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Thionolactone as Resin Additive to Prepare (bio)degradable 3D Objects via VAT Photopolymerization

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Supporting information for this article is given via a link at the end of the document.

Abstract: 3D printing and especially VAT photopolymerization leads to cross-linked materials with high thermal, chemical and mechanical properties. Nevertheless, such stability is incompatible with degradability and re/upcyclability. We showed here that thionolactone and especially dibenzo[c,e]-oxepane-5-thione (DOT) could be used as an additive (2 wt%) to acrylate-based resins to introduce weak bonds into the network via a radical ring-opening polymerization process. The low amount of additive allows to only slightly modify the printability of the resin, keep intact its resolution and maintain the mechanical properties of the 3D object. The resin with additive was used in UV microfabrication and 2-photon stereolithography setup and commercial 3D printers. The fabricated objects were shown to degrade in basic solvent as well in a home-made compost. The rate of degradation is nonetheless dependent of the size of the object. This feature was used to prepare 3D objects with support structures that could be easily solubilized.

Introduction

Additive manufacturing and more specially 3D printing has revolutionized the classic industrial manufacturing by creating directly a 3D object that was designed on a computer using successive layering of materials.^[1] The rapid development of this technique was first made by the ease of the fused deposition modeling (FDM) technique that allows to prepare 3D objects by the computer-controlled layer by layer deposition of molten or semi-molten polymer via an extrusion nozzle.^[1] Nevertheless, 3D printing has become extremely popular with the development of light-cured processes that are summarized by the term VAT photopolymerization.^[1] Among these processes, Digital Light Processing (DLP)^[1-2] in particular has attracted attention due to several attractive features, such as fast build, low resolution (<100 μm features), wide ink viscosity tolerance and low cost. The 3D object is thus obtained by the cross-linking of a liquid resin consisting mainly of multifunctional (meth)acrylates derivatives. The photopolymerization of acrylates occurs rapidly, with high yields, and generates almost no byproducts. This led

to a cross-linked material whose mechanical properties could be tuned by the monomers structure. Moreover, such object is constituted by a C-C bond covalent network that impart a high thermal and chemical stability. This permanent cross-linked network could also be detrimental for diverse reasons. First the high stability is incompatible with facile degradability and re/upcyclability. The high volume/amount of 3D-printed thermoset will be incinerated or stored in landfills following use, making this so promising manufacturing process not environment-friendly or sustainable.^[3] Secondly, this high stability is also not compatible with subtractive manufacturing,^[4] that is a technique where printed materials could be removable or erasable after its formation. Such approach^[5] is very interesting to easily remove templates or sacrificial parts of 3D objects, a technique that is widely used when the object is a positive print before casting and lastly decomposed such as in jewelry or to prepare ceramics. Recently very elegant approaches were proposed by Barner-Kowollik and coworkers that developed new monomers and resins for two-photon lithography based either on thiol-ene chemistry,^[6] TAD-polyether ligation,^[7] silane-based monomers,^[8] o-nitrobenzyl ester monomers,^[9] and chymotrypsin-cleavable monomers.^[10] With these chemistries, stimuli and/or controlled degradation could be obtained. Specific and home-made di or multi-(meth)acrylate monomers with a core containing an acid-degradable acetal^[11] or basic-degradable poly(beta amino ester)^[12] were also prepared and presented a good degradability. In the context of biomaterials, poly(propylene fumarate) (PPF) was also used to print stents for example.^[13] To increase the degradability Bowman and Anseth^[14-17] as well as Patton and coworkers^[18-19] showed that the use of similar specific thiol-ene monomers containing a degradable core could be used. In that case the use of thiol-ene chemistry allowed the preparation of more homogeneous networks that impart good degradation profile.^[16] Nevertheless, such thiol-ene polymers also tend to be too soft for many applications and are more devoted to biomaterials such as hydrogels.^[1]

