Supplementary Information (SI) for Green Chemistry.

Supporting Information

Metal-Free, Scalable Synthesis of Degradable Polyester Resins for High-Resolution DLP 3D Printing via Organoboron-Catalyzed ROCOP

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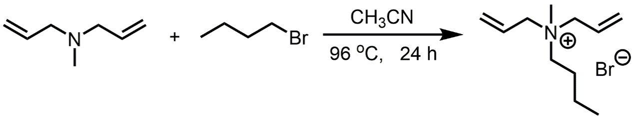
1. Synthetic procedures and materials

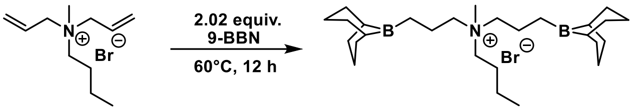
All manipulations involving air- and/or water-sensitive compounds were carried out in a glove box or with the standard Schlenk techniques under argon atmosphere. Tetrahydrofuran (THF), ethyl acetic (EA), cyclohexane, acetonitrile, n-hexane were purchased from Shanghai Titan Scientific Co., Ltd. 9-borabicyclo[3.3.1]nonane (9-BBN), diallylmethylamine, bromobutane, allyl glycidol ether (AGE), phthalic anhydride (PA), pentaerythritol tetra(3-mercaptopropionate) (PETMP), diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO), ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPOL), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), bis(4-methylphenyl)phosphoryl-(2,4,6-trimethylphenyl)methanone (TMO), 2-hydroxy-2-methylpropiophenone (1173), 2,2,6,6-tetramethyl-1-piperinedinyloxy (TEMPO), Sudan I, $CDCl_3$, calcium hydride(CaH_2) were purchased from Energy Chemical Co. AGE was dried over CaH_2 overnight, followed by vacuum distillation, and then stored in the glovebox. PA was purified by filtering after dissolving in dichloromethane, then recrystallization from chloroform. THF and n-Hexane were distilled over sodium/benzophenone then stored in the glovebox. $CDCl_3$ were distilled over CaH_2 for overnight and then stored over activated Davison 4 Å molecular sieves. All the raw materials of the catalysts were used without further purification.

Synthesis of N,N-diallyl-N-methyl-N-butylammonium bromide



A round bottom flask equipped with stir bar was charged with a solution of diallylmethylamine (2.78 g, 25 mmol, 1.00 equiv) in acetonitrile(25 mL), bromobutane (3.425 g, 25 mmol, 1.0 equiv) was added via a dropping funnel. The reaction mixture was then heated to 96 °C for 24 h before cooling to room temperature. The reaction mixture was concentrated in vacuo to afford the crude product that was further purified by washing with a mixed solvent (ethyl acetate:n-hexane = 1:1) for three times. The white solid was isolated by vacuum filtration and was dried at 50 °C in vacuo overnight.

Synthesis of bifunctional organoboron catalyst



In a glovebox,to a flame-dried Schlenk tube was added N,N-diallyl-N-methyl-N butylammonium bromide (1.24 g, 5.0 mmol, 1.00 equiv) and 9-BBN (20.2 mL, 10.1 mmol, 2.02 equiv) was added via cannula. The reaction mixture was then heated to 60 °C for 12 h before cooling to room temperature. The reaction mixture was concentrated in vacuo to afford the crude solid product that was further purified by washing with n-hexane for several times, then the white solid product was dried in vacuo at 30 °C overnight.

2. General information

Nuclear magnetic resonance (NMR) Spectroscopy

NMR (500 MHz) spectra were recorded on a Bruker AVANCE-500 spectrometer, and chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ as internal reference for ^1H NMR (δ = 7.26 ppm) and ^{13}C NMR (δ = 77.00 ppm) and BF_3*Et_2O as internal reference for ^{11}B NMR (δ = 0 ppm).Structural analysis were made from ^1H-^1H COSY experiments.

Gel permeation chromatography (GPC)

The number-average molecular weight of prepared polymer was determined by gel permeation chromatography equipped with a RI2000 refractive index detector and Shodex DVB column (1000 Å,300 mm × 7.5 mm) using DMF as eluent at 1 mL/min; the column temperature was maintained at 40 °C. Polystyrene(PS) standards were used for molecular weight calibrations.

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF) Mass Spectrometry

MALDI-TOF MS analyses were conducted on a Bruker Microflex LRF MS 1 spectrometer equipped with a 337 nm nitrogen laser operating at a positive ion, linear mode (modified according to experiments). The polymer samples (10 mg mL-1), trans -2[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, 25 mg*mL^{-1}) and CF3COONa (5 mg*mL^{-1}) were dissolved in THF and mixed in a volume ratio of 20:5:5.

