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Investigation of Lewis photobase-catalysed oxa-Michael addition for hot lithography

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In lithography-based additive manufacturing, step-growth polymerization is a highly desired mode as the resulting polymer networks are usually more homogenous and therefore tougher than ones obtained by free radical chain growth polymerization. Therefore, thiol–ene chemistry sees widespread use, however, the employed thiols are accompanied by strong odor, limited availability and limited storage stability of the formulation. Replacing the thiols with alcohols resolves these problems as a wide variety of odorless alcohols is available. The oxa-ene reaction presented here is a base-catalysed Michael-type reaction for which a highly active Lewis base catalyst is known. Our work shows the preparation of photocaged Lewis base catalysts for this oxa-Michael addition, its implementation into photochemistry and the accompanying new mechanism compared to the regular thermal catalysis. Additionally, the storage stability of such formulation was investigated at different temperatures. Finally, the developed system is applied in additive manufacturing using hot lithography approaches with both linear and non-linear absorption of light.

New concepts

We are working on pushing the limits of additive manufacturing in multiple directions by developing Lewis photobase generators for step-growth photopolymerization. With employing the oxa-Michael system, we could demonstrate the ability of phosphine-based Lewis photobase generators in a model reaction as excellent photolabile catalysts. Not only is our system highly reactive upon irradiation, it is also stable when stored under light exclusion at both room temperature and 60 °C. During our investigation, we also gained a first insight into the respective mechanism. Transitioning the developed model system towards a photopolymerizable formulation, we achieved the first light-induced oxa-Michael polymerization by Lewis catalysis using the hot lithography technology. In two different setups – laser stereolithography and digital light processing – highly resolved 3D-printed objects could be produced. Pushing the limits further, the systems was tested in a heated two-photon-polymerization (2PP) setup. Hereby, the first hot-2PP-lithography can be reported. All in all, our system opens up a versatile platform for further research in the fields of the oxa-Michael reaction, photobase generators, hot lithography, and (hot)-2PP-lithography.

The Michael addition is a fundamental reaction in organic chemistry featuring the base-catalysed addition of a nucleophile (Michael donor) to an α,β-unsaturated carbonyl compound (Michael acceptor) (Fig. 1a).[1] The portfolio of viable nucleophiles ranges from various C–H acidic compounds such as malonates or aliphatic nitriles to different heteroatoms such as primary and secondary amines, thiols and alcohols (Fig. 1b).[2] Especially, the oxa-Michael addition, where an alcohol is selected as the nucleophile, sparked increasing interest as both the high availability as well as the low cost of both alcohols and acrylates make for a great combination.[3] Typically, Brønsted bases such as amidines (**DBN**), guanidines (**TMG**), and phosphazene (**P_2-*t*Bu**) are used as the catalyst for thermal oxa-Michael addition (Fig. 1c).[3] The phosphazene **P_2-*t*Bu** remains the gold standard, however, the drawbacks of this compound are its high price, and its toxicity.[4] Systems catalysed *via* the Brønsted approach start by the deprotonation of the Michael donor by the Brønsted base. The newly generated anion reacts with the β-carbon of the acceptor giving the adduct intermediate with carbanion in the α-position. This carbanion is stabilized by the neighbouring electron withdrawing group (EWG). In the final step, the protonation of said carbanion takes place yielding the final Michael addition (Fig. 1a).[3,5]

In contrast to the widely used Brønsted catalysed addition, Lewis base catalysis is gaining more traction as cheaper yet comparably efficient catalysts are discovered. The recent use of electron-rich triaryl phosphines showed promising results regarding the catalytical capabilities. Various phosphines have been investigated and ordered in their efficiency. The best performing phosphine was tris(2,4,6-trimethoxyphenyl)phosphine which has the highest number of electron-donating moieties and therefore

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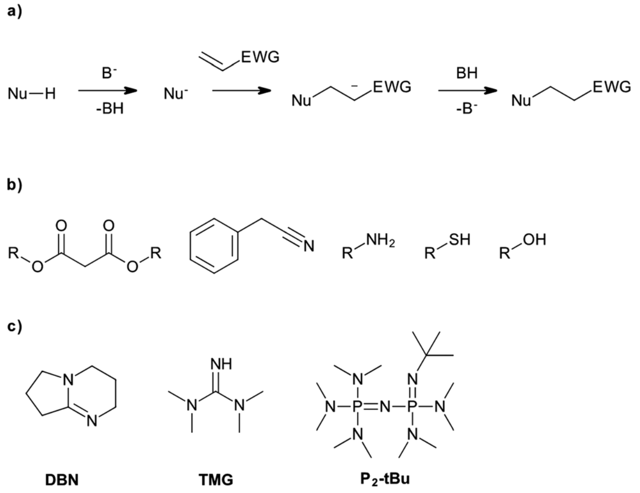

Fig. 1 (a) General mechanism of the Michael addition; (b) different nucleophiles for the Michael-type addition; (c) conventional Brønsted bases **DBN**, **TMG** and **P$_2$-*t*Bu**.