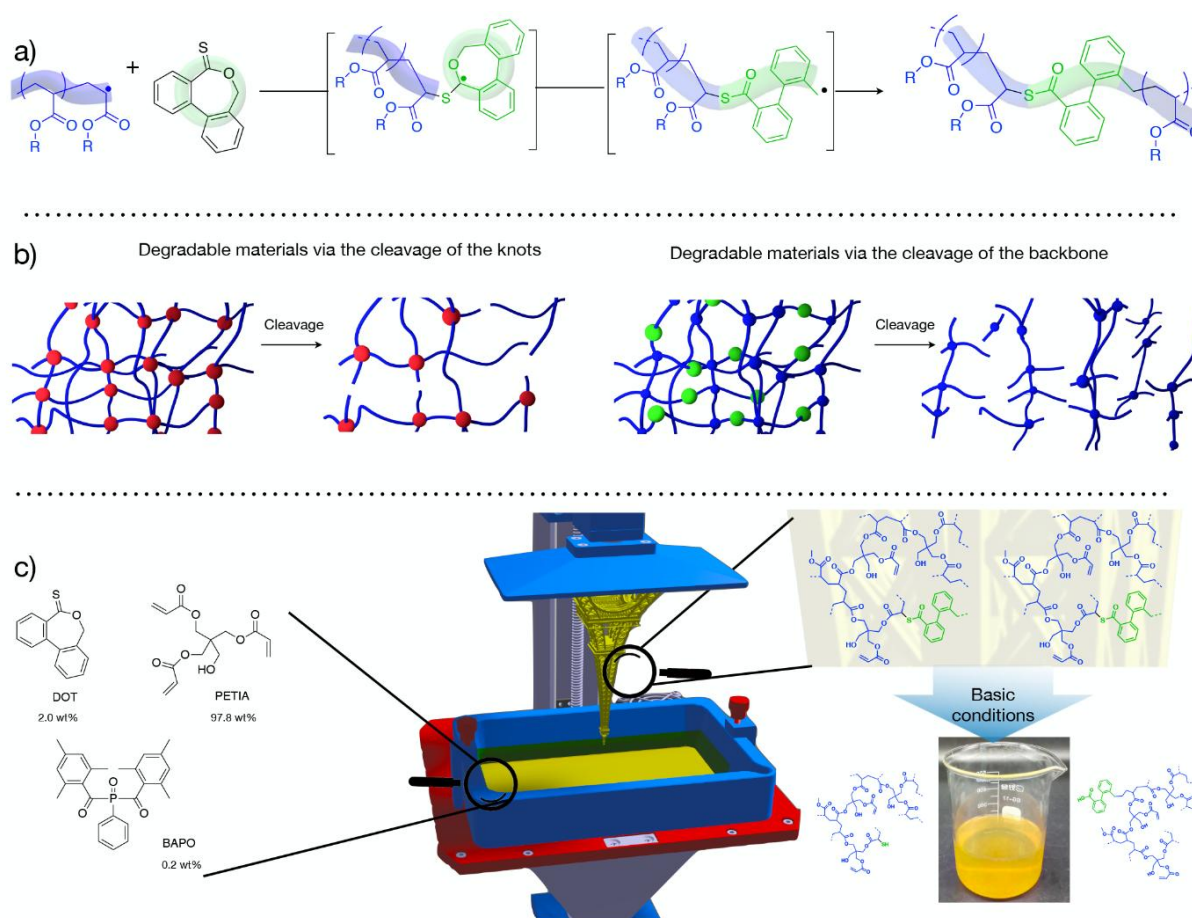


Figure 1. Schematic representation of the writing/erasing process. a) structure and mechanism of the radical polymerization involving the DOT/acrylate monomer pair. b) efficient cleavage of the thermoset via the comonomer approach (cleavage of 10 bonds in the case of both cleavable knots or cleavage linkage in the polymer backbone) adapted from ref. [19], c) Resin formulation, preparation of 3D objects via VAT 3D printer and cleavage mechanism.

The groups of Zhao^[20] and Bowman^[21] reported the 3D printing of linear polymers as a way to impart reprintability or recyclability to the printed object. Nevertheless, such materials have a lower chemical resistance due to the polymer solubility in organic solvent.

Another possibility to induce recycling of cross-linked 3D objects could be to use the concept of dynamic covalent networks^[22] also known as vitrimers. Such approach in combination with 3D printing has been already investigated.^[23-25] In contrary to these techniques the polymer ablation of conventional resins has received less attention,^[26-27] since this technique is more difficult to achieve and seems less promising.

All the previously mentioned techniques either require to prepare specific monomers with degradable core that are the main component of the resins and thus cannot be readily used (due to the high quantity of monomers that has to be prepared for each 3D printing) on commercially-available resins/printers. Moreover, the properties of the photopolymers are impacted by such structure and it is difficult to find the optimized composition to target both degradability and desired mechanical properties. Herein we thus introduce a new approach to impart degradability of 3D objects by adding a comonomer, here the dibenzo[c,e]-oxepane-5-thione (DOT) only as an additive (2 wt%) to impart

degradability to conventional acrylate resin (Figure 1.a). This approach is also based on the comonomer approach that has been developed by Johnson *et al.*^[28-29] on thermoset made by Ring-Opening Metathesis Polymerization (ROMP), where he showed that if the labile/degradable linkage is located into the backbone instead of the knots, fewer amount of labile/degradable moieties is required (Figure 1.b). This study showed that the cleavable monomer approach with only a few wt% of additive is possible,^[29] leading to materials with similar mechanical properties but that could be turned soluble after degradation.

Radical ring-opening polymerization (rROP) is a technique that has been developed in the 80s and that allows the incorporation of heteroatoms in the polymer backbone via a mechanism of addition/fragmentation.^[30] This technique has been rejuvenated recently by the copolymerization of common vinyl monomers and such cyclic derivatives to impart (bio)degradation of conventional materials.^[30] Two main cyclic monomer families emerged, the cyclic ketene acetals (CKAs)^[30-31] and the thionolactones^[32-33]. The non-favorable reactivity ratio between CKA and (meth)acrylates (r_{CKA} close to 0.01 and $r_{(\text{meth})\text{acrylate}}$ close to 4)^[34] led to a low and non-homogeneous incorporation of the labile group in the materials.^[35] To impart good degradability, high initial amounts of CKA are required or a

continuous feed of monomers^[36] could be used to counterbalance it. In the case of (meth)acrylate resin for 3D printing, both solutions cannot be implemented since high rate of polymerization is required implying using CKA only as additive and only bath resin can be used in 3D printer. As a reference, preliminary tests were performed using CKA inserted in (meth)acrylate resin and do not lead to any degradation (see Table S1 for details).

Unlike CKAs, thionolactones and in particular dibenzo[c,e]-oxepane-5-thione (DOT) introduced by Roth and coworkers^[32] followed by Gutekunst *et al.*^[33] presented an efficient copolymerization behavior (statistical incorporation of the two monomers) with acrylate derivatives, imparting homogeneous degradation that could occur via either hydrolysis or aminolysis (Figure 1.c). The combination of DOT/acrylate polymerization and VAT photopolymerization could be an efficient way to prepare (bio)degradable 3D objects. It has been shown that only few percents (5-10 vol%) of cleavable units are required to impart degradability of thermosets^[28-29] and also that DOT has a slightly higher rate of incorporation^[33] than acrylate derivatives during their copolymerization, allowing to use a very low amount of DOT as additive.

