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Chemical Circularity in 3D Printing with Biobased Δ -Valerolactone

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Digital Light Processing (DLP) is a vat photopolymerization-based 3D printing technology that fabricates parts typically made of chemically crosslinked polymers. The rapidly growing DLP market has an increasing demand for polymer raw materials, along with growing environmental concerns. Therefore, circular DLP printing with a closed-loop recyclable ink is of great importance for sustainability. The low-ceiling temperature alkyl-substituted δ -valerolactone (VL) is an industrially accessible biorenewable feedstock for developing recyclable polymers. In this work, acrylate-functionalized poly(δ -valerolactone) (PVLA), synthesized through the ring-opening transesterification polymerization of VL, is used as a platform photoprecursor to improve the chemical circularity in DLP printing. A small portion of photocurable reactive diluent (RD) turns the unprintable PVLA into DLP printable ink. Various photocurable monomers can serve as RDs to modulate the properties of printed structures for applications like sacrificial molds, soft actuators, sensors, etc. The intrinsic depolymerizability of PVLA is well preserved, regardless of whether the printed polymer is a thermoplastic or thermoset. The recovery yield of virgin quality VL monomer is 93% through direct bulk thermolysis of the printed structures. This work proposes the utilization of depolymerizable photoprecursors and highlights the feasibility of biorenewable VL as a versatile material platform toward circular DLP printing.

impact in various areas from aerospace and medical engineering to consumer products. Due to its advantage in fabricating parts with complex geometries, 3D printing has experienced explosive growth over the past decade, becoming increasingly mature and accessible. Various 3D printing techniques have been developed, such as fused filament fabrication, direct ink writing, selective laser sintering, stereolithography, digital light processing (DLP), etc.^[1] Among these commonly used techniques, DLP stands out for its ability to rapidly produce highly precise 3D objects. As a vat photopolymerization-based technique, DLP uses photocurable polymers as the precursor material. Upon UV exposure, layer-wise photopolymerization, typically induced with free radicals, solidifies the liquid resin.^[2–5] With continuous building in the z-direction, DLP can rapidly form 3D objects,[6-8] and can also print multimaterial-like structures.^[9-14] Depending on the pixel size in the projector, DLP's resolution is typically 50 µm with fine feature control^[15–17] and can reach as

1. Introduction

Additive manufacturing, also known as 3D printing, has emerged as a disruptive manufacturing technology with a significant

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low as micrometer-scale.^[18] These advantages make the DLP technique increasingly popular for industrial applications.

With the fast growth of the 3D printing market, the demand for polymer raw materials is expected to increase dramatically.

J. Cho, B. Brettmann School of Chemical and Biomolecular Engineering Georgia Institute of Technology Atlanta, GA 30332, USA B. Brettmann, R. Ramprasad School of Materials Science and Engineering Georgia Institute of Technology Atlanta, GA 30332, USA H. J. Qi Rewable Bioproduct Institute Georgia Institute of Technology Atlanta, GA 30332, USA However, concerns about the sustainability of plastic materials, stemming from heavy reliance on the petrochemical industry for production and the large volumes of unmanageable plastic waste, have posed significant challenges to our environment and sustainable development.^[19] Therefore, there is a growing need for sustainable feedstock materials with recyclability for 3D printing.

For DLP, developing circular 3D printable materials has become more prominent, as it typically prints parts from chemically crosslinking polymers, which are known to be difficult to recycle. Efforts have been made to develop recyclable DLP printable precursor materials. One approach is to print thermoplastics with controllable molecular weight, allowing the polymerized thermoplastic to dissolve into its monomer solution, achieving a long chain polymer-monomer mixture for reprinting or utilizing the remoldability of thermoplastics through melting for recycling and reusing.^[20,21] Another approach involves using thermosets with dynamic covalent bonds, which have shown promise in achieving reprocessability through exchange reactions and have been introduced for recyclable DLP printing.^[22-25] However, in both approaches, to make the recycled material printable via DLP, they have to be mixed with virgin liquid resin, thus hindering true circularity. To address this, researchers have also explored degrading the printed structures through exchange reactions, such as dynamic transesterification reactions, for repeated DLP printing.^[26] Although the network can be partially restored through exchange reactions, there is a decrease in properties along the reprinting process. To date, most approaches involving degradation produce reusable oligomers or small molecules, but not the original feedstocks, and thus are unable to achieve truly closed-loop circular DLP printing.

