation rate by the

liberated counterion, as it controls the equilibrium of the active cationic oxazolinium species and the dormant covalent species.<sup>16,17</sup> Clearly, the efficient CROP of 2-oxazolines is determined by the precondition of high temperature on the one hand, as well as the stabilization of the living cationic character by the suppression of termination processes on the other.

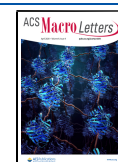
In fact, very similar effects have been observed in the cationic photopolymerization using onium salt photoacid generators (PAGs).<sup>18</sup> Many cationically ring-opening monomers have been considered for potential cationic photopolymerization initiated by PAGs, whereas only a few monomers, such as oxiranes and oxetanes, provide sufficient ring-strain to readily photopolymerize at room temperature.<sup>19,20</sup> Except for the photochemical generation of the initiating species, all processes in the initiation are thermally driven and kinetically dependent on temperature.<sup>21</sup>

In the strive for high acid strengths and low ion-pairing, superacid forming BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup>, and SbF<sub>6</sub><sup>-</sup>, but also

Received: January 22, 2020

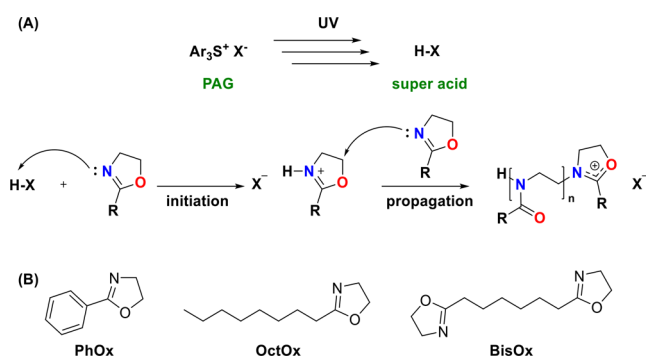
Accepted: March 23, 2020

Published: March 25, 2020



advanced weakly coordinating anions (WCAs) such as  $\text{BARF}_4^-$  and, recently,  $\text{Al}(\text{OC}(\text{CF}_3)_3)_4^-$  were applied in most powerful photoinitiators due to their explicitly low nucleophilicity.<sup>22,23</sup> The potential of onium salts to photoinitiate the CROP of low reactive heterocyclic monomers has been investigated for related benzoxazine monomers.<sup>24</sup> However, the factual cationic photopolymerization of 2-oxazolines by onium salt PAGs remained uninvestigated to date, despite considerations to use WCAs and direct protonation for the thermal induction of 2-oxazoline CROP.<sup>25,26</sup> In consequence, the photoinitiation and direct protonation by a photoacid with subsequent ring-opening polymerization of a 2-oxazoline monomer is proposed herein and illustrated in Scheme 1A.

**Scheme 1.** (A) Photoacid Generation with Subsequent Initiation of 2-Oxazoline CROP by Direct Protonation; (B) Model Compounds 2-Phenyl-2-oxazoline (PhOx), 2-Octyl-2-oxazoline (OctOx), and 1,6-Bis(4,5-dihydrooxazol-2-yl)hexane (BisOx)