Results and Discussion

Resin formulations were prepared by mixing only 2 wt% of DOT with pentaerythritol triacrylate (PETIA) as model multi-acrylate

monomer and 0.2-0.5 wt% of bis(2,4,6-trimethylbenzoyl)-phenyl phosphine oxide (BAPO) as photoinitiator. Figure 2.a compares the absorption spectra of the resins, with and without DOT. The monomer chosen is transparent in UV ($\lambda > 350$ nm) and the photoinitiator was chosen for its absorption at the wavelength of interest in this work (365-385 nm), both for laser microstructuring and for the DLP printer. DOT, added at 2 wt%, shows significant absorption in the UV and visible (< 500 nm) range. This absorption corresponds to a yellow coloration of the resin and is due to the (C=S)-O- group. Once polymerized and due to the isomerization (Figure 1.a), the resulting ring-opened (C=O)-S-thioester bond loose its color. It should thus be noted that this coloration also decreases strongly after UV irradiation (Figure 2.a). Nevertheless, since the overall conversion is not complete during the printing, the 3D objects are still yellow. The absorption of the DOT slightly modifies the reactivity of the resin but does not alter too much the polymerization rate. It has to be reminded that UV resins for 3D printing usually comprise photoabsorbers to control the penetration depth of actinic light. The kinetics of the photopolymerization were studied to quantify the effect of the DOT on the photopolymerization process. The kinetics are plotted in Figure 2.b. They are based on monitoring the C=C conversion of the acrylate functions in the monomer. With a BAPO concentration of 0.5 wt%, the polymerization is efficient, leading to a final conversion of more than 60 % and a conversion plateau quickly reached. This type of kinetics is classical for such a triacrylate monomer.

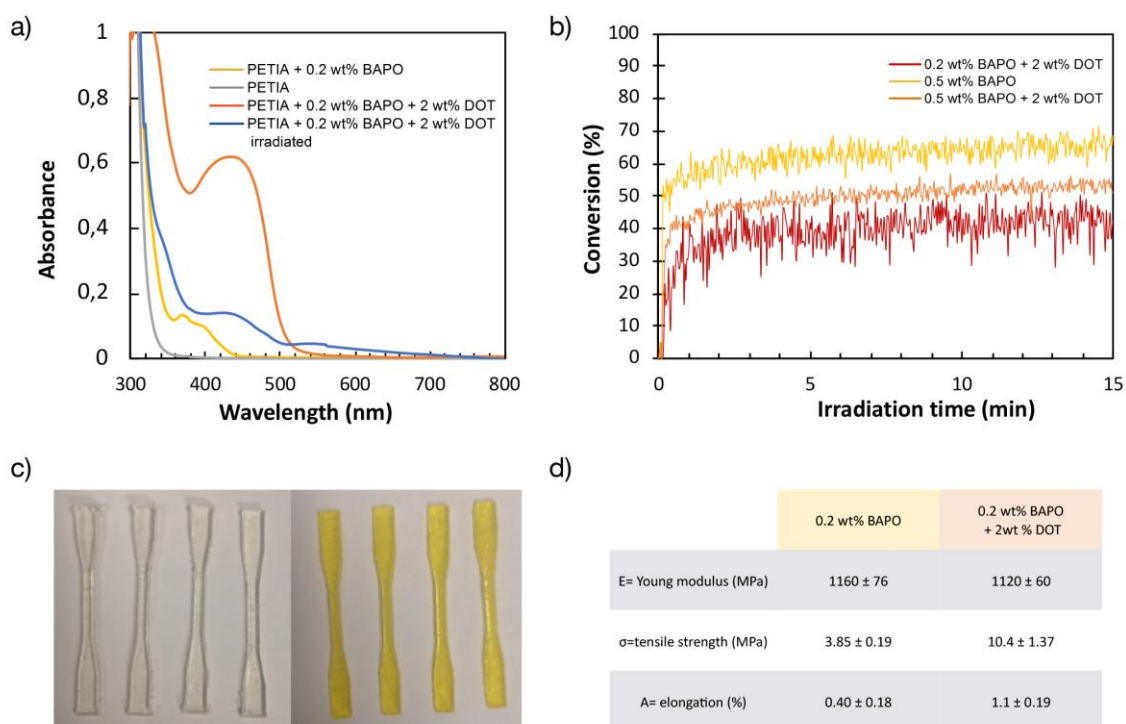


Figure 2. a) UV-vis absorption spectra of monomer (PETIA), monomer + photoinitiator (BAPO, 0.2 wt%), monomer + photoinitiator + DOT (2 wt%) before and after UV irradiation. b) Photopolymerization kinetics followed by FTIR (conversion of C=C band at 1635 cm^{-1}) under UV exposure for the photopolymer loaded or not with DOT (2 wt%). c) Samples prepared by 3D-printing for mechanical properties testing. d) Comparison of main mechanical properties of material with and without DOT.

The trifunctional character ensures a very fast initial polymerization speed, then the rapid increase in viscosity leads to an important gelification of the medium which stops the polymerization and prevents a higher conversion. The addition of DOT (2 wt%) decreases, as expected, the efficiency of the photopolymerization, both for the initial speed and the final conversion (50 %), but keep them still totally compatible to an 3D printing process. This effect can be easily explained by the absorption of DOT which acts as a filter effect for the BAPO, decreasing the amount of light available for photolysis of the photoinitiator. It should also be noted that a decrease of the kinetics during the copolymerization of acrylate derivatives and DOT is already observed during the thermal polymerization in solution.^[32-33] Finally, it can be observed that it is possible to reduce the concentration of BAPO to 0.2 wt%, while maintaining effective polymerization, with in particular sufficient cross-linking of the polymer to confer interesting mechanical properties to the material, as observed qualitatively after irradiation. This result justifies the percentage of 0.2 wt% of BAPO used in the following.

Figure 2.c shows that it is possible to use DLP-UV to very easily fabricate polymer specimens that can be used to quantitatively

evaluate the mechanical properties of the formed polymers. It can be seen that the addition of DOT only slightly modifies the mechanical properties of the polymer by leading to a slightly softer and less brittle polymer (Figure 2.d). This property can be correlated with the reduced photopolymerization efficiency induced by the addition of DOT. Nevertheless, Young modulus, tensile strength and elongation values remain in the same order of magnitude, meaning that DOT can be added up to 2 wt% without changing too significantly the mechanical properties of the polymerized material.

