Designing Sustainable Polymers: Lactate Esters for 3D Printing and Upcycling

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Abstract

The search for sustainable polymer systems is key to tackling the current climate crisis. However, the use of bio-based polymers does not suffice to achieve this goal. Additionally, new chemical approaches enabling the re- or upcycling of polymer materials need to be explored. Herein, we exploit lactate esters with different substituents as readily available bio-based molecules for the synthesis of printable monomers. The synthesis of these lactate ester-based monomers follows green chemistry principles by establishing a solvent-free, one-pot approach, relying on a reusable catalyst, and achieving high conversions (84 – 100%) at mild conditions. Further, these monomers are utilized in 3D printable ink formulations for digital light processing (DLP) for the first time in combination with a recycled crosslinker. The resulting 3D printed structures display complex geometries with high resolution. A key attribute of the presented system is that the 3D printed polymer material can be upcycled via aminolysis affording a pre-cursor of the crosslinker, which is in turn incorporated into the further ink formulations, introducing a material circularity into the system. These results demonstrate a powerful approach by combining bio-based monomers and chemical upcycling with sustainable 3D printing techniques.

Introduction

Polymers are essential materials in everyday life, with applications ranging from medical devices to packaging and most consumer goods, making our world barely imaginable without them. However, the high volume of polymer production requires us to move towards sustainable non-fossil alternatives.[1] The masses of polymer waste ending up in landfills or as microplastics in the ocean[2] also make it necessary to transition from a linear to a circular polymer economy. This can be achieved by designing materials with so-called end-of-life options such as recycling, upcycling or reprocessing in mind.[3,4] Further, green chemistry principles must be observed when creating sustainable polymers to not only obtain a sustainable end-product but to make the entire process as environmentally friendly as possible.[5,6] This means avoiding the use of toxic chemicals where possible, using widely available feedstocks and limiting waste generation and high energy usages. While significant efforts have been done in the search of bio-based monomers, the implementation of both green chemistry principles and end-of-life fates is still in its infancy.[7]

In recent years, new fabrication techniques have emerged alongside new materials. One such technique, which can be described as inherently sustainable, is additive manufacturing, or 3D printing.[8] It produces less waste and consumes less energy than conventional production methods. Light-based 3D printing, digital light processing (DLP) in particular, offers further advantages including high resolutions and fast building speeds.[8–11] The materials used in light-based 3D printing, also called inks or resins, are typically a mixture of petroleum-based monomers and crosslinkers. However, when aiming to move towards more sustainable DLP inks, the aforementioned criteria - using renewably sourced monomers, implementing end-of-life options and following green chemistry principles – need to be fulfilled.[8] While the main focus has so far been on bio-based monomers,[12–18] an interest in devising end-of-life options for printed materials has recently grown. Since most DLP-printed polymers are thermosets, reprocessing or recycling them often requires the breaking of covalent bonds.[19,20] While chemical recycling is a promising end-of-life option for thermosetting polymers, it has not been fully exploited yet.[21,22] There are only few reports of systems combining end-of-life strategies with renewably sourced, DLP-compatible monomers, as the chemistries available for the photopolymerization process – mainly radical polymerization – limit the polymer design.[23]

Lactate esters are small bio-based molecules that have mainly been used as green solvents,[24,25] with some further applications as additives in food and cosmetics.[26,27] They can be obtained by esterification of lactic acid, which is industrially sourced by fermenting carbohydrates,[28] with the desired alcohol.[29] Recently their scope has been expanded to applications in polymer chemistry. [29–33]

However, to the best of our knowledge, there have been no reports of their application as printable and recyclable materials.