Rheological Measurements

Complex viscosity was measured on n = 1 sample using a Haake Mars40. Samples were loaded on 60 mm parallel plate geometry with a 0.052 mm gap at ambient temperature (25 °C). The complex viscosity was collected over a frequency sweep from 0.1 rad/s to 100 rad/s at 10% strain. Viscosity of samples was determined as the complex viscosity at 10 rad/s, following protocols published by Becker[1].

Photopolymer resins formulation

3D printing resins formulation were prepared by mixing diluwent EA, thiol crosslinker PETMP, photosystems (include initiator BAPO, inhibitor TEMPO, and opaquing agent Sudan I). A general procedure for photopolymer resin involved a brown bottle equipped with stir bar was charged with a solution of BAPO (0.2 g, 0.5 wt%), TEMPO (0.004 g,0.01 wt%), Sudan I (0.012 g,0.03 wt%) in EA (8.00 g), and mixed with the polyester (40.0 g) until a homogenous solution at ambient temperature. Finally, PETMP were incorporated into the solutions and mixed for 30 mins.

Print cure time optimization by using scanning electron microscopy (SEM) imaging

Elegoo Mars 4 DLP 3D printer was used for this study. The optimal print cure time was determined through droplet cure tests prior to formal printing. General procedure: approximately 0.1 mL of photopolymer resin was dispensed onto a glass slide using a syringe, followed by irradiation for varying durations to induce photopolymerization. The uncured resin was then washed away with ethyl acetate (EA), and the thickness of the cured resin was measured via scanning electron microscopy (SEM).

Digital light processing (DLP) 3D printing

All 3D-printed models were sourced from www.MakerWorld.com or custom-designed using software suites such as Blender or Cinema 4D (C4D). All printing object were washed using EA, isopropanol, and deionized water. After air drying, the printed objects were post-cured in an Elegoo Mercury plus 2.0 UV oven (48 W, λ = 405 nm) for 20 minutes. Then the printed objects were dried in vacuum oven at 60 °C for 3 days.

Thermogravimetric Analysis (TGA)

Thermal analysis was performed on a TA Instruments Discovery TGA 550. Sample was prepared by loading 10 mg of material onto a platinum TGA pan. The temperature was ramped to 100 °C form 25 °C at 10 °C/min, held isothermally for 30 minutes, equilibrated at 30 °C, and finally ramped from 30 °C to 600 °C at 10 °C /min all under N_2 gas flow. Degradation temperature (T_d) was determined as the temperature at 5% mass loss.

Differential Scanning Calorimetry (DSC)

Thermal analysis was performed on a TA Instruments Discovery DSC 250. Each sample was prepared by loading 10 mg of material into an aluminum DSC crucible. The temperature range scanned was -50 °C to 70 °C at a 10 °C /min ramp rate under N_2 gas flow. Two cycles were completed: the first to reset the material's thermal history and the second to collect representative data. All measurements are reported against a sealed, empty reference crucible. Glass transition temperature (T_g) was determined as the midpoint of the transition in the second heating cycle.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed on a Tescan Mira4 LMH. The sample was mounted on a cross-sectional stage and placed into the SEM. The stage was tilted along the Z-axis from -15 to 25 degrees, and the electron beam was rotated by 180° to acquire the target image. The thickness of the cured resin was subsequently measured using dedicated analytical software. And the magnification was maintained between 50× and 100×, with angular adjustments ranging from −10 to 25 degrees, to achieve precise imaging of the printed object with microstructural features.

Uniaxial tensile test

3D printed dogbones Tensile bars (ASTM D368 Type V, 63.5 x 9.5 x 3.2 mm) were uniaxially tested until failure at a clamp separation speed of 10 mm/min.

Degradation Analysis

The experiment (n=5) was conducted at 37 °C using 0.1M NaOH solutions. 3D printed bars (20 x 30 x 2 mm) were weighed. The bar were complete submerged in 6 mL of solution and incubated 3 days. the samples were removed from the solution and washed with DI water and blotted dry. The bar were then weighed before the addition of new, fresh solution, with the process repeated until the pucks are fully eroded.