PETIA monomer is a reference monomer in microstructuring applications, 2D and 3D.^[37-39] It is shown in the following that the addition of DOT does not degrade the resolution and the possibility to use it for 2D and 3D stereolithography applications, at the micro and macroscopic scale. In a first approach, a laser microstructuring configuration is used to demonstrate the ability of the material to be used for laser-induced 3D microfabrication. It is a laser microstructuring configuration at the output of optical fibers that has demonstrated its interest for applications in photonics or sensors.^[40-42] Here, we use this configuration essentially as a microstructuring setup (Figure 3) that allows to test a new material in this microstructuring context with respect to its reactivity and resolution.

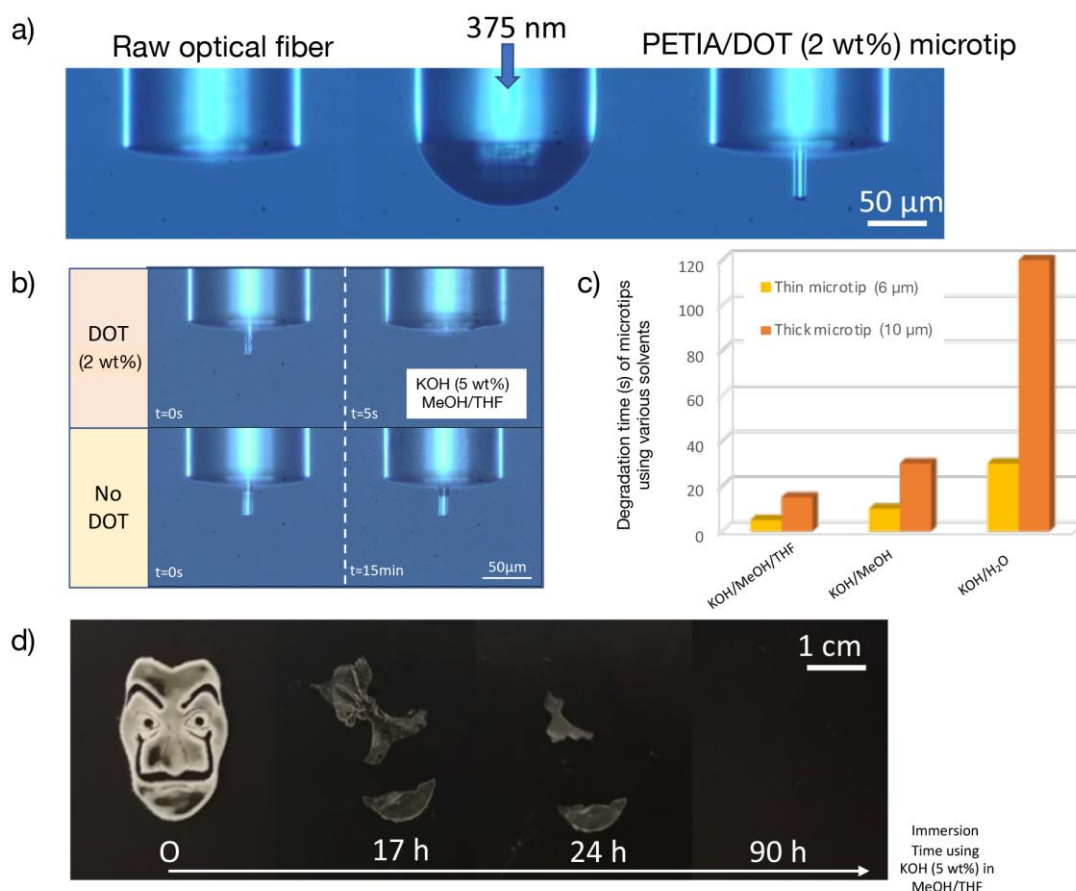


Figure 3. a) Steps of process for preparing polymer microtips at the end of optical fiber showing the photopolymer drop deposition, exposure through the optical fiber and microtip after development (loaded with 2 wt% DOT in this case). b) Dissolution experiments with KOH (5 wt%) in MeOH/THF showing the efficiency of

DOT on the dissolution kinetic of the microtip. c) comparison of degradation times for different solvents (in seconds), for thin and thick microtips (resp. 6 and 10 μm diameter). d) Dissolution of a macroscopic object (resin PETIA + 2 wt% DOT printed with a DLP-UV set-up) using KOH (5 wt%) in MeOH/THF.

The experimental procedure is described schematically in Figure 3.a. Further experimental details can be found in SI and reference [37]. Briefly, an optical fiber is cleaved and the resin is deposited at the cleaved end of the fiber. A 375 nm laser is coupled into the optical fiber and the light emerging from the fiber induces photocrosslinking in the volume located in the extension of the core of the optical fiber. After rinsing by immersion for a few seconds in ethanol, the microtip is obtained on the optical fiber. The photonic conditions (power, time), the geometrical and mechanical properties of the polymer formed allow to apprehend the reactivity of different photopolymers in this context of microfabrication. As shown in Figure 3.b, the microstructuring can be efficiently carried out using the DOT doped formulation. As expected after examination of the polymerization kinetics, the reaction is less efficient and the irradiation parameters need to be adjusted, by increasing the irradiation power and/or time (see SI for details).

From this result, we now consider the possibility of degrading the polymer after photopolymerization, as described schematically in Figure 1. To do this, we observe the behavior of microtips with or without DOT, in different solutions, a priori suitable to degrade the polymer.