the highest Lewis basicity.[3,4,6] The mechanism of the Lewis base catalysed oxa-Michael addition differs from the classical Brønsted mechanism as in the first step an equilibrium between the phosphine, the Michael acceptor and their adduct is reached (Fig. 2). As a side reaction, the zwitterionic species can initiate the anionic homopolymerization of the electron deficient double bond. However, in the presence of an alcohol, the proton transfer to the α-carbanion is favoured. The resulting alkoxide is a strong nucleophile and can perform the β-addition to the double bond of the acceptor. After proton transfer, the product is obtained and another alkoxide is formed to resume the catalytic cycle (Fig. 2).[6]

Since the planned application for the oxa-Michael reaction is in the field of light-based additive manufacturing (AM), the system needs to be translated to photochemistry. AM – first introduced in the 1980s – is a technique allowing for precise and highly customised fabrication of three-dimensional objects.[7] As a subcategory of AM. Vat photopolymerization was patented 1984 using light patterning in a liquid resin.[8] Most resins today are based on radical photopolymerization of (meth)acrylates which yield rather brittle materials due to their tightly crosslinked and irregular networks.[9] This problem can be countered by utilizing step-growth systems such as the thiol–ene reaction, which has seen widespread use.[9–11] Beside the accompanying nauseating smell of the thiol, thiol–ene based resins struggle with short shelf-life stability.[12] In contrast, the oxa-Michael polymerization is also based on a step growth-mechanism, but the alcohols are more pleasant to work with. As the reaction is base catalysed, photobase generators are needed. Photobase generators are a substance class which liberate a base after light irradiation, which was first reported in 1990 using photoactive carbamates.[13,14] While at first only weak bases such as primary amines could be liberated, progress was made towards stronger base using quaternary amines which cleave off one residue and therefore give a tertiary amine.[15] However, the limited basicity of tertiary amines accompanied by low solubility, thermal stability and stability in solution asked for further development in this field. While 1,1,3,3-tetramethylguanidine (**TMG**) is a strong neutral base,[16,17] the introduction of photobase generator salts consisting of the protonated base and a photoactive anion such as tetraphenylborate, ketoprofen or thioxanthone carboxylate allowed for the preparation of stronger organic bases.[14,18–20] However, to the best of our knowledge, only Brønsted-type bases were prepared in that manner and the aforementioned Lewis base phosphines have not yet been introduced to the world of photochemistry and additive manufacturing.

Results and discussion

Preparation of Lewis photobase generators

The use of photobase generator (PBG) salts provides a platform allowing different combinations of both base and photoactive anion to be easily varied (Fig. 3a), which also made it into

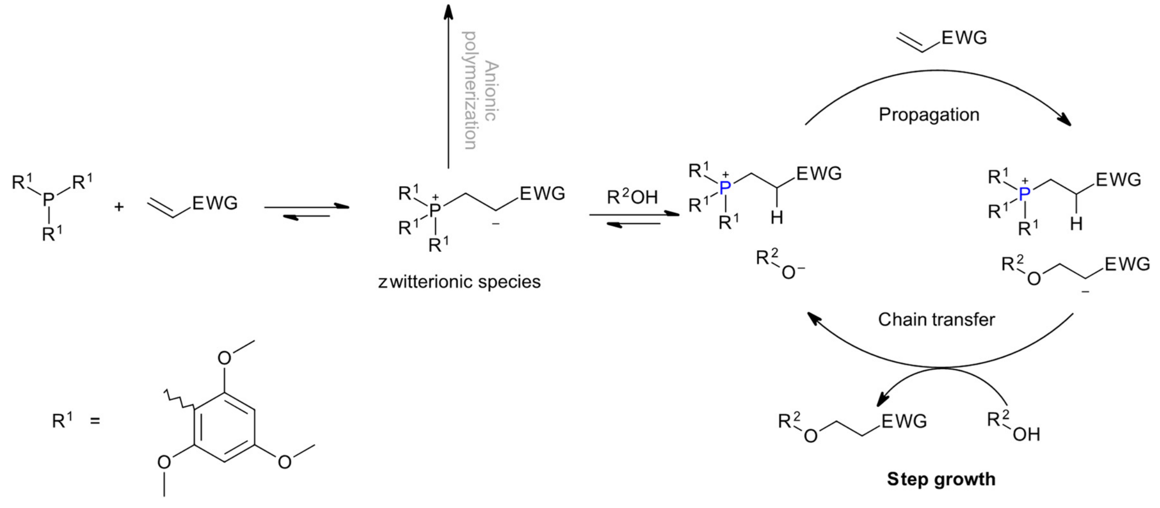

Fig. 2 Mechanism of the Lewis-base catalysed oxa-Michael addition.[6]