To fill this gap, we have envisioned lactate esters as a promising source for establishing a new family of bio-based monomers for light-based 3D printing. Lactate esters are excellent candidates due to their wide availability, low toxicity[34] and low cost. Additionally, the variation of their alkyl chain length enables the tunability of material properties and their high content of ester groups allows for targeted degradation and chemical recycling/upcycling. Thus, we here propose a printable system based on lactate esters (Figure 1) that implements an end-of-life strategy by choosing a crosslinking unit for the ink formulation, which can be obtained by upcycling the printed structures and then reused in a new ink formulation.
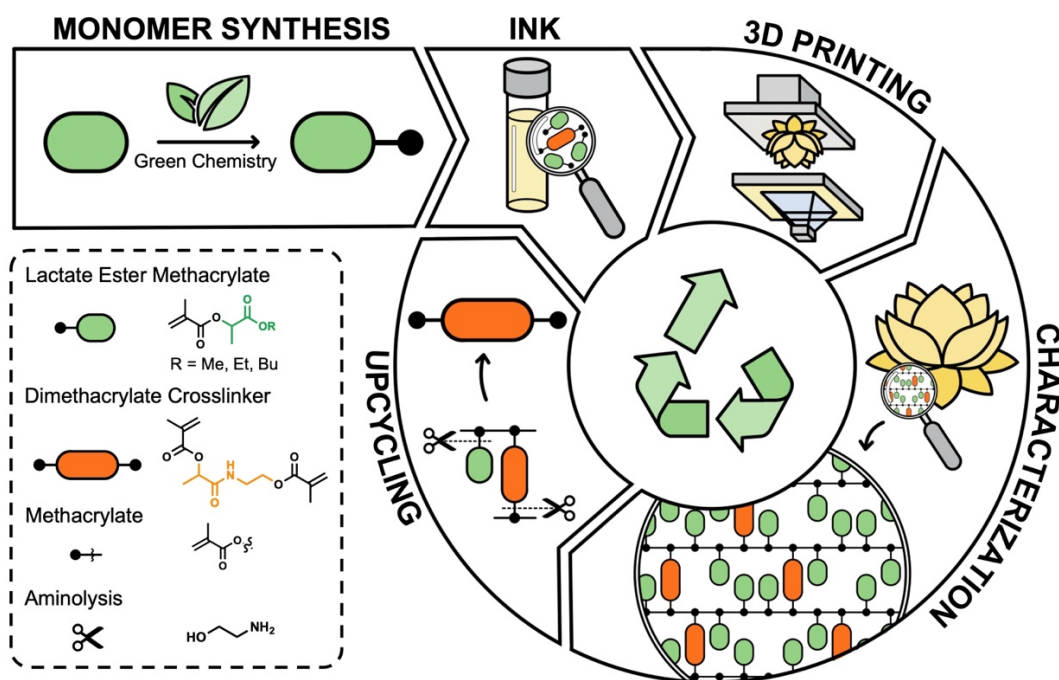

Figure 1. *Schematic illustration of the monomer synthesis, ink formulation, 3D printing and upcycling process.*

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Experimental

Materials

2-Propanol (≥99.8%, Honeywell); Amberlyst® 15 (hydrogen form, Sigma-Aldrich); n-Butyl lactate (99%, thermos scientific); Chloroform-*d* (99.8 atom % D, Sigma-Aldrich); Dichloromethane (DCM) (≥ 99%, Fisher Scientific); Diethyl ether (≥99.5%, Honeywell); Dimethyl sulfoxide-d_6 (DMSO-d_6) (99.8 atom % D, Sigma-Aldrich); Ethanolamine (≥ 99.0%, Sigma-Aldrich); Ethyl acetate (≥99%, fisher); Ethyl lactate (> 98.0%, TCI); Methacrylic acid (99%, containing 250 ppm MEHQ as inhibitor, Sigma-Aldrich); Methacrylic anhydride (≥ 94%, containing 2,000 ppm topanol A as inhibitor, Sigma-Aldrich); Methyl lactate (>98.0%, TCI); $NaSO_4$ (≥ 99%, Acros Organics); NaCl (99%, Honeywell Fluka); $NaHCO_3$ (99%, Grüssing GmbH); Phenyl-bis-(2,4,6-trimethylbenzoyl)-phosphinoxid (BAPO) (97%, Sigma Aldrich). All chemicals were used as purchased without further purification unless otherwise stated. Amberlyst® 15 was washed three times with ethyl acetate and dried with air prior to its first usage and washed once with DCM after each usage.

Instrumentation

[underline]1H and 13C NMR[/underline] spectra were recorded on a Bruker Avance III 300 (300 MHz), Avance DRX 300 or Avance III 400 device. Chemical shifts (d) in ppm were measured in reference to the solvent signal of $CDCl_3$ or DMSO-d_6 respectively.

Digital Light Processing (DLP) was performed using an Asiga MAX X27 UV DLP 3D printer with an LED light source of 385 nm and a pixel resolution of 27 mm. A custom aluminum build platform with a surface of 25 x 25 mm was used. The commercial vats were modified accordingly with an aluminum inlet held in place by Slygard 184 silicone elastomer.[35] Printing was performed with a layer thickness of 100 mm at room temperature. The light intensity was fixed at 28 mW/cm^2. After printing, the structures were carefully removed from the build platform with a thin blade and washed by ultrasonication in isopropanol for 1 min. The structures were dried and post-cured in an Asiga UV chamber for 2 min.

Digital microscope images of the 3D printed structures were taken using a Leica DM2700 M digital microscope equipped with a FLEXACAM C1 microscope camera.

Dynamic mechanical analysis (DMA) was performed using a TA instruments DMA 950 device. Strips with dimensions of 20 x 3 x 2 mm were 3D printed for each measurement. The measurements were conducted with a tensile test configuration in a temperature range of 10 to 150 °C with a ramp of 3 °C/min and a frequency of 1 Hz. The amplitude was set to 0.01% after an amplitude sweep of all three samples.