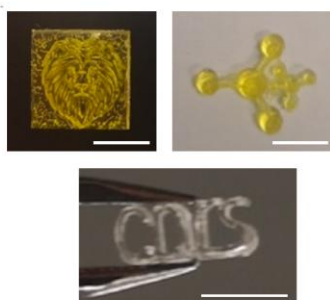
First, a KOH/MeOH/THF mixture is used. In this mixture, KOH acts as a base for the hydrolysis of the polymer. The MeOH/THF mixture is selected to solubilize KOH and provide a solvent that can swell the polymer and thus promote its dissolution. As can be seen in Figure 3.b, the results after immersion are very different with and without DOT in the photopolymer: without DOT, the microtip remains attached to the end of the optical fiber after 15 min, showing the chemical resistance of this highly cross-linked polymer. With DOT in the resin, it is removed after only 5

seconds. Degradation is also obtained in different mixtures, as shown in Figure 3.c. KOH/MeOH (without THF) and KOH in water also degrade the microtip, but with less efficiency, as demonstrated by longer degradation times. Degradation is in any case longer for objects with various sizes, which is consistent with a degradation process as shown in Figure 1. At this stage, however, it is difficult to exclude a mechanism that would implement a detachment of the microtip from the fiber end by degradation of the polymer at the interface. The results shown in Figure 3.d confirm the degradation of the material in the volume. Indeed, in this experiment, a macroscopic object (Dali mask) was fabricated by DLP-UV.

This object was then immersed in the KOH/MeOH/THF solution. After 17 h, the object is taken out of the solution and placed on a substrate to be photographed. One can easily notice the already started degradation of the object. After 24 h, this degradation is even more marked and finely, after 90 h, the object is no longer visible in the solution. This result therefore undoubtedly confirms the role of DOT in the degradation mechanism. Very remarkably, a DOT concentration of only 2 wt% allows this property to be obtained.

It seems quite logical that the degradation of macroscopic objects is significantly longer than that of microscopic objects. Moreover, the use of THF is important for these macroscopic objects to allow KOH access to hydrolysable functions. Based on this result, we further demonstrate the possibility of manufacturing various objects by VAT photopolymerization. Different objects are manufactured, with different geometries, as shown in Figure 4.a and Figure 4.b using both setups, which are interesting to build 2.5 and 3D objects with arbitrary shapes.

a) DLP



b) 3D printing



c)

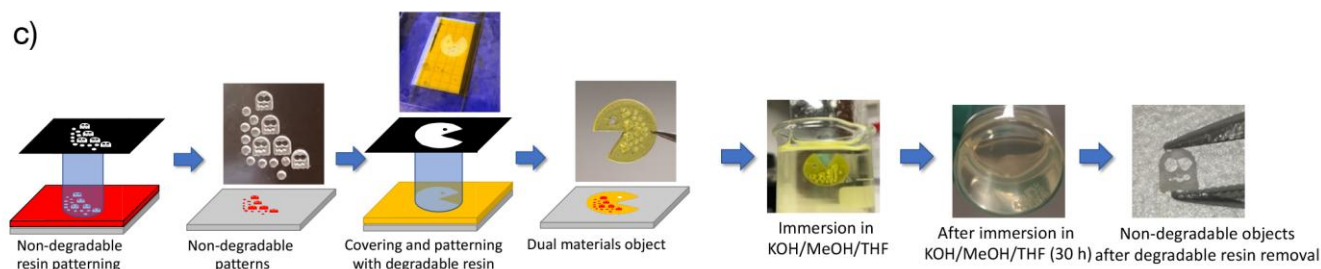


Figure 4. a) Examples of objects made by DLP-printing, b) 3D-printing (scale bar is 1 cm) and c) Embedding a non-degradable object in the degradable resin: example of a degradable Pacman head containing ghosts and balls that are non-degradable.