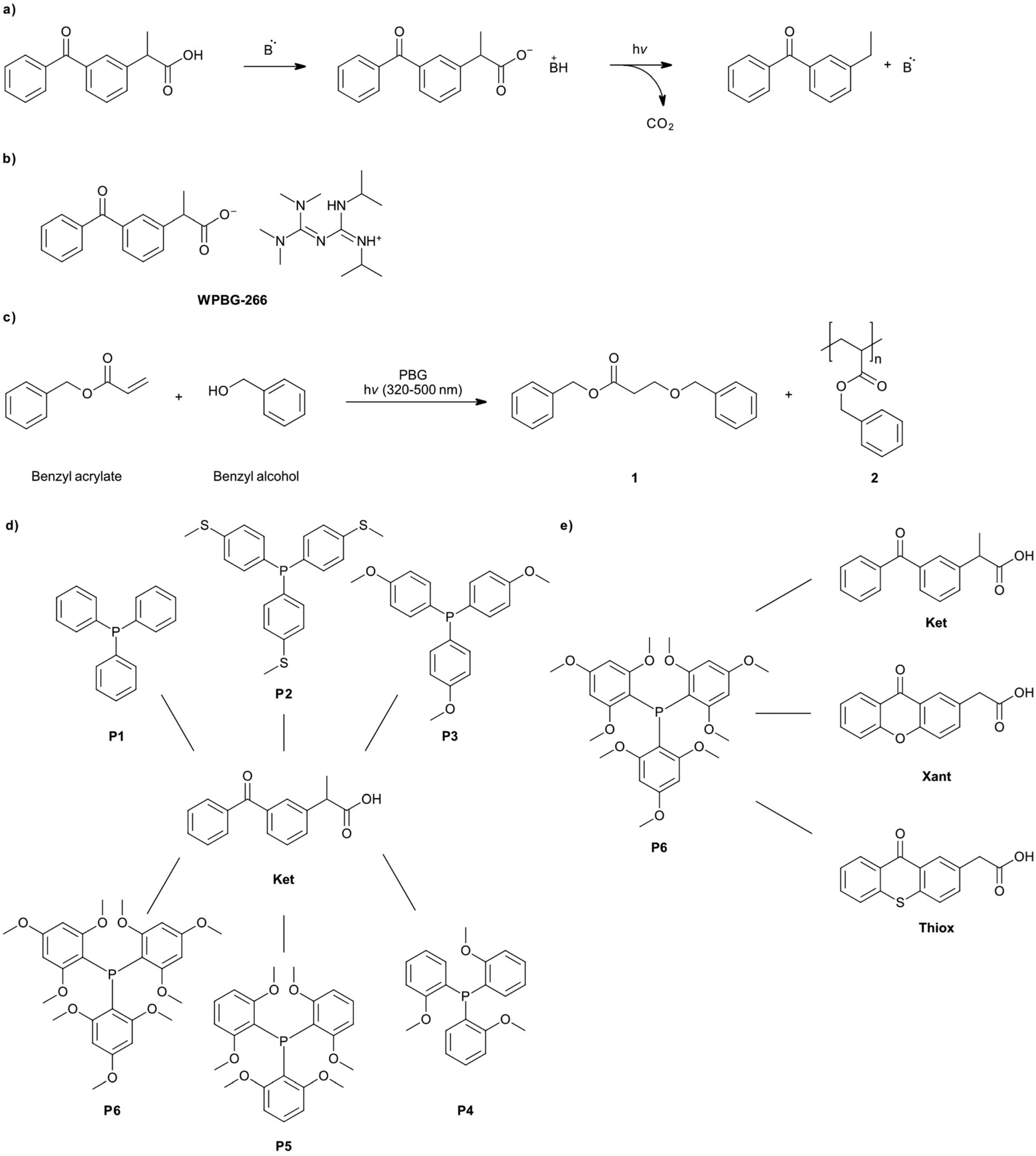

Fig. 3 (a) General synthetic approach for PBG salts using ketoprofen and subsequent photo-decarboxylation and liberation of the base.[21–23] (b) Structure of the ketoprofen based commercial photobase generator WPBG-266 form FUJIFILM Wako Chemicals Europe GmbH.[23] (c) Oxa-Michael model reaction for the screening of various PBG salts to the desired oxa-Michael product and the possible homopolymer of benzyl acrylate **2**. (d) Structure of the triaryl phosphines (**P1** to **P6**) and ketoprofen (**Ket**) (e) structure of the phosphine base **P6** and the different photoactive acids **Ket**, (9-oxo-2-xanthenyl)acetic acid (**Xant**) and (10-oxo-9-thiaanthr-3-yl)acetic acid (**Thiox**).

commercial products such as **WPBG-266** from FUJIFILM Wako Chemicals Europe GmbH (Fig. 3b).[21–23]

Herein, we adopted this strategy by converting a set of six different triaryl phosphines (compounds **P1** to **P6**) with varying electron donating moieties with ketoprofen (**Ket**) to PBGs (Fig. 3d). As according to literature, the phosphine with the highest electron density was expected to perform the best in an oxa-Michael system, it was also used for the synthesis of two further PBGs with xanthone- and thioxanthone carboxylic acids (**Xant** and **Thiox**, respectively) (Fig. 3e).[4] A major difference in our set of various Lewis PBGs to conventional Brønsted PBGs was that we obtained a solid mixture of the acid and the phosphine-bases rather than a phosphonium carboxylate salt.