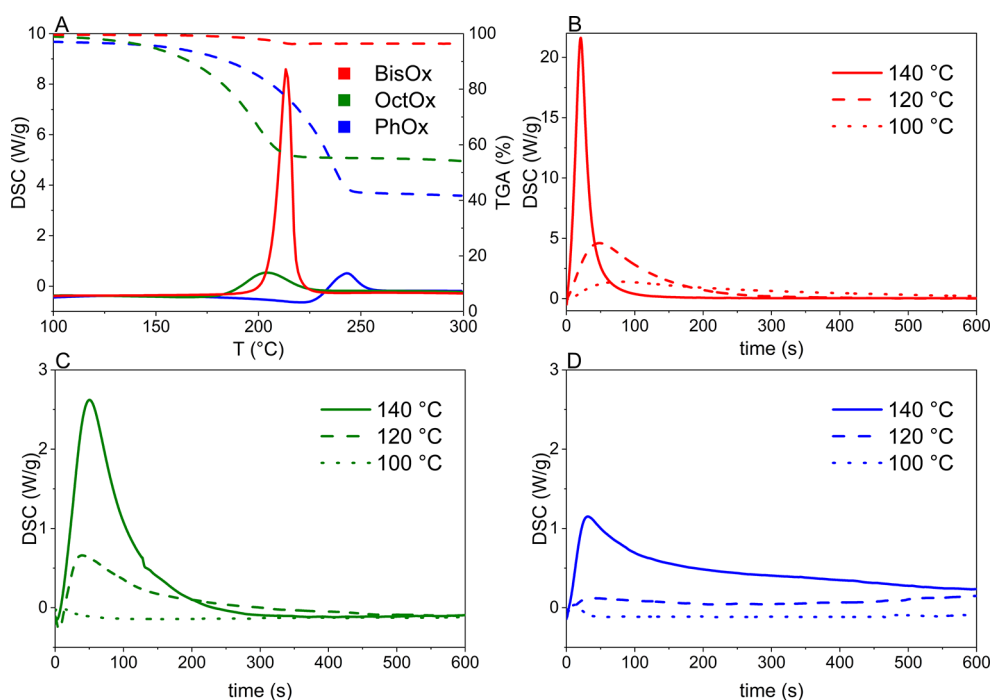
As a prerequisite for a solely light-induced initiation at elevated temperatures, a PAG that provides inherent thermal

stability, yet, selective and efficient photodecomposition upon irradiation, is required.

Well-described triarylsulfonium salt PAGs ( $\text{Ar}_3\text{S}^+\text{X}^-$ ) exhibit outstanding thermal stability of over 300 °C, as well as efficient photodecomposition arising from the nature of the cation.<sup>18</sup> In combination with a weakly coordinating anion (WCA), such as  $\text{BARF}_4^-$ , efficient propagation is facilitated by the non-nucleophilic character of the released counterion.<sup>22,23,27</sup> Therefore, the herein presented investigations on the cationic photopolymerization of 2-oxazolines were conducted using the triarylsulfonium tetrakis(pentafluorophenyl)borate PAG S-B (Irgacure 290) to enable the efficient and selective photoinitiation at elevated temperatures.

Moreover, it is considered that the substituent in 2-position of the monomer exhibits a decisive electronic interaction with the propagating oxazolinium moiety and crucially influences the propagation rate.<sup>4</sup> An electron-donating aliphatic substituent provides higher reactivity to the ring by raising its nucleophilicity, whereas an aromatic system leads to significant retardation by mesomeric stabilization of the propagating oxazolinium species.<sup>14,28–30</sup>

Based on a one-step synthesis route from corresponding nitriles, the aliphatic-substituted monofunctional 2-octyl-2-oxazoline (OctOx) and difunctional 1,6-bis(4,5-dihydrooxazol-2-yl)hexane (BisOx) were synthesized as model compounds and examined together with the commercially available 2-phenyl-2-oxazoline (PhOx) regarding the specific requirements of UV-induced CROP at elevated temperatures (Scheme 1B).<sup>3,31</sup> It was expected that formulations of the respective model compounds with the PAG S-B would exhibit different thermal stability limits and susceptibility to thermal polymerization.<sup>22</sup> Hence, simultaneous thermal analysis (STA) showed the thermal stability of photoreactive formulations of the 2-oxazolines PhOx, OctOx, and BisOx containing 0.5 mol % S-B per 2-oxazoline reactive group in a range from 25 to 300 °C



**Figure 1.** STA and photo-DSC of photoreactive formulations with 0.5 mol % S-B per reactive group; (A) STA analysis by DSC (solid) and TGA (dash) (B-D) photo-DSC of BisOx, OctOx, and PhOx at 100, 120, and 140 °C.

regarding thermogravimetric loss (TGA) and thermally induced onset of polymerization (DSC; Figure 1A). It is concluded that the 2-oxazoline formulations show high thermal stability limits of 165 °C for OctOx and BisOx, and even above 200 °C for PhOx. Still, mass loss by evaporation becomes prominent at temperatures above 160 °C. Thus, the 2-oxazoline formulations were examined in photo-DSC studies at elevated temperatures of 100–140 °C due to the observed sufficient thermal stability and only insignificant mass loss by evaporation of monomers within this range.