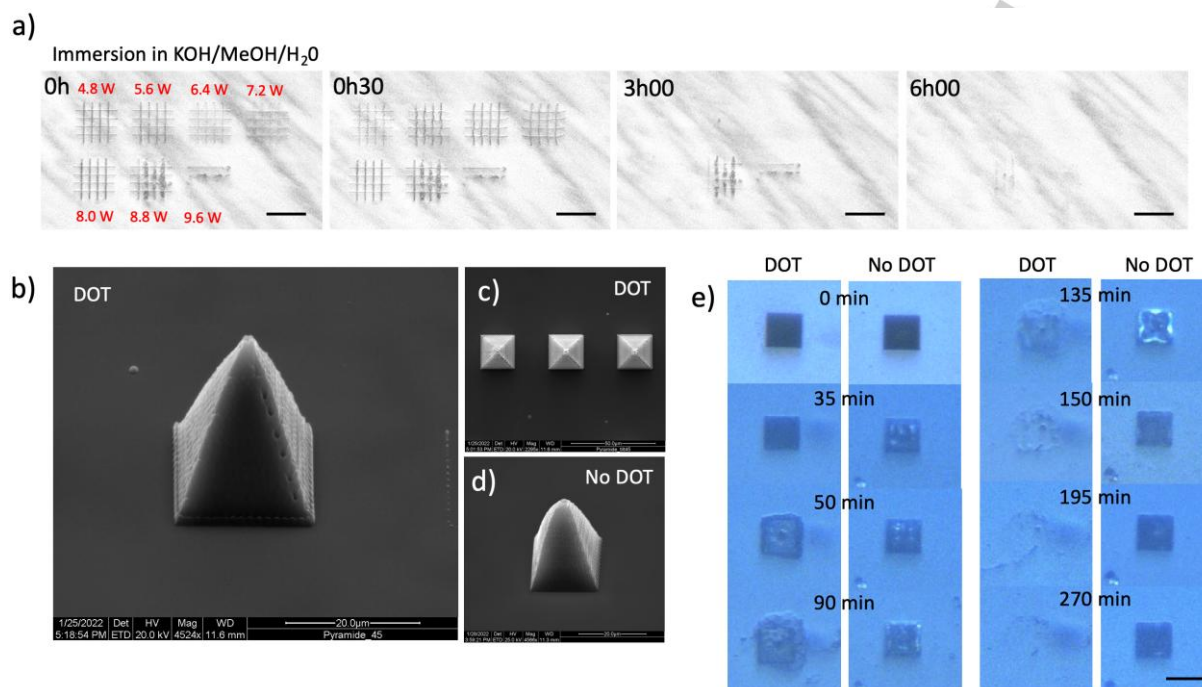


Figure 5: a) Two-photon stereolithography of 50x50 μm microgrid structures and their dissolution in KOH/MeOH/H₂O. Grids were written using a 40X, 0.65-NA objective with increasing laser input power from 4.8 to 9.6 W. b) SEM images of a 20x20x19 μm pyramid prepared by TPS with a resist doped with DOT. c) top view of 3 pyramids prepared with DOT. d) Example of pyramid with the same formulation without DOT. e) Optical microscopy images of dissolution tests of the micropylramids prepared with (left column) and without DOT (right column). Scale bar is 20 μm .

As can be seen, the residual yellow coloration is visible but the parts keep their transparency. For relatively thin objects such as the CNRS logo, the coloration can be attenuated after bleaching.

The degradation property of PETIA/DOT combined with the stability of PETIA makes it possible to consider manufacturing objects with degradable and non-degradable parts using the same DLP-UV printer. This possibility is demonstrated in Figure 4.c. In this example, the strategy is as follows: in a first step, objects (ghosts and balls) are made with the non-degradable PETIA/BAPO resin. The object is then placed in the degradable resin with 2 wt% DOT and a second pattern is printed (Pacman figure). At the end, the object is a Pacman head in which objects are included. This matrix is soluble in the usual solution (5 wt% KOH in MeOH/THF) and its dissolution releases the included objects which are not degraded in the time necessary for the disappearance of the degradable matrix. This example is only intended to show the proof of concept of this new approach and the perspectives opened.

Figure 5 demonstrates that DOT-doped resin can also be used in two-photon stereolithography (TPS). To demonstrate this (Figure 5.a), micrometer grids (50x50 μm) were produced with different laser power (irradiation wavelength 800 nm). As for UV microfabrication, the resin doped with DOT was slightly less reactive but it could be used with photoreactivity in the same order of magnitude. A test of dissolution of the microgrids

showed a complete degradation after 6 hours. Interestingly, it appeared that the dissolution time was increased when laser power was increased. This can be explained by a higher crosslinking of the polymer network at higher laser power. This proof of concept opens the doors towards 3D fabrication of arbitrary structures at the microscale as shown in Figure 5.b and 5.c. The micro-pyramid shown in the SEM image illustrates that no significant loss of resolution is visible as compared to the reference formulation not doped with DOT (Figure 5.d). Dissolution tests (Figure 5.e) clearly shows that objects doped with DOT can be dissolved, unlike objects non-doped with DOT.

In this last section, we further explore the degradation conditions for 3D objects. Before the 3D printing, cm-scale small tablets were prepared using a polypropylene mold previously printed by FDM (see Figure S1 for details) to find the best degradation conditions. The weight and visual aspect of these tablets were monitored during the decomposition process (Figure 6). According to the literature data, the degradation of the copolymers bearing thioesters weak bond could be done either via aminolysis using primary amines^[32-33] or using strong bases such as TBD or KOH/NaOH. We thus started the degradation at room temperature using a 50 vol% of N-isopropylamine in dichloromethane, 2.5 wt% of TBD in THF and 5 wt% of KOH in MeOH/THF. We also prepared a pellet without DOT as a reference. After 3 months there is no degradation for both pellets using either N-isopropylamine or TBD (see SI for details). This

could be related to the difficult diffusion of such compounds into the dense PETIA-based 3D network. Nevertheless, the use of 5 wt% of KOH in MeOH/THF led to the complete dissolution of the pellet in 1 week whereas the reference pellet was not degraded

in 3 months (Figure 6a). To speed-up the degradation, we thus increase either the concentration of KOH or increase the temperature.