Fourier transform infrared spectrometry (FTIR) spectra were recorded on a JASCO FT/IR-4600 FT-IR spectrometer in a range of 500 – 4000 cm^{-1}.

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Mass spectra were recorded on a Bruker timsTOFleX instrument in atmospheric pressure chemical ionization (APCI) mode.

Thermal gravimetric analysis (TGA) was conducted on a TGA 2 Mettler Toledo instrument. Previously dried, 3D printed cylinders with a diameter and height of 2 mm were placed in an aluminum pan and heated to 500 °C at a rate of 10 °C/min under inert atmosphere.

Synthetic Procedures

Methyl Lactate Methacrylate (MeLMA). Methyl lactate (132 mmol, 1.0 eq.), methacrylic anhydride (132 mmol, 1.0 eq.) and Amberlyst 15 (1.9 mmol, 0.015 eq.) were added to a round bottom flask. The mixture was stirred for 10 min at RT and then heated to 70 °C for 1 h while stirring. At the end of the reaction time, Amberlyst 15 was removed by filtration and diethyl ether was added to the reaction mixture. The aqueous phase was extracted with diethyl ether. The organic phase was washed with water, 1 M HCl, saturated $NaHCO_3$ solution and brine and dried over $NaSO_4$. The solvent was removed under reduced pressure. Methyl lactate methacrylate (MeLMA) was obtained as a colorless liquid (102 mmol, 77%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.15 (s, 1H), 5.59 (s, 1H), 5.09 (q, J = 7.1 Hz, 1H), 3.70 (s, 3H), 1.92 (s, 3H), 1.48 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 171.26, 166.61, 135.63, 126.40, 68.76, 52.23, 18.10, 16.92. FTIR: ν_{max} /cm^{-1} 2996 and 2956 (C–H), 1758 (C=O$_{ester}$), 1719 (C=O$_{a-b-unsat.\ ester}$), 1637 and 814 (C=C). APCI-MS (m/z): 173 (M+1).

Ethyl Lactate Methacrylate (ELMA). Ethyl lactate (176 mmol, 1.0 eq.), methacrylic anhydride (176 mmol, 1.0 eq.) and Amberlyst 15 (2.6 mmol, 0.015 eq.) were added to a round bottom flask. The mixture was stirred for 10 min at RT and then heated to 70 °C for 2 h while stirring. At the end of the reaction time, Amberlyst 15 was removed by filtration and diethyl ether was added to the reaction mixture. The aqueous phase was extracted with diethyl ether. The organic phase was washed with water, 1 M HCl, saturated $NaHCO_3$ solution and brine and dried over $NaSO_4$. The solvent was removed under reduced pressure. Ethyl lactate methacrylate (ELMA) was obtained as a colorless liquid (130 mmol, 74%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 6.20 (s, 1H), 5.62 (s, 1H), 5.11 (q, J = 7.1 Hz,1H), 4.20 (q, J = 7.1 Hz, 2H), 1.96 (s, 3H), 1.53 (d, J = 7.0 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 170.84, 166.73, 135.72, 126.35, 68.93, 61.30, 18.18, 16.96, 14.11. FTIR: ν_{max} /cm^{-1} 2987 and 2941 (C–H), 1755 (C=O$_{ester}$), 1720 (C=O$_{a,b-unsat.\ ester}$), 1637 and 814 (C=C). APCI-MS (m/z): 187 (M+1).

Butyl Lactate Methacrylate (BuLMA). Butyl lactate (133 mmol, 1.0 eq.) methacrylic anhydride (133 mmol, 1.0 eq.) and Amberlyst 15 (1.9 mmol, 0.015 eq.) were added to a round bottom flask. The mixture was stirred for 10 min at RT and then heated to 70 °C for 14 h while stirring. At the end of the reaction time, Amberlyst 15 was removed by filtration and diethyl ether was added to the reaction mixture. The aqueous phase was extracted with diethyl ether. The organic phase was washed with

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water, 1 M HCl, saturated NaHCO$_3$ solution and brine and dried over NaSO$_4$. The solvent was removed under reduced pressure. Butyl lactate methacrylate (BuLMA) was obtained as a colourless liquid (112 mmol, 84%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 6.19 (s, 1H), 5.62 (s, 1H), 5.12 (q, J = 7.1 Hz, 1H), 4.15 (td, J = 6.6, 2.1 Hz, 2H), 1.96 (s, 3H), 1.70 – 1.56 (m, 2H), 1.53 (d, J = 7.1 Hz, 3H), 1.43 – 1.30 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 170.76, 166.55, 135.66, 126.16, 68.83, 64.98, 30.48, 18.94, 18.04, 16.87, 13.52. FTIR: ν_{max} /cm^{-1} 2960, 2937 and 2875 (C–H), 1755 (C=O$_{ester}$), 1721 (C=O$_{a,b-unsat.\ ester}$), 1638 and 813 (C=C). APCI-MS (m/z): 251 (M+1).