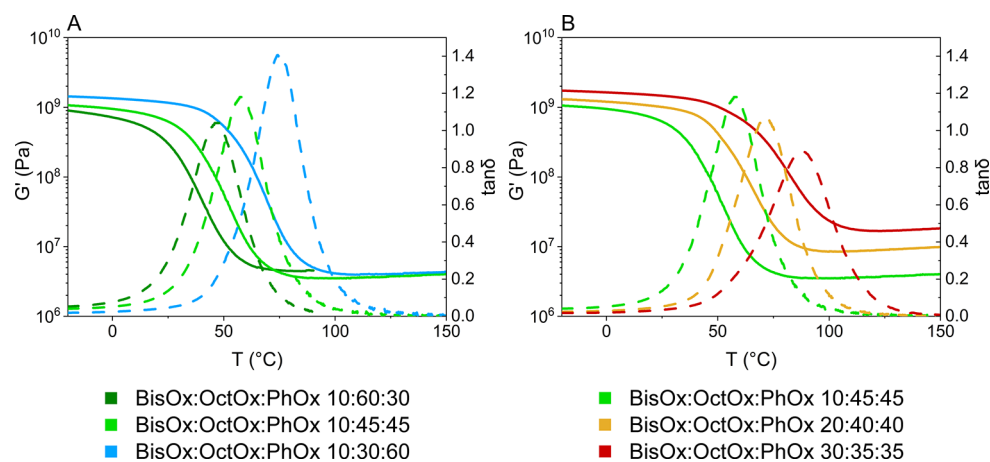
As already observed from the distinct DSC peak in STA analysis, the ring-opening reaction of 2-oxazolines generates high specific amounts of heat and is therefore particularly suitable for photo-DSC analysis to follow a UV-induced polymerization. In fact, subsequent photo-DSC measurements (320–500 nm, 130 mW cm<sup>-2</sup>) clearly confirm the ability for photopolymerization at 100, 120, and 140 °C, as the formulations showed distinct exothermicity of polymerization and resulted in glassy transparent photopolymers with light yellow discoloration (Figure S1). Still the comparative photo-DSC analyses showed expectedly different reactivities and photopolymerization behavior of the examined monomers PhOx, OctOx, and BisOx in mixtures comprising the triarylsulfonium PAG S–B (Figure 1B–D). The determination of theoretical functional group enthalpy ( $\Delta H_{op} = 73.1 \pm 0.9$  kJ mol<sup>-1</sup>) from separately conducted photo-DSC measurements and subsequent <sup>1</sup>H NMR measurements of OctOx at 120 °C allowed for the direct evaluation of conversion (*C*) and rate of polymerization (*R<sub>p</sub>*) as the most significant parameters (Table 1). The juxtaposition of monofunctional monomers PhOx and OctOx showed the clearly impeded photopolymerization of aromatic PhOx.