Depolymerizable or low-ceiling temperature polymers that can revert back to their constituent monomers have been demonstrated as appealing circular polymers.^[27–29] A number of closedloop ring-opening polymerization systems with low-ceiling temperatures (T_c) that depolymerize under mild conditions have been developed.^[29–32] The depolymerization of these polymers takes advantage of the low ring strain in the monomer, making depolymerization enthalpically favorable.^[33] Among the reported polymers, polyesters derived from the ring-opening transesterification polymerization (ROTP) of biobased lactones are especially attractive.^[34] The six-membered cyclic lactone (δ -valerolactone) family, with alkyl substitutes, exhibits low ceiling temperatures ranging from 100 to 200 °C and has recently shown great promise as a platform material for establishing a "monomer-polymermonomer" circular loop.^[30,35–37]

The ceiling temperature decreases with an increase in alkyl substitute size. In this study, a biobased 7-alkyl-substituted δ -valerolactone (VL) is employed as the monomer for preparing a recyclable photoprecursor, aiming to enhance resin circularity in DLP 3D printing. The chosen δ -valerolactone, characterized by a moderate ring strain, exhibits both a high polymerization yield at room temperature and a high monomer recoverability due to its low ceiling temperature. Additionally, its low boiling point (\approx 140 °C) facilitates easy separation and collection during the recycling process. In contrast to semicrystalline polycaprolactone, which is in a solid state at room temperature and poses challenges in mixing with other photoresins and additives for DLP printing, the substituent group of δ -valerolactone disrupts crystallinity to form an amorphous polyester. This maintains a

liquid state, facilitating miscibility with other photoresins and additives. The aliphatic structure of δ -valerolactone also enhances the resin's elasticity, biodegradability, and resiliency.

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This work focuses on significantly improving chemical circularity in DLP 3D printing by introducing low-ceiling-temperature δ -valerolactone based polymer as a platform photoprecursor. The biobased alkyl-substituted δ -valerolactone monomer is first polymerized through ROTP with 2-hydroxyethyl acrylate (2HEA) as a functional initiator to introduce the photocurable acrylate group to facilitate the DLP printing. The synthesized photocurable poly(δ -valerolactone) acrylate (PVLA) is then used as the base component, comprising ≈85 wt% in a typical resin formula, along with various photocurable monomers as reactive diluents (RDs) to formulate DLP printable resins. The printed materials can be either a thermoplastic or a crosslinked thermoset by varying the reactive diluents and additives for different applications. Importantly, the PVLA segment of the photocured structure retains the intrinsic ability to depolymerize and recover the VL monomers in their pure state, with a yield of 93 wt%. Figure 1 illustrates the concept of circular DLP printing with the depolymerizable photoprecursor as the platform material. In a typical loop, VL is polymerized into PVLA, which is then mixed with RDs and additives for DLP printing of thermoplastics or thermosets. The printed structures can be further depolymerized to recover VL monomer with virgin quality for reuse. The recovered VL monomers can then be repolymerized into PVLA that can be used again for DLP printing by mixing with other RDs and additives, closing the loop and enhancing circularity in the DLP 3D printing process.

Herein, this work represents the first instance where the majority of the chemical (85 wt%) achieves "monomer-polymermonomer" closed-loop recycling in DLP 3D printing. Introducing a low-ceiling-temperature-based photopolymer with inherent recyclability substantially improves the chemical circularity in DLP 3D printing. The industrially accessible biobased δ valerolactone monomers with the well-developed ROTP synthetic route facilitate the large-scale production of this depolymerizable photoprecursor for application.