Model reaction

The newly prepared PBGs alongside WPBG-266 were subjected to a model reaction consisting of benzyl acrylate as the Michael acceptor and benzyl alcohol as the respective donor as the combination of acrylate and primary alcohol has been shown in literature to achieve good double bond conversion using the free **P6**.[4] The reaction was performed using the photo-DSC as this device allowed for the automatic measurement of all

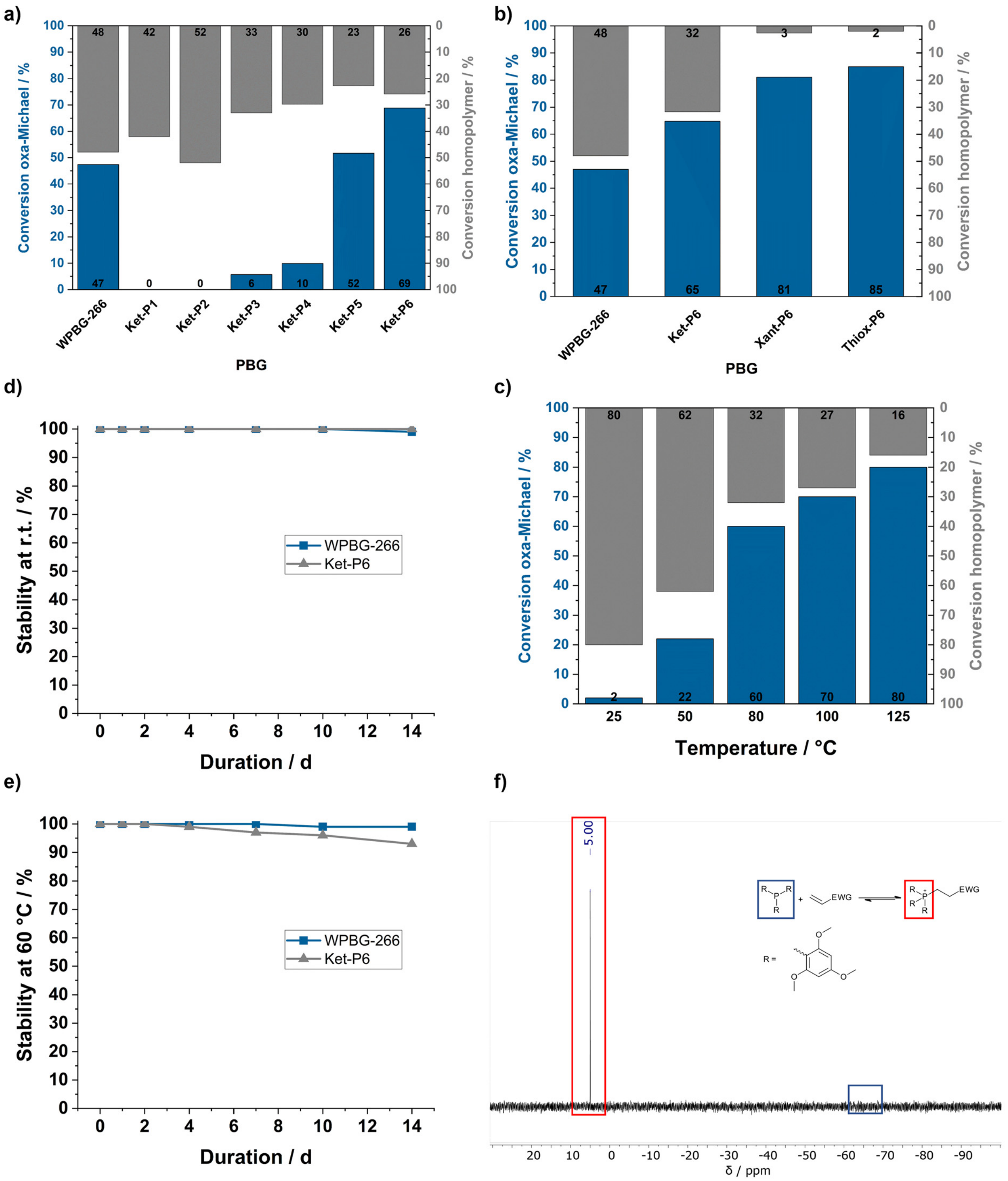

Fig. 4 (a) Conversion in the model reaction to the desired ether product **1** and to the homopolymer **2** using the reference **WPBG-266** in comparison to the new phosphine PBGs **Ket-P1** to **Ket-P6** according to ^{1}H-NMR after photo-DSC experiments at 80 °C. (b) Conversion in the model reaction to the desired ether product **1** and to the homopolymer **2** using the reference **WPBG-266** in comparison to the new phosphine PBGs **Ket-P1** to **Ket-P6** according to ^{1}H-NMR after photo-DSC experiments at 80 °C; (c) conversion of the model oxa-Michael reaction at various temperatures using **Ket-P6**; (d) and (e) stability of an oxa-Michael formulation containing **Ket-P6** or **WPBG-266** as the PBGs at room temperature (d) and at 60 °C (e); (f) ^{31}P-NMR of **Ket-P6** in oxa-Michael model formulation of the stability study after homogenization.

formulations under controlled temperature and irradiation conditions. Said samples were prepared with equimolar amounts of benzyl acrylate and benzyl alcohol alongside 2 mol% PBG, 2 mol% 3,5-di-*tert*-butyl-4-hydroxytoluene (**BHT**) as a radical inhibitor (Fig. 3c). After the reaction in the photo-DSC, the samples were dissolved for NMR analysis to calculate the conversion. A control experiment without any PBG was performed as well and did not yield any oxa-Michael product (SI). The **BHT** content was also varied (SI).