N-Lactoyl Ethanolamine (N-LEA). The synthesis of *N*-LEA for the initial batch of crosslinker was done by recycling PLA following a literature procedure.[3] DLP-printed structures consisting of different lactate ester inks with DME crosslinker were dried in a vacuum oven at 40 °C overnight. The polymer was cut up or ground into pieces small enough to allow stirring and placed into a flask equipped with a reflux condenser. After purging with nitrogen, ethanolamine was added in a 10:1 (wt) ratio. The mixture was heated to 150 °C while stirring for 18 h. After full dissolution of the structures was observed, the reaction was stopped, and excess ethanolamine was removed by vacuum distillation. The excess ethanolamine could be recovered and reused for further upcycling batches, avoiding waste. The remaining residue was extracted by addition of isopropanol and ultra-sonification. The solution was filtered, and the solvent removed under reduced pressure. *N*-lactoyl ethanolamine (*N*-LEA) was obtained as a viscous brown liquid. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 7.59 (s, 1H), 5.49 (s, 1H), 4.69 (s, 1H), 3.94 (q, J = 6.8 Hz, 1H), 3.40 (t, J = 6.1 Hz, 2H), 3.14 (m, J = 6.1, 1.6 Hz, 2H), 1.20 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$): δ (ppm) = 174.48, 67.87, 59.81, 40.95, 21.05. FTIR: ν_{max} /cm^{-1} 3306 (O–H), 2977, 2935, 2879 (C–H), 1635 (C=O$_{amide}$), 1537 (N–H$_{bending}$).

Dimethacrylate Ester (DME) Crosslinker. The procedure was adapted from literature.[3] The solid product could be obtained in a 93% yield. Further purification was performed for analysis purposes by dissolving the product in a minimal amount of DCM and careful addition of a layer of pentane, leading to the precipitation of the pure product. However, washing with water also led to a printable crosslinker for ink formulations and avoided loss of product. The resulting analytic characterization was in accordance with literature. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) = 6.51 (s, 1H), 6.19 (s, 1H), 6.11 (s, 1H), 5.67 (s, 1H), 5.60 (s, 1H), 5.30 (q, J = 6.8 Hz, 1H), 4.28 (m, 2H), 3.61 (q, J = 5.7 Hz, 2H), 1.98 (s, 3H), 1.93 (s, 3H), 1.51 (d, J = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, CDCl$_3$): δ (ppm) = 170.78, 167.64, 165.89, 135.98, 135.85, 126.82, 126.39, 70.87, 63.34, 38.92, 18.44, 18.39, 17.93. FTIR: ν_{max} /cm^{-1} 3277 (C–N), 3110 (C=C), 1715 (C=O$_{a,b-unsat.\ ester}$), 1656 (C=O$_{amide}$), 1634 and 816 (C=C).

Preparation of Ink Formulations

In a small vial, the DME crosslinker (10 wt% in terms of monomer+crosslinker) was dissolved in the lactate ester methacrylate monomer (90 wt % in terms of monomer+crosslinker). Methacrylic acid (10 wt% in terms of both monomer + crosslinker) and BAPO (2 wt% in terms of all methacrylated species) were added. The formulation was ultrasonicated for 10 − 30 min until all species fully dissolved. This formulation was adapted for MeLMA and ELMA. When adopting the formulation for BuLMA, the quantities were calculated based on mol instead of weight to ensure a comparable monomer to crosslinker ratio resulting in a formulation of BuLMA:DME in a mol ratio of 93:7 (set as 1 eq.), 0.22 eq. MA and 0.01 eq. BAPO.

Single Layer Exposure Test

Single layer exposure tests were performed using the same Asiga MAX X27 UV DLP 3D printer used to print 3D structures. A droplet of the ink was placed at the center of a 0.17 mm thin microscope slide. A 2.00 mm circular spot was projected onto the bottom of the slide with varying intensity and exposure times. The uncured ink was rinsed off with isopropanol and the cured spot was dried with compressed air. The cure depth (C_d) of the material was measured using a digital caliper with a 0.01 mm precision. The E_c of each material could be determined from the C_d values at each energy via the Jacobs working curve.[36]