2. Results and Discussion

In order to create photocurable PVLA, 2HEA is utilized as the initiator. The hydroxyl group can initiate the ROTP reaction of VL, meanwhile the acrylate group can introduce photocurable functionality as shown in Figure 2A. The bulk ROTP of VL is a lowtemperature favorable reaction that exhibits high rates at room temperature, carrying out with the efficient organoacid diphenyl phosphate (DPP) catalyst.^[38,39] The molar mass of the resulting PVLA is regulated by adjusting the monomer-to-initiator (VL-to-2HEA) ratio. To assess the printability of PVLA with different molecular weights, three variants are synthesized with molecular weights of 1800, 2700, and 3600 g mol⁻¹. After a 24-h reaction, the monomer conversion exceeds 90% for all variants. GPC (gel permeation chromatography) analysis reveals purified PVLA with a narrow polydispersity in the range of 1.22-1.28, closely matching the expected molecular weight as shown in Figure 2B. The widths and the heights are identical and narrow, indicating that the ROTP reaction is well controlled regardless of the molecular weight. The acrylate functionality of PVLA is also confirmed







Figure 1. Illustration of circular in DLP printing with depolymerizable photoprecursor.

with NMR (nuclear magnetic resonance) spectra as shown in Figure 2C with the acrylic protons appearing between 6.5 and 5.8 ppm. This demonstrates that the synthetic route is a highly effective and well-controlled approach for producing the PVLA photoprecursor. It is worth mentioning that the ROTP of VL is conducted at room temperature on a 100 g scale. The renewable VL monomer is low-cost and large-scale industrially accessible. The results demonstrate a scalable, controllable, and reproducible synthesis route of PVLA as the photoprecursor for DLP printing.

The resultant PVLA is an amorphous aliphatic polyester with a low glass transition temperature, which makes it desirable as a soft block in a materials platform.^[40] The molecular weight of PVLA not only affects the printability of the formulated DLP ink but also influences the thermal and mechanical properties of printed structures after photopolymerization. When using PVLA as the base component in the material platform, two criteria regarding DLP printability should be carefully considered: 1) the viscosity of the formulated liquid resin, and 2) the kinetics and conversion of the photopolymerization of the liquid resin.^[41] Since PVLA with a molecular weight of 1800 g mol⁻¹ has the lowest viscosity, it is chosen as the example photoprecursor for further printing. As shown later, PVLA possesses relatively high viscosity and low reactivity for DLP printing. Therefore, a suitable RD is used to adjust the printability and modify the physicochemical properties of the printed structure. A suitable RD should exhibit good miscibility with PVLA and reduce the viscosity of the mixed resin, and the copolymerization during printing should solidify the liquid resin rapidly enough for 3D printing. After a preliminary screening, acrylate acid (AA) is first selected as the RD to mix with PVLA. Aliphatic polyesters are well-established biocompatible and biodegradable polymers that have been used



Figure 2. Synthetic route of acrylate functionalized poly(δ -valerolactone) via ROTP. A) Schematic of the 2HEA initiated ROTP reaction. B) GPC curves for PVLA. C) Overlays of ¹H NMR spectra (23 °C, CDCl₃) of the synthesized PVLA compared to VL. Inset shows peaks at 5.8–6.6 ppm corresponding to the double bond protons of acrylate.