Influence of the substitution pattern of the phosphine

At first the influence of the different phosphines **P1** to **P6** in their PBG salts with **Ket** were investigated at 80 °C with an overall reaction time of 30 min. The conversion to the oxa-Michael adduct **1** was determined *via* ^{1}H-NMR, as well as the conversion to the homopolymer **2** (eqn (S1) and (S2), SI). First of all, the expected trend of triaryl phosphines with a high amount of electron donating moieties proved to be also applicable for phosphine PBGs. When looking closer at the results, the completely unsubstituted **Ket-P1** yielded no ether under the respective conditions. Adding one methoxy group to each ring in the *para* position (**Ket-P3**) allowed for 6% conversion to the ether **1**. However, using thiomethyl substituents instead showed no conversion at all (**Ket-P2**), even though both methoxy and thiomethyl being electron donating moieties. Changing the methoxy position from *para* to *ortho* increased the conversion to 10% (**Ket-P4**). Even more drastic was the increase when adding two methoxy substituents in both *ortho* position (**Ket-P5**), which increased the conversion to 52% and thus outperforming the commercial Brønsted PBG **WPBG-266** (47%). Adding an additional third methoxy moiety in the *para* position (**Ket-P6**) pushed the conversion to 69%. What was also observed was the formation of poly(benzyl acrylate) as a side product. Its formation was most prominent in the commercial **WPBG-266** as well as **Ket-P1** and **Ket-P2**. The two PBGs to yield more oxa-Michael product than homopolymer were **Ket-P5** and **Ket-P6** (Fig. 4a).

Therefore, the set of phosphine-PBGs with different substitution patterns could successfully be applied to the photochemically triggered oxa-Michael addition in a model system. The observed conversion trend of the Lewis-PBG was in line with literature about the performance of free phosphines in oxa-Michael systems.[4,6]

Influence of the photolabile protective group

Three different carboxylates were investigated as photocaging agents. While **Ket** was commercially available, both **Xant** and **Thiox** were synthesized according to their respective literature (SI).[24,25] Regarding the performance of the three PBGs with different carboxylates, their conversion in the model oxa-Michael reaction was compared. As shown above, **Ket-P6** outperformed the reference **WPBG-266.** With both **Xant** and **Thiox** this result could even be improved to 81 and 85%, respectively (Fig. 4b). Furthermore, the use of **Xant** and **Thiox** also lead to only minimal formation of homopolymer −3 and 2%, respectively. Additionally, **P6** without any photolabile was measured on the photo-DSC with irradiation in a control experiment, which showed 85% conversion (SI). Although **Xant-P6** and **Thiox-P6** performed better in the model reaction, further testing was done with **Ket-P6** as this PBG relies on inexpensive, commercial starting materials.

Temperature dependency

Previous model reactions for the investigation of the performance of different PBGs were conducted at 80 °C, however, the reaction speed and conversion are of course dependent on the temperature. Thus, a general screening of the model reaction at 25, 50, 80, 100 and 125 °C using **Ket-P6** was conducted (Fig. 4c). While at low temperatures in the period of 30 min only 3% oxa-Michael conversion was achieved and homopolymer formation prevailed, a continuous increase in the conversion towards the oxa-Michael product was observed when moving to higher temperatures reaching 80% at 125 °C. This temperature dependency is particularly useful for hot lithography applications, which allows processing of formulations above 100 °C.[26,27]

Stability study

One concern for hot lithography is the stability of the used systems as unintended reaction of the monomers would lead to gelation of the formulation in the vat. Therefore, the model system with **Ket-P6** or **WPBG-266** was monitored over 14 days at room temperature (r.t.) and at 60 °C using both ^{1}H- and ^{31}P-NMR spectroscopy. The proton NMR was used to investigate the stability of the monomers and to detect any formed ether. The acquired spectra of those experiments were evaluated three times and the respective results varied by less than 1%. The results showed that after 14 days no conversion of the reactants to the ether without any external trigger occurred, while at 60 °C the conversion climbed to 3 and 7% for **WPBG-266** and **Ket-P6,** respectively (Fig. 4d and e). With these results in mind, the application in hot lithography can be pursued as a spontaneous polymerization of the formulation is unlikely. ^{31}P-NMR was used to investigate the stability of the phosphine species in the formulation and whether it oxidized or not. On day 0, no oxidation was observed, however, the phosphine signal itself at −66 ppm was also not present anymore. The detected phosphorous signal at 5 ppm belonged to phosphonium species which would be expected to only form after irradiation to liberate the phosphine. As this suggests that the addition of the phosphine to the acrylate already happened before any irradiation took place, a closer look at the mechanism was necessary (Fig. 4f). Nevertheless, this phosphonium adduct was stable throughout the stability study.