Swelling and mass loss Analysis

3D printed bars (20 x 30 x 2 mm) were weighed (denoted as W_0) then submerged in 20 mL of ethyl acetate after 48 hours at room temperature (n=5). The bar was immediately weighed upon removal from ethyl acetate (denoted as W_s), followed by drying in a vacuum oven at 50°C for 2 days prior to reweighing (denoted as W_d).

$$swelling\ (\%) = \frac{W_s - W_d}{W_s} * 100\ \%$$

$$Mass\ loss\ (\%) = \frac{W_0 - W_d}{W_0} * 100\ \%$$

3. Supplementary Figures and Tables

^{1}H and ^{13}C NMR spectra of synthesized catalyst

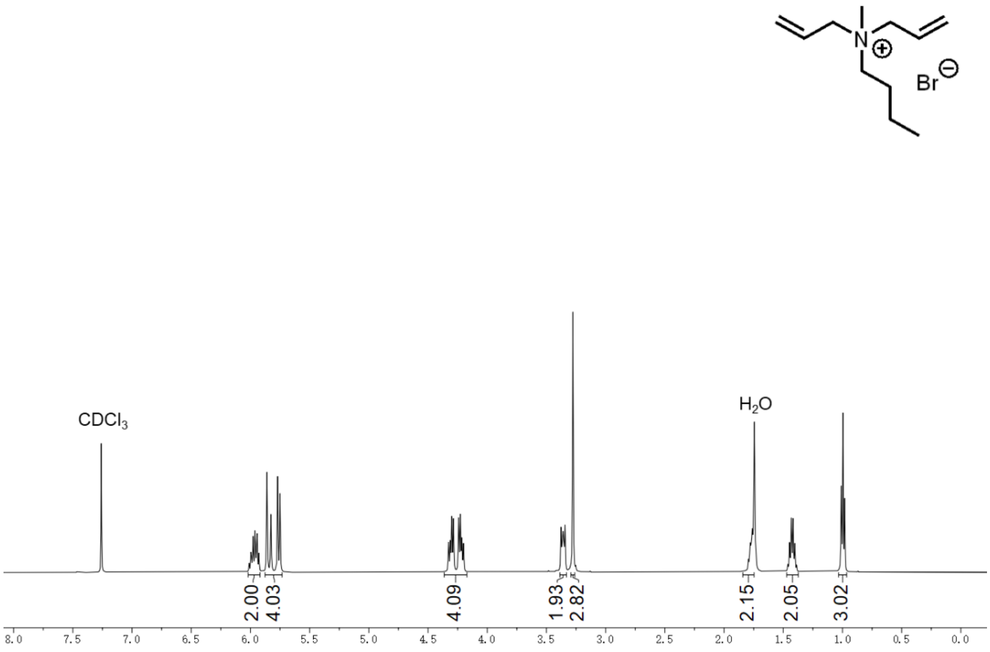


Figure S1. ^{1}H NMR spectrum of the N,N-diallyl-N-methyl-N-butylammonium bromide.

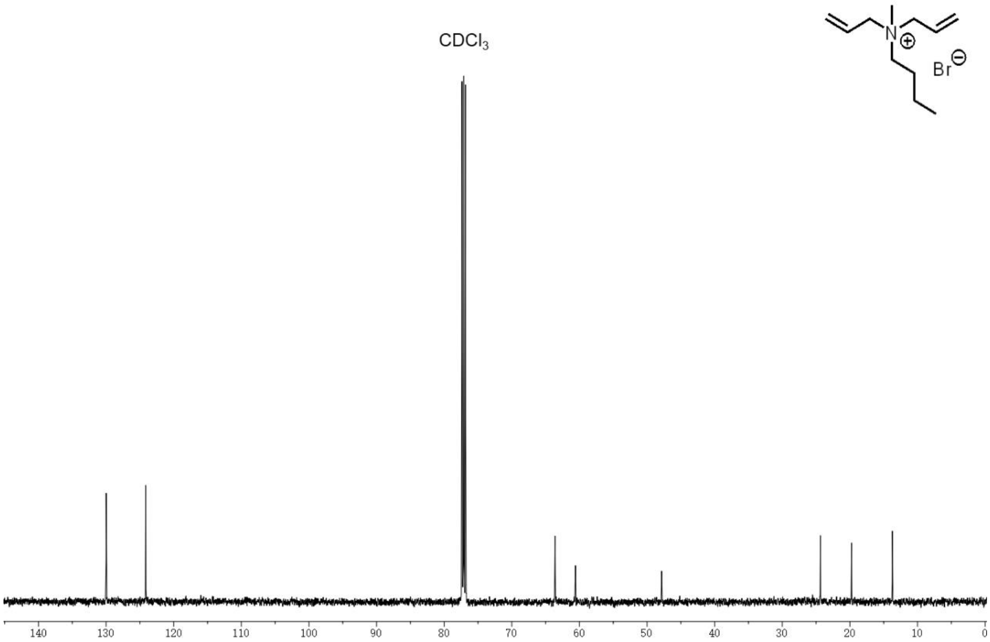


Figure S2. ^{13}C NMR spectrum of the N,N-diallyl-N-methyl-N-butylammonium bromide.