Results and Discussion

Synthesis of Lactate Ester Methacrylates

As a first step, we established a functionalization procedure that fulfils green chemistry principles to convert bio-based lactate esters into printable monomers. To this aim, three lactate esters (methyl, ethyl, butyl) were functionalized with methacrylate groups using a reusable catalyst (Figure 2). Special attention was paid to the reaction conditions: the use of organic solvents was avoided and choosing chemicals with low toxicity, high yields and a high atom economy, were a main priority.
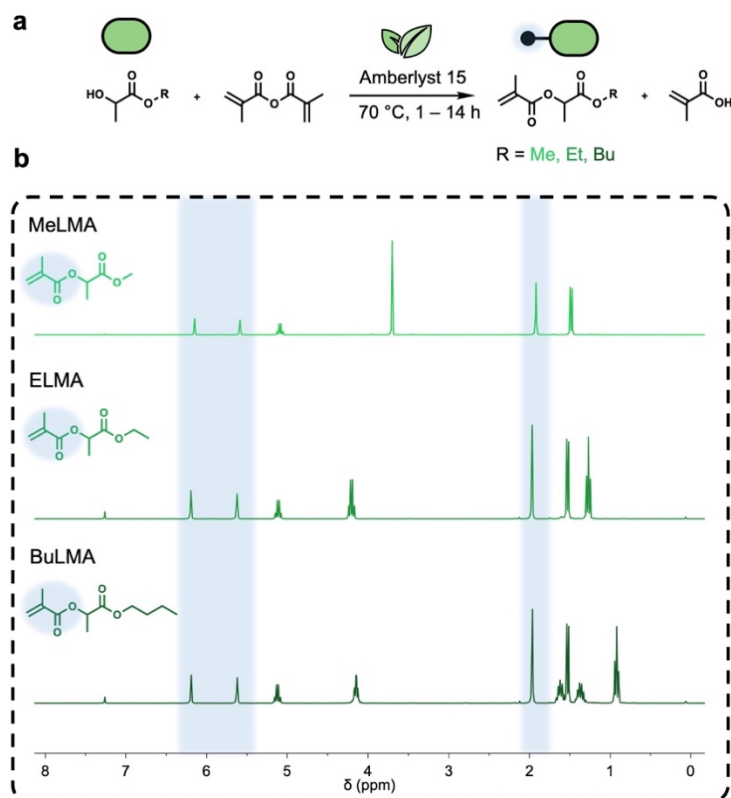
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Figure 2. *(a) Reaction scheme of the synthesis of monomers based on lactate esters, (b) ¹H-NMR spectra of methyl lactate methacrylate (MeLMA), ethyl lactate methacrylate (ELMA) and butyl lactate methacrylate (BuLMA).*

Following these criteria, a solvent-free reaction of the lactate esters with methacrylic anhydride using the ion exchange resin Amberlyst 15 as a means of heterogeneous catalysis was found to be a very efficient method for incorporating photopolymerizable groups. Using Amberlyst 15 as a catalyst provides the main benefit of being easily recoverable and reusable for subsequent reactions.[37] The reaction conditions were initially established for ethyl lactate. Impressively, > 95% conversion was obtained after just 1 h of reaction at 70 °C with a final yield of 77% after an aqueous work-up to remove methacrylic acid. The successful introduction of the methacrylate group was confirmed by NMR spectroscopy (Figure 2b), with characteristic peaks at 6.19, 5.62 and 1.96 ppm stemming from the two alkene protons and the methyl group. Notably, testing the re-usability of the catalyst by using it in 10 consecutive reactions showed no decrease in the conversion (SI Figure S13). Furthermore, we compared the use of Amberlyst 15 with 4-(dimethylamino)pyridine (DMAP), a commonly chosen catalyst for methacrylation reactions.[38] Using DMAP resulted in a conversion of 81% after 5 days, while Amberlyst 15 shortened the reaction time to just 1 h with an even higher conversion of 96%. In a second step, the reaction was adapted to methyl and butyl lactate to provide a wider range of bio-based monomers that can later be used for 3D printing. As before, the reactions were monitored using NMR spectroscopy (Figure 2b). When comparing the results of the functionalization reactions using

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the different lactate esters, it could be observed that the alkyl chain length of the lactate esters inversely correlates with the reaction time and conversion (see Table 1).

Table 1. Reaction times and conversion of lactate ester methacrylation.

Product	Reaction time [h]	Conversion [%][a]	Yield [%][b]
MeLMA	1	100	77
ELMA	1	96	74
BuLMA	14	84	84

[a] from NMR analysis, based on amount of starting material, [b] after work-up based on amount of starting material.

While methyl lactate reached a conversion of 100% after 1 h, the functionalization of butyl lactate progressed more slowly with a conversion of 88% after 14 h. An effect of the chain length on the reaction times was expected, as the use of an ion exchange resin leads to sterical hindrance governing the reaction kinetics, while the inductive effect of the alkyl chain plays a subordinate role.[29,39,40] Notably, the overall reaction yields of 77%, 74% and 84% for MeLMA, ELMA and BuLMA, respectively, exhibit an opposite trend. This is caused by an increase in the hydrophobicity with longer alkyl chains, which lowers product loss during the aqueous work-up. The present reaction conditions outperform those previously reported[30,33,41] in terms of efficiency and from a green chemistry standpoint by using a reusable catalyst.