Mechanistical investigations

We first anticipated on basis of pK_a values for **Ket** (5.9 in aqueous solution) and protonated **P6** (11.0 calculated for aqueous solutions) the formation of the corresponding salt.[28–30] However, ^{31}P-NMR spectroscopy of neat **Ket-P6** in benzene-d_6 revealed only one peak at −66 ppm, which was assigned to the phosphine of **P6.**[4] No considerable salt formation was observed

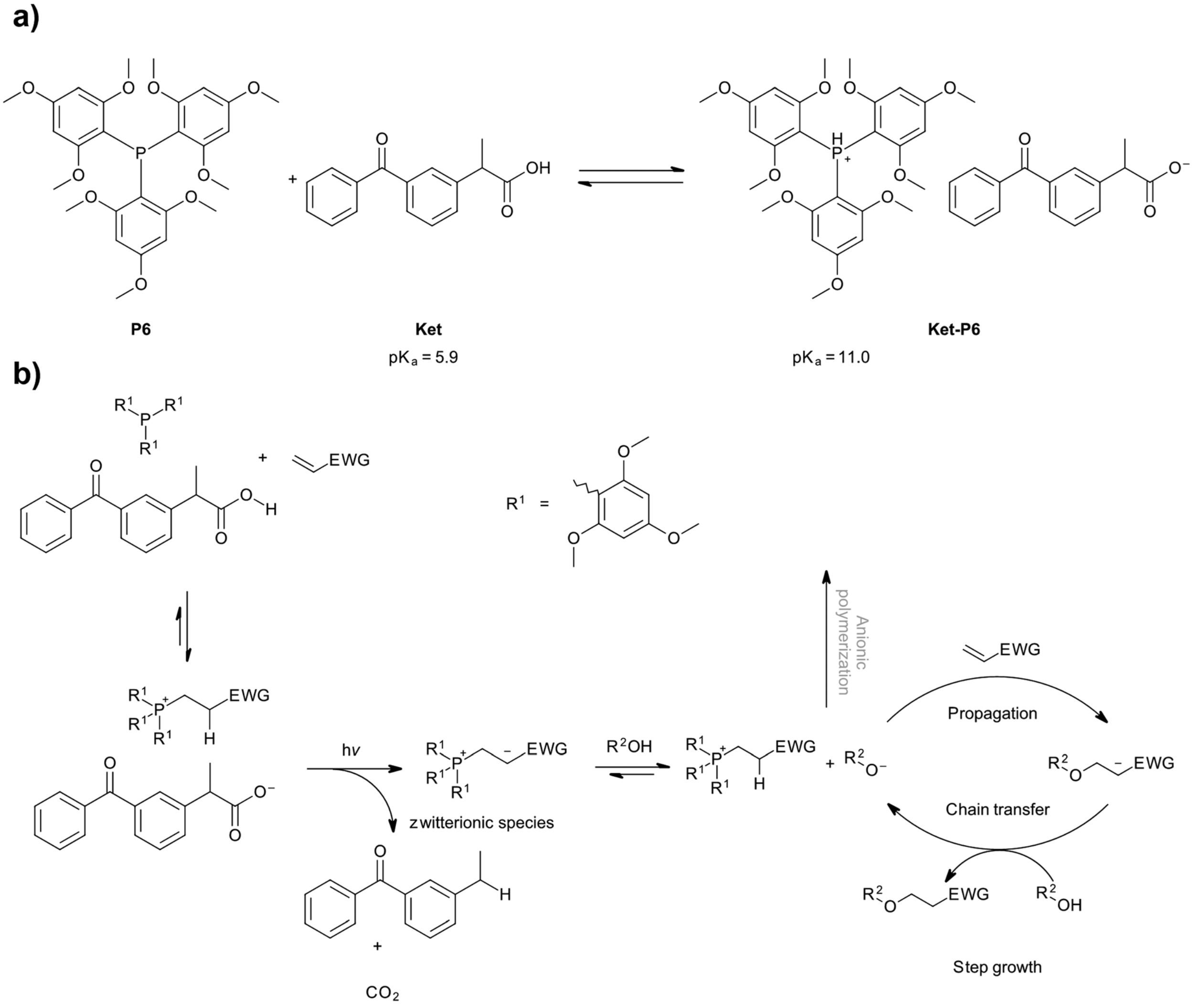

Fig. 5 (a) Acid/base equilibrium of the **P6** and **Ket** with corresponding pK_a-values for **Ket** and protonated **P6**;[28–30] (b) proposed oxa-Michael mechanism with the new Lewis PBG **Ket-P6**.

under these conditions. Therefore, the equilibrium of the acid/base reaction was on the neutral side (Fig. 5a, left side).

This updated version of **Ket-P6** now allowed for the explanation of the phosphonium peak in the phosphorous spectrum of the stability study at day 0 as the phosphine **P6** was not hindered by **Ket** to react with the benzyl acrylate of the oxa-Michael system.

With the updated form of the Lewis-PBG-adduct in mind and why irradiation is needed nonetheless, a new overall mechanism was proposed in which the formation of a protonated phosphine-double bond adduct and the subsequent photodecarboxylation of the carboxylate was integrated (Fig. 5b, for further information see the SI).

With those results in mind the system was taken to the next step by replacing the monofunctional model compounds with multifunctional monomers for additive manufacturing.

Additive manufacturing experiments

To demonstrate the potential of the presented oxa-Michael system for additive manufacturing, hot lithography techniques were employed, that enable fabrication at temperatures up to 140 °C. The following lithography-based additive manufacturing approaches have been evaluated at elevated temperatures.