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Figure 3. DLP printability of PVLA as photoprecursor. A) Schematic illustration of the photopolymerization of PVLA with acrylate acid (AA). B) Complex viscosity of PVLA with different molecular weights (3600, 2700, and 1800) and in a mixture with 85 wt% PVLA and 15 wt% AA (1:4.4 mol mol⁻¹). C) Photo-rheology of PVLA with and without 15 wt% AA as reactive diluent. D) Conversion of PVLA photopolymerization with and without 15 wt% AA as reactive diluent.

for various biomedical applications.^[42,43] AA is also a widely used precursor monomer in biomedical applications.^[44–46] The resulting resin mixture is expected to be a good candidate for biomedical structure printing. Here, both AA and PVLA are monofunctional precursors. Upon UV exposure, the free radical induced copolymerization of the acrylate groups forms a branched thermoplastic, as illustrated schematically in **Figure 3**A.

The complex viscosity measurement (Figure 3B) shows that PVLA itself has relatively high viscosity that increases with increasing molecular weight. A lower viscosity resin with good flowability is favorable for fast DLP printing. Decreasing the molecular weight of PVLA or increasing the loading of an RD can both serve this purpose. To achieve a higher proportion of recyclable chemicals while maintaining suitable printability for DLP 3D printing, a formulation with 85 wt% PVLA of 1800 g mol⁻¹ and 15 wt% AA is selected for further demonstration (marked as 15AA in Figure 3B–D). The viscosity of the mixed resin is close to 1 Pa s, which is favorable for DLP printing. The reaction kinetics of the resin is investigated through photo-rheology testing with a photo rheometer, which monitors the gelation of the resin during photopolymerization. To slow down the photochemical reaction, we use a relatively small amount 0.5 wt% of photoinitiator Irgacure 819 (compared to 1 wt% for printing). The photorheology results in Figure 3C show that PVLA itself exhibits a long induction time, with the shear moduli (G' and G'') starting to increase around 12 s after the UV light is turned on, indicating slow photopolymerization kinetics. Also, the storage modulus is always lower than the loss modulus after 140 s UV irradiation, suggesting that the gelation cannot be achieved (Figure S1, Supporting Information). In contrast, for the mixed resin with 15 wt% AA, the shear modulus immediately increases once the UV light is turned on and reaches the gelation point (where the storage modulus crosses over with the loss modulus as shown in Figure 3C) within 10 s due to the entanglement of the photopolymerized high molecular weight branched polymer. The presence of the small molecular reactive diluent between the PVLA segments during copolymerization can decrease the hindering effect of the branched long polymer chain. Consequently, the reactivity of PVLA effectively increases with an increasing amount of reactive diluent, resulting in a shorter induction time (Figure S2, Supporting Information).

Next, the double bond conversion during photopolymerization is investigated using FTIR (fourier-transform infrared spectroscopy). The change in absorbance of the acrylate double bond peak at 1604–1648 cm⁻¹ (Figure S3, Supporting Information) is monitored with UV exposure time. Here, we use the ink with a regular amount of photoinitiator (1 wt%). As shown in Figure 3D, the formulated ink shows conversion immediately upon UV irradiation and reaches an average conversion of around 80% within 15 s. In contrast, the photopolymerization of PVLA is very slow, with a very small initial conversion after 5 s and a conversion below 50% after 30 s. These results suggest that the presence of the





Figure 4. Printing quality and properties of PVLA as a photoprecursor. A) A 10 cm length lattice structure and B) an 8 mm length lattice structure printed with PVLA and 15 wt% AA as reactive diluent. C) Dog bone sample printed with 15 and 30 wt% ACMO as reactive diluent and stretching of the dog bone sample printed with different ACMO loading. D) Schematic of the calcium crosslinked network and printed 3D structures. E) Strain stress curves with different calcium loading.

RD is necessary to facilitate DLP printing when PVLA is used as the photoprecursor.

Subsequently, the mixed resin is utilized for DLP printing to demonstrate its printability by constructing a diverse set of 3D structures. A bottom-up DLP printer, as shown in Figure 1, is used in this work. As displayed in **Figure 4A**, B, the resin exhibits good printing quality under the optimized printing conditions with a layer thickness of 50 μ m and a curing time of 5 s per layer. An overhanging lattice with a length of 10 cm and 1mm thick beam and an 8 mm cubic lattice with 200 μ m thick beams could both be smoothly printed with detailed features. These results demonstrate that PVLA is a promising photoprecursor for DLP printing, enabling the production of high-resolution and sophisticated structures.