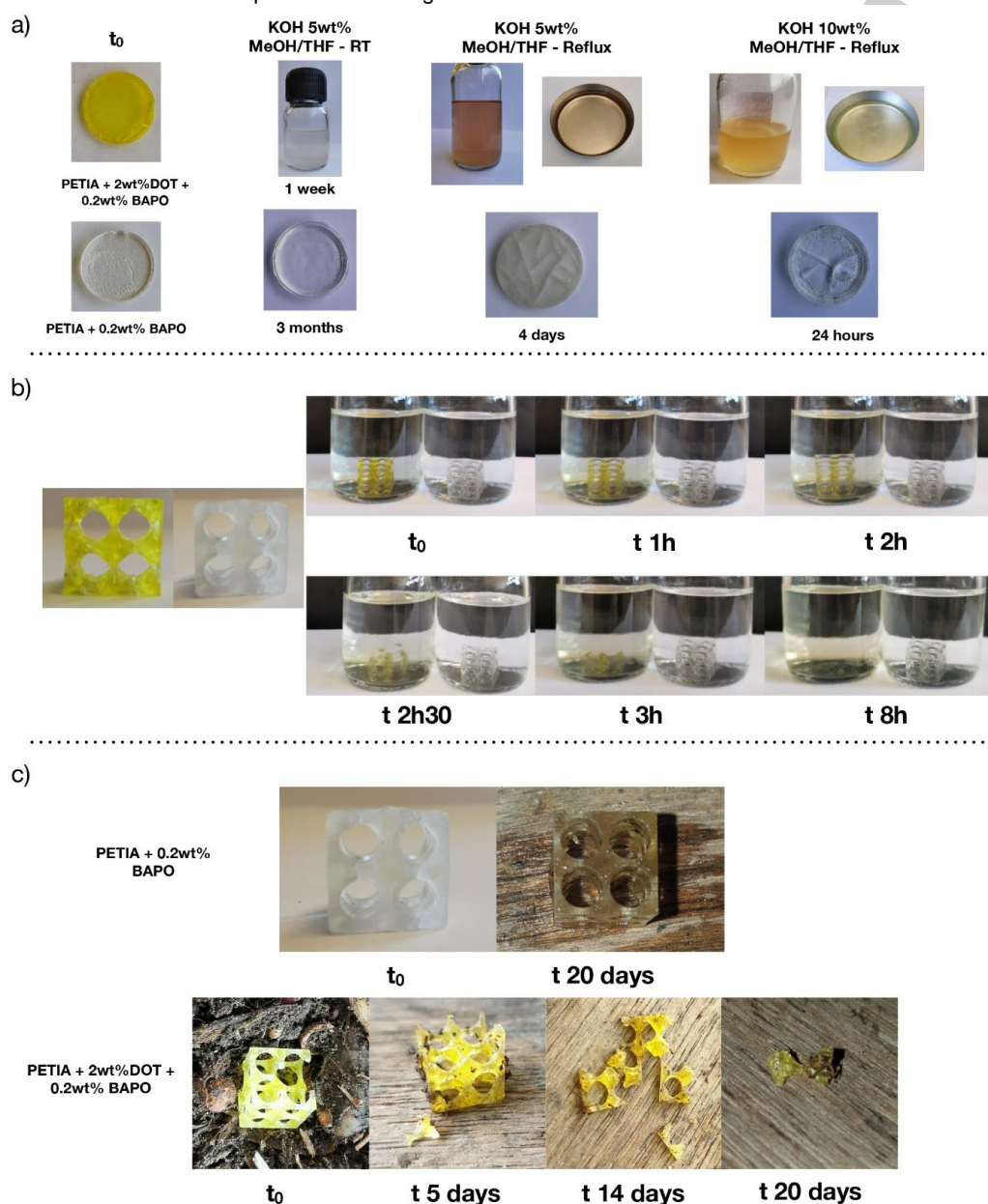


Figure 6. a). Degradation of the PETIA-based pellets using various degradation conditions. b) 3D printing of hollow cubes using a MiiCraft 125 UV-printer and their degradation (5 wt% of KOH in MeOH/THF at room temperature and without agitation). c) Biodegradation of the hollow cubes in a home-made compost.

Such kind of degradation conditions (120 °C, 10 wt% KOH in EtOH, 24 h) were already used by Mecking *et al.*^[43] to perform the degradation of solid polyethylene objects containing weak ester linkages. Using these improved conditions, the complete dissolution of this dense cm-scale object could be obtained in 24 h (Figure 6a).

The main goal of this study was the 3D printing of a degradable objects and we thus used our formulation (PETIA + 2 wt% DOT + 0.2 wt% BAPO) and the reference PETIA resin with a commercial 3D printer (MiiCraft 125, 385 nm). The complete

parameters used for these printings are given in ESI and the same parameters were used for both resins. We first printed a hollow cube as a proof of concept. The printed objects are depicted in Figure 6b. It can be seen that the introduction of DOT inside the formulation do not modify the 3D printing since a similar object is obtained. Such cubes were then subjected to degradation. In this case, due to the porosity of the cube we choose to perform the degradation using 5 wt% of KOH in MeOH/THF at room temperature and without agitation.

After 8 h the hollow cube that was prepared with 2 wt% of DOT totally degraded (see the video in SI and Figure 6b) whereas the reference cube was not affected. This experiment validates the concept of degradable thermoset via the introduction of weak bond via radical ring-opening polymerization. These hollow cubes (the pristine PETIA and the DOT doped cube) were also subjected to biodegradation using a home-made compost. Both cubes were inserted into the compost and the degradation monitored visually. The results are presented in Figure 6c. After 20 days in the compost, the DOT-doped cube is quite totally degraded whereas the PETIA one was not affected.

To further showcase the interest of our approach, an Eiffel Tower was also printed to ensure that a 3D object with a high resolution could be obtained and degraded. The results are gathered on Figure 7a and confirmed that this approach could be used on cm-scale 3D objects with a high resolution. The degradation of this Eiffel Tower presented an inhomogeneous degradation with the thinner part being degraded before the thicker ones. This feature is in good agreement with our previous findings correlating the rate of degradation with the size of the object. This prompt use to

investigate the potential use of this approach to address the issue of support structures. Indeed, printing complex geometries with VAT photopolymerization usually require support structures that have to be manually removed afterward. In some cases, such structures are not easily accessible, and their removal could be difficult to perform or could be time consuming since it has to be done manually. Moreover, the preparation of easily removable/cleavable support structure could enable the printing of stacked 3D objects in the z-dimension. To illustrate this feature, we prepare two dices that are printed vertically (z-direction) using support structures (Figure 7b).

The dices were printed either using the PETIA and the DOT-doped resins. In both cases the 3D objects were obtained and were immersed in a gentle basic solution (5 wt% KOH in MeOH, RT, without agitation). After one hour, the dices printed with the DOT-doped resin dissociated (Figure 6b) whereas the reference still possessed its support structures.