**Table 1. Photo-DSC Results of PhOx, OctOx, and BisOx Formulations with 0.5 mol % S–B per Reactive Group**

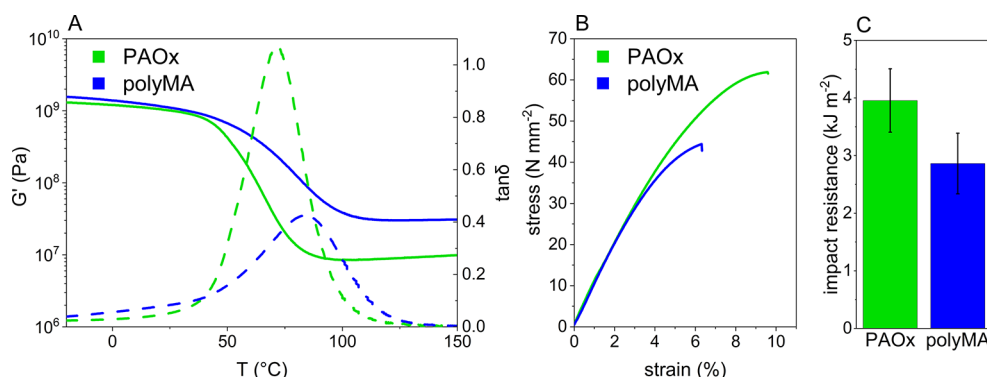
<i>T</i> (°C)	monomer	<i>C</i> (%)	<i>t</i> <sub>max</sub> (s)	<i>t</i> <sub>95</sub> (s)	<i>R<sub>p</sub></i> (×10 <sup>-3</sup> mol·L <sup>-1</sup> ·s <sup>-1</sup> )
100	BisOx	56	80	535	9
120	BisOx	91	48	299	32
	OctOx	27	39	322	9
140	BisOx	94	21	108	158
	OctOx	69	51	211	35
	PhOx	38	31	558	15

Only insignificant photopolymerization could be observed for the aromatic PhOx below 140 °C, whereas OctOx showed apparent photoreactivity at temperatures above 100 °C. By gel permeation chromatography (GPC) the structural analysis of poly(OctOx) was conducted for samples photopolymerized at temperatures of 100, 120, and 140 °C, as well as with varied PAG concentrations of 0.5, 1.0, and 1.5 mol % S–B (Table S2). As expected, higher temperatures lead to an enhanced ring-opening propagation and, therefore, higher monomer conversion, while this is also well reflected in an increased molecular weight. Furthermore, it is also well expected that an increase of PAG concentration causes lower molecular weights in the cationic photopolymerization of OctOx. Generally, the monofunctional model compounds showed high dependency on thermal energy input for effective propagation. The difunctional monomer BisOx, however, showed outstandingly rapid photopolymerization and high susceptibility to thermal input, reaching conversions of 94% at 140 °C.

This exceptionally high reactivity of BisOx at elevated temperatures was considered for the investigation of cross-linked 2-oxazoline photopolymers. Based on earlier reports of thermally cross-linked bis(2-oxazoline)-terminated building blocks, promising (thermo)mechanical properties were expected from materials after cationic photopolymerization of difunctional 2-oxazolines.<sup>32</sup> Formulations of BisOx in mixtures with the monofunctional monomers OctOx and PhOx were prepared to yield sufficiently resistant photopolymers for (thermo)mechanical investigations by DMTA. The aliphatic OctOx was considered to provide sufficient flexibility in a mixture with the aromatic PhOx, which gives a glassy photopolymer with high rigidity. Moreover, the concentration of the difunctional cross-linking BisOx was varied between 10 and 30 mol % to investigate the effect of higher cross-link density on the structural strength of the resulting material. The photopolymer specimens of a series of 2-oxazoline mixtures were prepared comprising increased amounts of PAG (1 mol % S–B per reactive group) to ensure high conversions in photopolymerizations at 140 °C using 320–580 nm irradiation at 120 mW cm<sup>-2</sup>. Equally heated samples without irradiation confirmed the thermal stability of the formulations in the absence of light. As seen from DMTA results in Figure 2, the variation of the ratio BisOx/OctOx/PhOx yielded in adjustable glass transition temperatures (*T<sub>g</sub>*) between 40 and 90 °C.



**Figure 2.** DMTA screening of 2-oxazoline photopolymers with (A) the variation of the ratio of OctOx/PhOx with 10 mol % BisOx and (B) the variation of BisOx concentration in a mixture of monofunctional 2-oxazolines (OctOx/PhOx 1:1).



**Figure 3.** Mechanical testing of photopolymers of 2-oxazoline formulation (PAOx) and methacrylate reference formulation (polyMA) by (A) DMTA, (B) tensile testing, and (C) impact resistance.