3D Printing of Lactate Ester–Based Formulations

The functionalized lactate esters were implemented as new bio-based monomers for DLP 3D printing (Figure 3). In order to obtain a printable formulation, the addition of a crosslinker is necessary. To this aim, the crosslinker *N*-lactoyl ethanolamine dimethacrylate ester, abbreviated to DME, (see Figure 3) was chosen as an ideal candidate, since it can initially be sustainably sourced by upcycling poly lactic acid (PLA) waste, which itself is sourced from biomass.[42] The final aim is then to re-synthesize DME by upcycling the structures printed with this first ink formulation (see section below). When developing the ink formulation, a ratio of 9:1 lactate ester monomer/crosslinker with 2 wt% of phenyl-bis-(2,4,6-trimethylbenzoyl)-phosphinoxide (BAPO) as the photoinitiator was found to be printable. However, some over-polymerization could be observed. This issue could be overcome by adding 10 wt% of methacrylic acid as a reactive diluent, resulting in a formulation with very good printability of finely detailed structures. Since methacrylic acid (MA) can be sourced from biomass, specifically citric acid and itaconic acid obtained from fermentation of sugar, its addition does not reduce the overall bio-based content.[43]
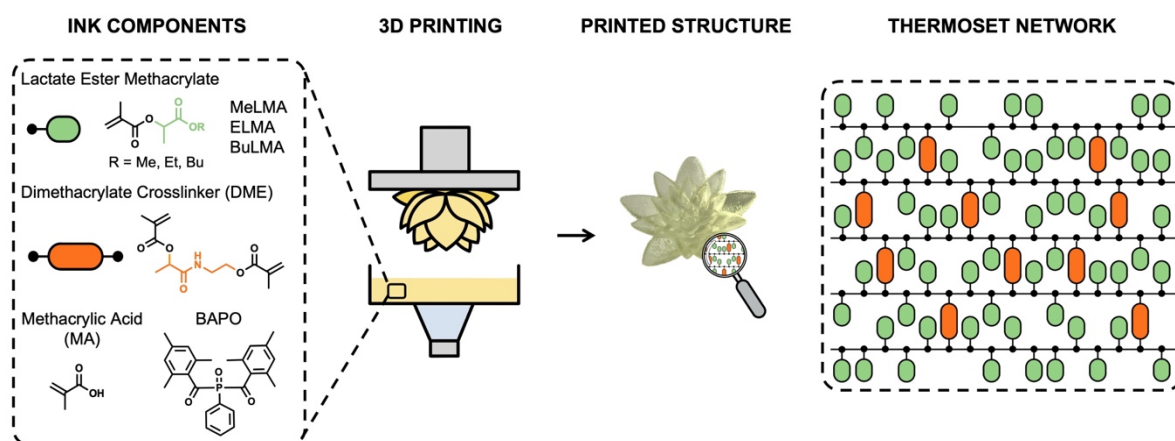
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Figure 3. *Illustration of the printing process of the optimized ink formulation (monomer/crosslinker 9:1, MA 10 wt%, BAPO 2 wt%) and the resulting thermoset network of the printed structure.*

All three inks were printable with comparable exposure times ranging from 22 – 28 s at an intensity of 28 mw/cm² for a layer thickness of 100 μm. Slight variations in the kinetics of the photopolymerization could be observed, which can be quantified by the critical energy E_c below which no photopolymerization occurs. The E_c values, listed in Table 2 again follow the previously observed trend of faster kinetics corresponding to shorter alkyl chain lengths.

Table 2. *Critical Energies of optimized MeLMA, ELMA and BuLMA based ink formulations.*

Formulation Monomer/Crosslinker 9:1*	Intensity [mW/cm²]	Critical Energy [mJ/cm²]
MeLMA/DME	28	428 ± 21
ELMA/DME	28	487 ± 19
BuLMA/DME	28	562 ± 47

*All formulations contain 10 wt% MA and 2 wt% BAPO.