The properties of the printed structures can be easily regulated by varying the composition of the RD. In addition to AA, there are numerous other photocurable monomers that can be used as RDs for PVLA, depending on the requirements of the target applications. Figure 4C shows an example of using 4acryloylmorpholine (ACMO), a rigid segment, to adjust the properties of the printed polymer. With 15 wt% ACMO, the resulting polymer is soft and stretchable, while increasing the proportion of hard segment to 30 wt% makes the polymer much stiffer, as shown Figure 4C. By altering the loading of the reactive diluent, multi-property structure can be printed, as shown in Figure 4C.

Besides altering the ink composition, properties can also be regulated with additives. Figure 4D demonstrates the addition of Ca^{2+} as an ionic crosslinker in the 15 wt% AA resin. The calcium cations interact with the carboxyl groups of AA to form ionic crosslinks within the polymer. By varying the loading of Ca^{2+} from 0.5 to 4.5 wt%, the modulus can be adjusted from 12 to 250 kPa, providing a more versatile approach to modulating the ink properties (Figure 4E).

The ceiling temperature for pure VL monomer is ≈ 130 °C. Above this temperature, the hydroxyl groups at the chain ends tend to favor backbiting into the polymer chain, leading to depolymerization back to the VL monomer. Since photopolymerization occurs only on the acrylate-capped side, and PVLA is branched along the polyacrylate backbone chain with its hydroxylterminated group on the other side, the photopolymerized PVLA is expected to have the ability to depolymerize back to the VL monomer once the activation barrier is overcome, as illustrated in **Figure 5**A. The thermal stability of PVLA and photopolymerized PVLA-AA polymer is examined using TGA (thermogravimetric analysis) (Figure 5B). The onset depolymerization temperature of PVLA is around 168 °C, and the majority of weight loss occurs below 300 °C. When the active hydroxyl chain-end

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Figure 5. Depolymerization of the DLP printed structure. A) Schematic of the depolymerization route of photopolymerized PVLA and the recovered VL monomer. B) TGA curves of PVLA and photopolymerized PVLA with 15 wt% AA. C) ¹H NMR spectra (23 °C, CDCl₃) of recovered VL monomer overlapping with the virgin VL and PVLA.

undergoes transesterification with its backbone ester to recover the cyclic monomers, the low boiling point VL (\approx 140 °C) evaporates simultaneously, further facilitating the depolymerization process. The initial weight loss stage of the photopolymerized PVLA-AA overlaps with PVLA, indicating depolymerization and evaporation of VL monomer and the second stage reflects the decomposition the polyacrylate backbone. This confirms that the photopolymerization does not suppress the depolymerizability of PVLA.

Based on the above observation, the DLP-printed bulk samples in Figure 4 are directly subjected to thermolysis at 200 °C using a vacuum distillation setup to collect the recovered VL monomer, leaving behind the polyacrylate backbone and additives. It is noteworthy that the thermolysis is carried out without the use of additional catalysts or solvents. After 4 h of thermolysis, an average of ≈93 wt% of the total input VL monomer is recovered in three different batches of thermolysis. The recovered VL monomer is further analyzed using ¹H NMR spectroscopy (Figure 5C), which shows the same spectra as virgin VL and confirms the complete depolymerization of VL from the bulk samples. The regenerated VL monomer is of the same quality as the starting VL and can be readily reused.