Laser scanning lithography

For the first printing experiments, laser scanning lithography (Laser-SLA) at 80 °C was used with a 375 nm Laser providing 60 mW of power. Printing was done with a layer thickness of 50 μm at a writing speed of 200 mm s^{-1}.[26] The tested formulation consisted of 1,1,1-trimethylolpropan (**TMP**) and 1,1,1-trimethylolpropan triacrylate (**TMPTA**) (Fig. 6a) alongside 2 mol% **Ket-P6**, and 2 mol% **BHT**. The obtained structures demonstrated a high resolution without signs of overpolymerization. In cationic photopolymerization, small amounts of base are typically added to neutralize protons that diffuse into non-irradiated areas, which can lead to overpolymerized regions.[31] However, no overpolymerization due to base diffusion was observed in this case. This can be attributed to the significant size difference between the alkoxide and a single

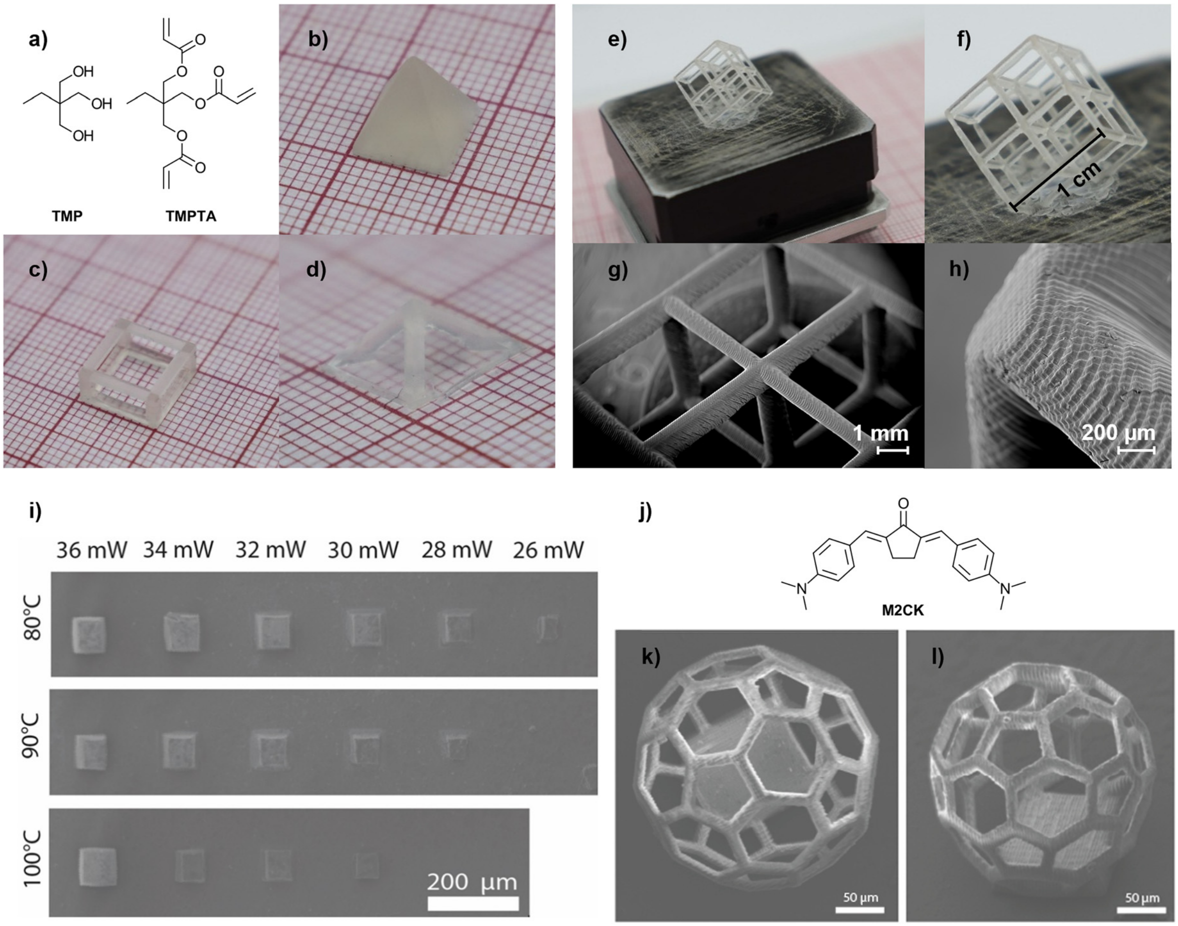

Fig. 6 (a) Structure of 1,1,1-trimethylolpropan (**TMP**) and 1,1,1-trimethylolpropan triacrylate (**TMPTA**); (b)–(d) objects produced by Laser-SLA on graph paper (large square 1 × 1 cm^2); (b) laser-SLA pyramid; (c) laser-SLA hollow cube; (d) laser-SLA hollow pyramid; (e)–(h) hollow cube with internal structures printed with the DLP BP10; (e) and (f) macroscopic view; (g) and (h) SEM images; (i) threshold tests to determine the fabrication window for 2PP. Cube structures (100 × 100 × 100 µm^3) were printed at different temperatures with increasing laser power. After development, the structures were inspected using SEM. (j) Structure of the 2PP-photosensitizer **M2CK**;[33] (k) and (l) micro scaffolds produced at 80 °C with 50 mW laser power. The structures were imaged using SEM in top view (l) and with 45° tilt (l), revealing high-resolution feature sizes in both, lateral and longitudinal directions.

proton, making it unlikely for the phosphine to diffuse in the same manner as protons typically do in cationic systems.