The printability of the three ink formulations containing the different lactate ester-based monomers was further tested with complex 3D models such as a lattice (SI Figure S15) and a water lily as test geometries, resulting in very defined structures for all three ink formulations, depicted in Figure 4a. Further, Figures 4b – 4d show a range of intricate printed structures, including a Klein bottle with a fine mesh surface and a gyroid geometry to illustrate the excellent printability. In both cases the structures exhibit high resolutions of small features without over-polymerization. To demonstrate the high xy-resolution, the Heidelberg University seal, containing a complex engraved image with feature sizes below 100 μm, was printed with the ELMA ink formulation (Figure 4d). Further details of the distinct features were imaged using a light microscope (see images in SI Figure S17).
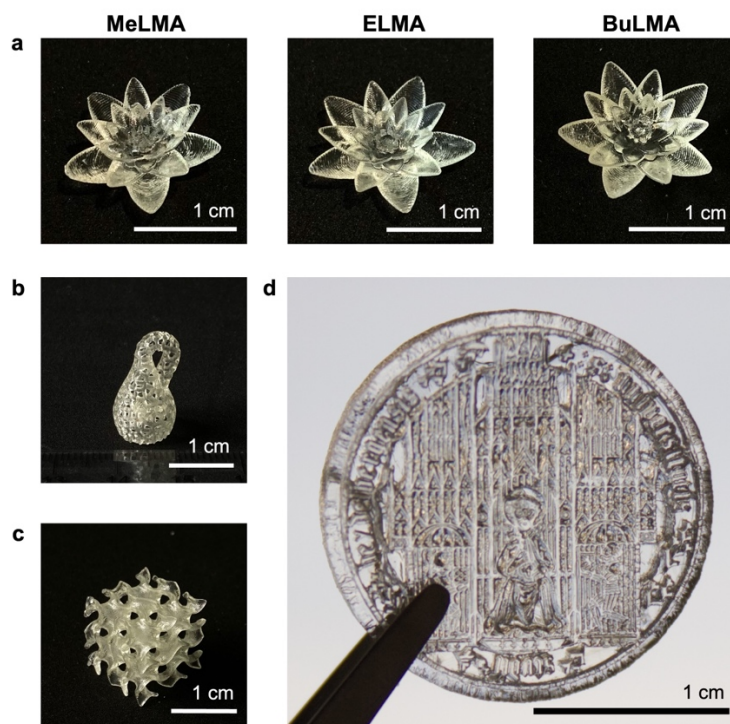
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Figure 4. (a) Water lily test geometry printed with MeLMA-, ELMA- and BuLMA-based inks, (b) Klein bottle printed with MeLMA-based ink, (c) gyroid structure printed with ELMA-based ink, (d) Heidelberg University seal printed with ELMA-based ink.

To further analyze the photopolymerization taking place during printing, the degree of double bond conversion (DOC) was calculated from FTIR spectra (SI Figures S18 – 23). The DOC values for the three lactate ester-derived polymers lie within the range of 76 – 86%, which is in accordance with values observed in literature for 3D printed samples.[35] Specifically, the DOC was calculated to be 86% for the MeLMA formulation, 76% for ELMA, and 79% for BuLMA. To gain further insights on the effect of the different alkyl lengths incorporated in the bio-based monomers of the formulation, the thermomechanical properties of the printed structures were analyzed by way of dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) (SI Figures S24 – 25). The storage modulus in the glassy state was found to be 1.78 GPa for MeLMA, 1.62 GPa for ELMA and 1.08 GPa for BuLMA at 25 °C. The decrease in the storage modulus may stem from the alkyl chains acting as plasticizers, leading to softer materials with increasing chain lengths. Overall, these values for the storage modulus are comparable to other thermosetting bio-based methacrylate inks containing vanillin- and eugenol-based monomers.[44] The glass transition temperatures T_g were determined at the maxima of *tan(d)* (SI Table S1). For the sample containing the MeLMA monomer the T_gs were determined at 82.4 and 120.3 °C, ELMA displayed T_gs at 82.5 and 106.1 °C and BuLMA at 85.5 °C. The occurrence of two T_gs can often be ascribed to a heterogeneous material with two phases.[45] A general trend can again be discerned of the main glass transition moving to lower temperatures with increasing chain length due

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to the alkyl chains acting as plasticizers. Analysis of the thermal stability of the printed structures through TGA measurements showed that the polymers are stable up to at least 180 °C. Please refer to the SI for further details.