Through consecutive ROTP of VL, DLP printing of PVLA, and thermolysis recovery of VL, closed circular DLP printing is achieved following the proposed route illustrated in Figure 1. To further validate the feasibility of PVLA as the material platform for circular DLP printing, we print structures targeting different applications through upcycling. First, the above-mentioned calcium crosslinked PVLA with 15 wt% AA reactive diluent (**Figure 6A**-i) is used to print a variety of structures (Figure 6A-ii), including a negative spring mold (Figure 6A-iii). The PVLA-AA polymer can be easily dissolved in a 70% isopropyl alcohol (IPA) solution at room temperature, making it ideal for a sacrificial mold, as demonstrated in Figure 6A-iii. IPA is separated by vac-

uum drying at room temperature from the dissolved polymer PVLA-AA, which is then go through thermolysis to recover the VL monomer. The recycled VL is repolymerized into PVLA to create a different resin. For the application of a pneumatic actuator, which typically requires a soft polymer with a relatively high elastic elongation, 15 wt% reactive diluent (1 wt% aliphatic urethane diacrylate (AUD) and 14 wt% ACMO) is used as the reactive diluent, forming a crosslinked thermoset network, as displayed in Figure 6B-i with good print quality (Figure 6B-ii). The loadingunloading test demonstrates good elastic recovery (Figure S4, Supporting Information). Then a well-performed pneumatic actuator is demonstrated in Figure 6B-iii.

The thermoset bulk samples displayed in Figure 6B are subsequently subjected to thermolysis under the same conditions as the thermoplastic samples, as mentioned earlier. Depolymerization of poly(δ -valerolactone) is initiated from the hydroxylterminated group, regardless of whether it is branched on a thermoplastic backbone or a thermoset network (Figure S5, Supporting Information). The VL monomer possesses a low boiling point of 140 °C and can be easily separated from the decomposed polyacrylate backbone and additives, including dye and photoinitiator. It can be successfully recovered from the thermoset network and undergoes repolymerization. Finally, an ion-conductive thermoset ink is formulated with 15 wt% reactive diluent (2 wt% poly(ethylene glycol) diacrylate (PEGDA) and 13 wt% AA) and additional 10 wt% lithium salt (lithium bis(trifluoromethanesulfonyl)imide). A well-performed solid-state conductive sensor is printed for demonstration, as displayed in Figure 6C and Figure S6 (Supporting Information).

The same batch of VL monomers undergo the depolymerization and repolymerization process, which is repeated for three consecutive cycles using different types of reactive diluents. After each cycle, the VL monomer is recovered with a high yield of about 93 wt%, and the reproduced PVLA exhibits identical



Figure 6. Chemical circularity in DLP printing with PVLA. A-i) Schematic of using Ca^{2+} crosslinked thermoplastic; ii) Printed structures and dissolution of them in a 70 wt% IPA solution; iii) A silicone rubber spring fabricated with the printed sacrificial mold. B-i) Schematic of thermoset network; ii) Printed structures; iii) Printed attructures and dissolution of thermoset network with lithium salt; ii) Printed all-solid ion-conductive pressure sensor. Different dyes were used for differentiation. All scale bar was 2 cm.

molecular weight and polydispersity (Figure S8, Supporting Information). Moreover, all the demonstrated formulations display good printability and achieve the expected performance. In general, PVLA demonstrated its capability as a platform photoprecursor material for DLP printing. PVLA-based ink can be easily adapted to conventional DLP printers, offering good printing quality. The mechanical properties can be adjusted by varying the type or loading of the reactive diluent, as well as incorporating suitable additives.

3. Conclusion

We have showcased the versatility of the renewable VL as a materials platform for improving the chemical circularity in DLP 3D printing. The bulk ROTP synthesis method for photocurable PVLA provides a well-controlled and scalable approach to produce the resin precursor. By incorporating a small portion of reactive diluent, we not only improve the printability of PVLA but also regulate the properties of the printed structures. Depending on the specific application requirements, a wide range of generally photocurable monomers can serve as reactive diluents for PVLA. Additionally, functional additives, as demonstrated, can be utilized to further modify the properties. The photopolymerized structures obtained from printing can undergo direct bulk thermolysis at the end of their service life without the need for additional catalysts or solvents. The inherent low ceiling temperature of VL allows for depolymerization. Regardless of the printed polymer type, a recovery yield of 93 wt% with the same quality as the virgin material can be achieved. The chemical circularity of the base component feedstock has significantly contributed to advancements in achieving a more sustainable additive manufacturing process.