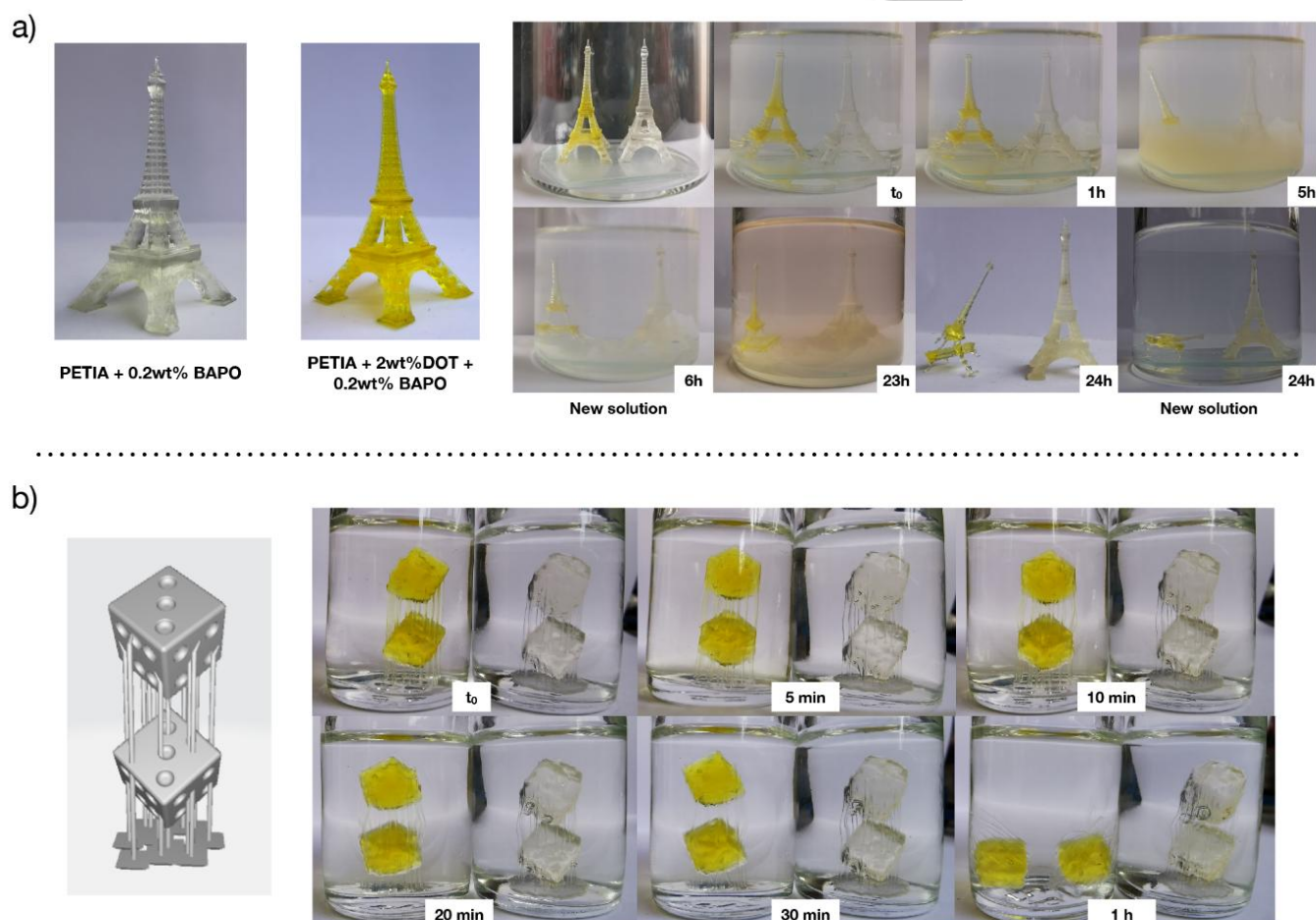


Figure 7. a) Preparation of the Eiffel Tower using the Miicraft 3D printer and its degradation using 5 wt% of KOH in MeOH/THF at room temperature and without agitation. b) Preparation of stack dices using the Miicraft 3D printer and its degradation using 5 wt% of KOH in MeOH/THF at room temperature and without agitation.

Conclusion

In conclusion, we showed in this work that the introduction of 2 wt% of a specific thionolactone, i.e. the dibenzo[c,e]-oxepane-5-thione (DOT) that is known to copolymerize efficiently with acrylate monomers, into an acrylate based- 3D resin confer a degradability property to the obtained 3D objects. Moreover, we showed that the mechanical properties of the final product are only slightly affected since only small amount of DOT was used as additive. This approach has then been applied to microstructuring configuration, two-photon stereolithography, DLP set-up and finally to commercial 3D printer. At all scales, the objects could be degraded using basic conditions. Such conditions are nevertheless dependent of the size of the object. In all cases the complete dissolution of the objects occurred that allow first to strongly decrease the volume of wastes that could be produced via VAT photopolymerization and secondly will make more feasible the use of subtractive manufacturing since only an additive could be added to common acrylate-based resins. As an example, using the size-dependent rate of degradation of the printed materials, stacked 3D object (z-directions) could be prepared and whose separation could be done gently in solution. This approach could thus be improved by developing new monomers of radical ring-opening polymerization that do not absorb in the UV range and whose reactivity with methacrylate derivatives is efficient (i.e. reactivity ratios allowing statistical incorporation of thioesters in the polymer backbone).

Acknowledgements

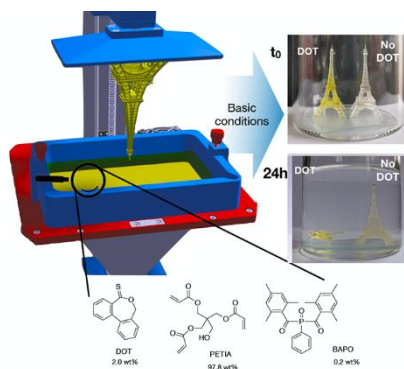
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Keywords: 3D printing • degradable materials • radical ring-opening polymerization • photopolymerization • thionolactone

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3D UV-printing produces cross-linked materials at the expense of degradability. The introduction of thionolactone (2 wt% of dibenzo[c,e]-oxepane-5-thione (DOT)) in acrylate-based resins confer (bio)degradability via the introduction of thioester units into the network via a radical ring-opening polymerization process. The resin was used in different set-up including commercial 3D printers and the objects were shown to degrade in basic solution.

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