From increased amounts of rigid aromatic structures (PhOx) and higher cross-link density (BisOx), the typical structure–property relationship of thermosetting photopolymers is observed, which is represented by a higher storage modulus at room temperature ( $G'_{20}$ ), an increase of glass transition temperature ( $T_g$ ), and increased storage moduli in the rubbery region ( $G'_r$ ; derived at  $T_g + 30$  °C). Overall, photopolymers with promising (thermo)mechanical properties and high glass transition temperatures are obtained, presumably arising from the characteristic polyamide backbone structure after cationic photopolymerization of 2-oxazolines.

As shown, the efficient photoinitiation of 2-oxazoline CROP by onium salt PAGs not only introduces a novel class of materials, but may also serve as a new approach for the toughening of photopolymer products, being currently in the focus of lithography-based additive manufacturing technology (L-AMT). Earlier cationic systems for L-AMT based on epoxides, oxetanes, and vinyl ethers, as well as radical-cationic hybrid systems, aimed for better product properties from low viscous formulations and the reduction of shrinkage by photopolymerization of ring-opening monomers. Still, low curing rates have obstructed their application to date.<sup>33–35</sup> The rapid free radical photopolymerization of low molecular (meth)acrylates has therefore been dominantly applied in L-AMT due to fast curing rates. However, this leads to the challenge of high brittleness and low toughness of the resulting photopolymerized products as well as significant shrinkage in the processing of these monomers.<sup>33,36</sup>

In an effort to reach desirable Thermoplast-like material properties, Hot Lithography has recently been introduced as a new L-AMT for polymers with increased toughness and impact resistance from inevitably high viscous formulations, which can only be processed when heated.<sup>37–39</sup> In Hot Lithography, temperatures up to 140 °C are applied to reduce viscosity and at the same time decisively enhance the reactivity of the photoreactive formulations upon laser irradiation, which potentially also facilitate the 3D printing of 2-oxazolines by the herein presented cationic photopolymerization method. To first evaluate the advantageous (thermo)mechanical properties of photopolymerized poly(2-oxazoline)s over poly(methacrylate)s, a mixture of the 2-oxazoline model compounds was compared to a corresponding methacrylate system by DMTA, tensile tests, impact resistance tests, and TGA. Therefore, a molar ratio of BisOx, OctOx, and PhOx of 20:40:40 was photopolymerized in a described manner via the PAG S–B at 140 °C, whereas the reference system of 1,4-butanediol dimethacrylate (BDDMA), aliphatic hexyl meth-

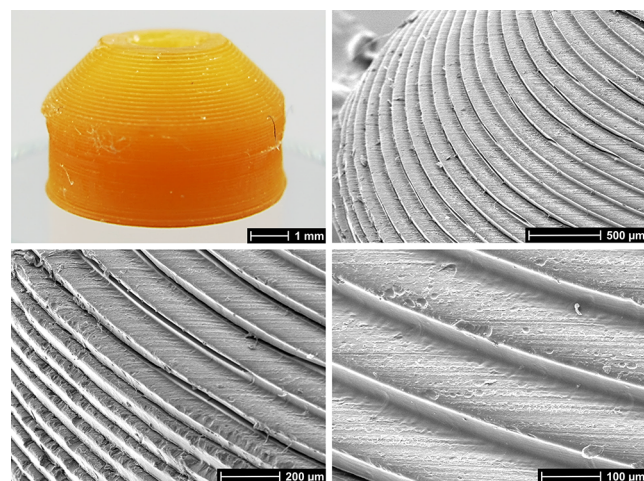
acrylate (HexMA), and aromatic benzyl methacrylate (BMA) was photopolymerized in the same ratio via the free radical photoinitiator bis(4-methoxybenzoyl)diethylgermanium (BMDG, 1 mol % per reactive group of monomer) at room temperature. As seen from the DMTA results in Figure 3, the resulting photopolymer materials of 2-oxazoline and methacrylate formulations, PAOx and polyMA, exhibit comparable  $G'_{20}$  and glass transitions at  $T_g$  of 73 and 84 °C, respectively. The distinctly higher storage modulus above the glass transition at  $G'_r$  of the methacrylate system indicates a higher cross-link density in the network generated by free radical photopolymerization. However, the examinations by tensile testing showed the advantageous properties of the 2-oxazoline-based photopolymer PAOx under mechanical stress, as the material exhibits distinctly higher stress and strain at break. The standardized Dynstat tests show the significantly higher impact resistance for the polyamide material of PAOx. Furthermore, TGA confirmed the expectedly high thermal resistance of PAOx up to 350 °C (5% mass loss, Figure S5).<sup>32</sup> With respect to the fundamentally different polymerization mechanisms, the UV-induced CROP of 2-oxazolines generates polyamide materials with advantageous properties, whereas the poly(methacrylate) gives brittle materials with low resistance to mechanical stress and temperature.