Upcycling of Printed Structures by Aminolysis

As discussed above, both using bio-based materials and integrating end-of-life strategies into material design are paramount to achieving a truly sustainable system. The latter is especially challenging when generating thermosets, which is the case for most 3D printed materials using light-based technology. In our case, the chosen strategy consists of chemically upcycling the 3D printing resulting in the same crosslinker used in the ink formulation. More specifically, performing an aminolysis reaction using ethanolamine affords *N*-lactoyl ethanolamine (*N*-LEA), a pre-cursor of the desired crosslinker. Methacrylation of the obtained diol following a reported procedure then leads to the synthesis of the dimethacrylate crosslinker (DME).[3] The reaction scheme of the upcycling procedure and subsequent functionalization of the product is shown in Figure 5.
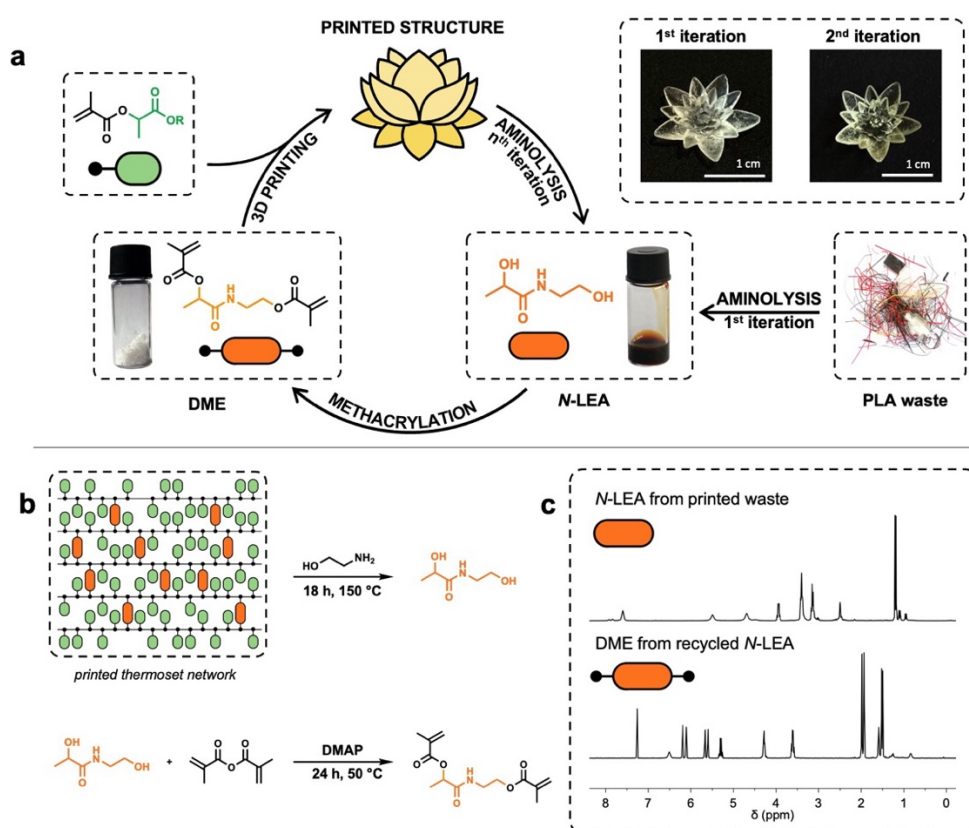

Figure 5. *(a) Illustration of recycling process, (b) Reaction scheme of DME synthesis by recycling, (c) ^{1}H-NMR spectra of N-LEA and DME from recycled N-LEA.*

A screening of reaction conditions found a temperature of 150 °C, a reaction time of 18 h and a feeding ratio of 10:1 ethanolamine: polymer (by weight) to be successful without employing a catalyst. The dissolution of the material after 10 – 12 h indicated the dissociation of the thermoset bonds.

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Increasing the temperatures further did not significantly impact the reaction speed. The reaction conditions are comparable to those of PET aminolysis, which progresses with ethanolamine at 150 °C. [46] The reaction was followed by a simple work-up procedure in which the ethanolamine could be distilled off and *N*-LEA was extracted from the highly viscous residue. The obtained product was confirmed by NMR spectroscopy (Figure 5c). The distilled ethanolamine can be reused for further aminolysis reactions, mitigating any concerns that the use of an excess amount would otherwise raise from a green chemistry standpoint. The upcycled *N*-LEA was used to re-synthesize the crosslinker (DME) by methacrylation and the successful reaction was confirmed by NMR spectroscopy (Figure 5c). To confirm the reproducibility, the upcycling procedure was repeated with printed samples of all three lactate esters and the desired product could be recovered each time (SI Figures S11 – 12). A representative upcycling procedure of a printed structure using the MeLMA formulation with a weight of 900 mg, yielded 844 mg of the DME crosslinker. Thus, printing new structures using the upcycled crosslinker obtained in this fashion could be achieved, proving the circularity of the process.

Conclusion

Three different lactate esters were functionalized with photopolymerizable groups in high yield reactions, followed by their successful implementation as novel bio-based monomers for ink formulations in 3D printing. Outstanding 3D printability was achieved with all three lactate ester ink formulations and the printed materials were characterized in depth. To implement an end-of-life option, the printed structures were upcycled via aminolysis. Following this procedure, the crosslinker employed in the ink formulation could be re-synthesized and used for subsequent printing. Beyond, green chemistry principles were followed throughout, taking bio-based inks for 3D printing a step towards full sustainability. We believe this work will open new avenues in the design of sustainable materials for 3D printing and contribute to the revaluation of bio-based 3D printed waste.

Acknowledgements

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