Digital light processing

Further additive manufacturing experiments using a digital light processing (DLP) setup were conducted. Hereby, it was possible to print highly complex hollow cubes with high resolution at 80 °C with a 385 nm light source (75 mW cm^{-2}, 50 µm pixelpitch, 18 s irradiation). Again, no overpolymerization was observed, in contrast, the projected pixels of the light engine could be observed with SEM after the printing (Fig. 6h).

Two-photon polymerization

Two-photon polymerization (2PP) is a subclass of lithography-based additive manufacturing, in which an ultra-short pulsed laser is used induce a photochemical reaction *via* a two-photon absorption process.[32] Structuring was performed at 800 nm using a scanning speed of 600 mm s^{-1}, a line-spacing of 0.5 µm and a layer-spacing of 2.5 µm. Again, **TMP** and **TMPTA** were used as the monomers for the 2PP-experiment (Fig. 6a) alongside 2 mol% **BHT**, 2 mol% **Ket-P6** and 0.02 mol% of the 2PP-photosensitizer **M2CK** (Fig. 6j).[33,34]

To evaluate the reactivity and usability of the presented oxa-Michael system for 2PP, the fabrication window was determined by testing the polymerization threshold at temperatures of 80 °C, 90 °C, and 100 °C. This was done by printing cubes (100 × 100 × 100 µm^3) with progressively increasing laser power (Fig. 6i). The highest reactivity was observed at 80 °C, with the first detectable polymerization occurring at 26 mW. With increasing temperature, the polymerization threshold was rising.

To demonstrate the potential of the developed oxa-Michael system for hot 2PP lithography, micro scaffolds inspired by Buckminster fullerene[35] were produced. Such micro scaffolds have been reported to be used for tissue engineering approaches such as fabricating macro-sized tissue constructs based on *e.g.* cartilage to improve the regeneration of tissue defects.[35,36] Besides its promising application in tissue engineering, the micro scaffold represents due to its complex design and high structural fidelity, a significant challenge for

2PP fabrication and can therefore serve as a benchmark for the performance of a resin.[37,38] Fabrication was performed at a material temperature of 80 °C using 50 mW laser power. The resulting structures were mechanically stable and exhibited high resolution in both lateral and longitudinal directions (Fig. 6k and l).

Conclusions

Overall, a set of different Lewis-type PBG could be developed of which four showed excellent performance (**Ket-P5**, **Ket-P6**, **Xant-P6**, and **Thiox-P6**) in an oxa-Michael model reaction by outperforming the reference PBG. With two of those PBGs – **Xant-P6** and **Thiox-P6** – also exhibiting a low tendency towards homopolymerization. These new Lewis-type PBGs expand the field of PBGs allowing in future a broader selection of available PBGs.[14] While proofing a storage stability of at least 14 days even at 60 °C, a closer insight into the mechanism of the Lewis-type PBG catalysed oxa-Michael system was gathered. As the phosphine could react freely to an adduct with an acrylate before the resulting carbanion was protonated by the carboxylic acid of **Ket**, which was found to be the actual dormant species, which starts the catalytic cycle upon irradiation. Therefore, the oxa-Michael reaction previously only accessible by thermal catalysis has been introduced to the area of photochemistry.[3] The newly developed system could also then be translated into first proof of concept additive manufacturing experiments using both Laser-SLA as well as DLP printing to produce complex structures with high resolution. Furthermore, while hot lithography in the context of 2PP has not yet been widely explored, 2PP could significantly benefit from this approach allowing it to use new material systems. By introducing this novel oxa-Michael system and fabricating complex micro scaffolds *via* 2PP, an important step in this direction has been made. With these results, great progress in replacing thiols with alcohols in the field of photo-catalysed Michael addition could be achieved. Building on these results, the investigation and optimization of oxa-Michael materials will be placed in the focus of future research.

Author contributions

Klaus Ableidinger: data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing – original draft, writing – review & editing. Dominik Laa: data preparation, formal analysis, investigation, methodology, validation, writing – review & editing. Franziska Chalupa-Gantner: data preparation, formal analysis, investigation, methodology, validation, writing – review & editing. Edma Gjata: conceptualization, data preparation, formal analysis, investigation, methodology, validation. Patrick Knaack: conceptualization, formal analysis, funding acquisition, methodology, resources, writing – review & editing. Aleksandr Ovsianikov: conceptualization, formal analysis, funding acquisition, methodology, resources, writing – review & editing. Jürgen Stampfl: conceptualization, formal analysis, funding acquisition, methodology, resources, writing – review & editing. Christian Slugovc: conceptualization, formal analysis, funding acquisition, methodology, resources, writing – review & editing. Robert Liska: conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The raw data supporting the conclusions of this article will be made available by the authors on request. The data supporting this article has been included in the SI. See DOI: **https://doi.org/10.1039/d5mh01050k**

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