As the hot lithography design comprises a heated bottom-up stereolithography (SLA) setup and high intensity UV-laser irradiation, it provides suitable conditions for the direct application of the investigated UV-induced CROP of 2-oxazolines in L-AMT (Figure S8). The performed proof of concept should not only exhibit the applicability of a novel cationically photopolymerizable system in L-AMTs in general, but also the enhancement in the 3D printing of low reactive formulations by Hot Lithography at temperatures beyond 100 °C.

For the experimental Hot Lithography printing of a 2-oxazoline monomer, the difunctional BisOx was used for rapid solidification upon irradiation and absence of evaporation throughout the printing process. Moreover, 9,10-dibutoxyanthracene was used to enhance the resolution of the selective photopolymerization in the irradiated area by its excellent spectral compatibility with the 375 nm laser ( $\lambda_{\max} = 381$  nm). This electron-transfer photosensitizer greatly supports the reactivity and the control over curing depth in the layer-by-layer cationic photopolymerization.<sup>40</sup> As the PAG S–B caused inevitable diffusional overpolymerization, the Hot Lithography of BisOx was conducted using a mixture of triarylsulfonium hexafluoroantimonate salts (S–Sb, 50 wt % in propylene

carbonate solution; Figure S6), which was previously examined in comparative photo-DSC analyses (Figure S7).

As seen from the SEM images in Figures 4 and S9, the successful structuring of defined 3D parts confirms the efficient



**Figure 4.** Photography and SEM images of poly(BisOx) parts 3D-printed by Hot Lithography at 120 °C.

application of the UV-induced CROP of 2-oxazolines in Hot Lithography. The nozzle-type cylindrical-conical object was structured in a layer-by-layer approach via a laser at 120 °C (Figure 4, 100 μm layer thickness). The high resolution of the printed layers confirms the selectivity of the light-induced curing reaction, whereas the high lateral precision is expressed by the accurate layer thickness without light-induced or diffusional overpolymerization.

In summary, the UV-induced CROP of 2-oxazolines by sulfonium salt PAGs at elevated temperatures was introduced as a promising polymerization method to overcome the limitations of this versatile, yet, inherently low reactive monomer class. Within the set of investigated model compounds, the exceptionally high reactivity of aliphatic difunctional BisOx was observed at temperatures between 100 and 140 °C and applied in the UV-curing and investigation of thermosetting 2-oxazoline-based photopolymers. The efficient photoinitiation of 2-oxazoline CROP gives access to novel materials, which showed inherently higher toughness in mechanical testings and may give rise to further development of advanced materials based on 2-oxazoline monomers. Moreover, the difunctional monomer BisOx was successfully printed to yield well-defined three-dimensional structures via Hot Lithography at 120 °C. The Hot Lithography platform pioneers in the 3D printing of low reactive monomers and might enable the fabrication of promising new materials from monomer classes, which have not been considered for photopolymerization to date.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00055>.

Materials, experimental procedures of synthesis and characterization, analytic devices and methods, structural analysis, material testing and sample preparation, 3D-printing by hot lithography (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge the TU Wien University Library for financial support through its Open Access Funding Program.

## ■ ABBREVIATIONS

CROP, cationic ring-opening polymerization; PAG, photoacid generator; UV, ultraviolet; DSC, differential scanning calorimetry; STA, simultaneous thermal analysis; TGA, thermogravimetric analysis; PAOx, poly(2-alkyl/aryl-2-oxazoline); PEG, polyethylene glycol; WCA, weakly coordinating anion

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