4. Experimental Section

Materials: δ-Dodecalactone (VL), diphenyl phosphate (DPP), 2hydroxyethyl acrylate (2HEA), acrylate acid, 4-acryloylmorpholine (ACMO), poly(ethylene glycol) diacrylate (PEGDA), calcium chloride, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), Irgacure 819, Sudan I and all the solvent used were purchased from Sigma-Aldrich (St. Louis, MO, USA). Oil soluble dye Solvent Blue 104 was from Clariant Corp. (Frankfurt, Germany) and Solvent green 5 was from Orichem International Ltd. (Hangzhou, Zhejiang, China). Aliphatic urethane diacrylate (AUD, Ebecryl 8413) was from Allnex (Alpharetta, GA, USA). VL monomers and 2HEA were thoroughly dried with a molecular sieve and kept in a nitrogen atmosphere.

Synthesis and Purification of PVLA: The bulk ring-opening polymerizations were performed on a scale of 100 g monomer. The monomer (VL), the initiator (2HEA) and the catalyst DPP were added into a 200 mL glass jar with molar ratio [monomer]:[initiator]:[DPP] of 8:1:0.08, 13:1:0.13 and 17:1:0.17. The reaction was conducted for 24 h at room temperature with stirring under a nitrogen atmosphere in a glove box. After the reaction, a small portion of the mixture was quenched with benzoic acid for NMR test to examine the monomer conversion. The remaining mixture was dissolved in 300 mL of acetone, and PVLA was extracted using a potassium hydroxide solution (2 mol L⁻¹). The product was then dissolved again in acetone and extracted with DI water repeatedly until the pH reached 7. The purified PVLA was dried using a rotary evaporator.

Ink Preparation: All presented inks were composed of PVLA (1800 g mol⁻¹) and UV-curable reactive diluents with an additional 1 wt% Irgacure 819 and 0.1 wt% photoabsorber (orange color was Sudan I; yellow color was Solvent Green 5, and blue color was Solvent Blue 104). Figure 4A,B contains 15 wt% AA (RD 1); Figure 4C with 15 and 30 wt% ACMO (RD 2); Figure 4D,E with 15 wt% AA and additional CaCl₂; Figure 6A with 15 wt% AA; Figure 6B with 1 wt% AUD and 14 wt% ACMO (RD 3); Figure 6C with 2 wt% PGEDA and 13 wt% AA (RD 4), with an additional 10 wt% LiTFSI. The mechanical properties and photocuring of those reactive diluent are presented in Figures S9 and S10 (Supporting Information).

DLP 3D Printing: 3D printing was performed with a bottom-up DLP printer that employs a 385 nm UV-LED light projector (PRO4500, Wintech Digital Systems Technology Corp., Carlsbad, CA, USA) and a linear translation stage (LTS150 Thorlabs, Newton, NJ, USA). A homemade container with an oxygen-permeable window (Teflon AF-2400, Biogeneral Inc., CA, USA) was used as the resin vat. The designed 3D structures were sliced into image files with a layer thickness of 0.05 mm. Samples were printed using a layer-by-layer approach with 8 s curing for each layer.

Depolymerization: Around 5 g printed structures were cut into small pieces and add into a round-bottom flask with a stirring bar. The temperature was then increased to 200 °C under reduced pressure for 4 h. The collected mixture was further distilled at 100 °C under reduced pressure for between 20 min and a few hours.

Detailed characterization and analysis are presented in the Supporting Information.

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

3D printing, additive manufacturing, recycling, upcycling, sustainability

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