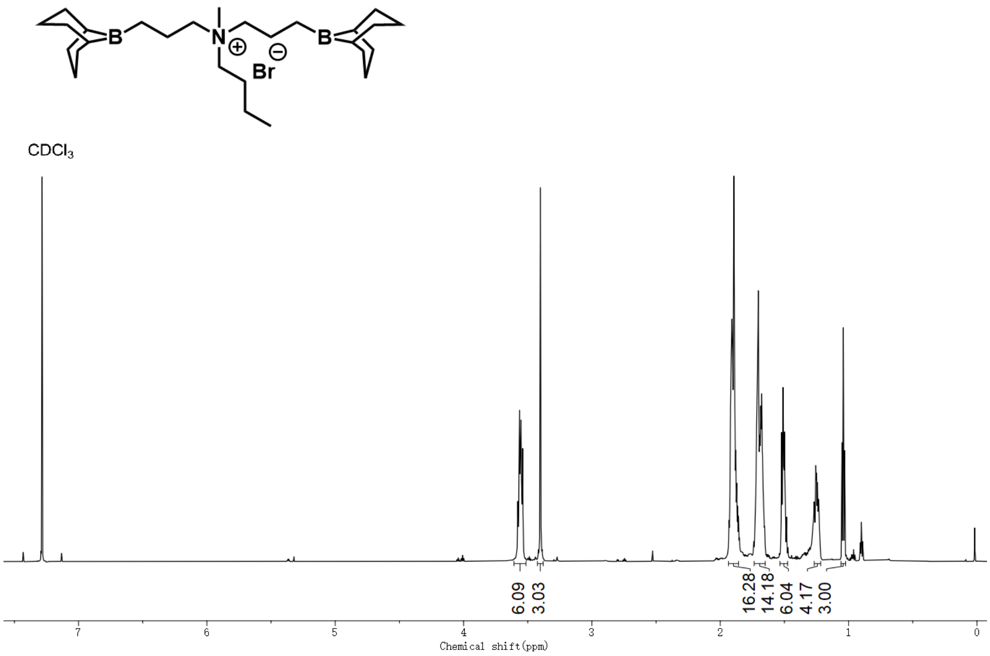


Figure S3. ^{1}H NMR spectrum of the bifunctional organoboron catalyst.

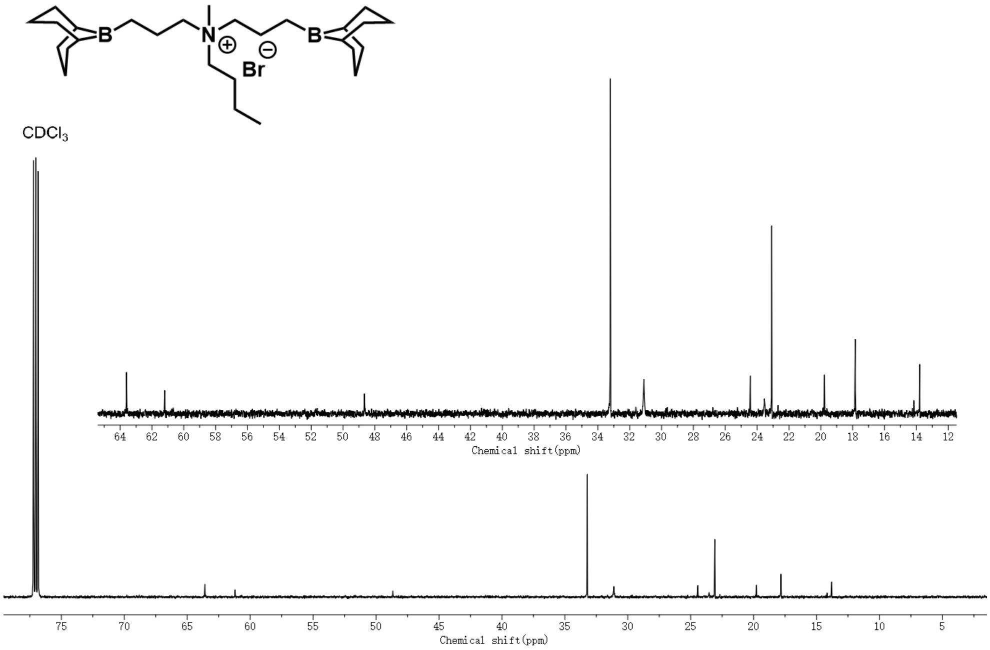


Figure S4. ^{13}C NMR spectrum of the bifunctional organoboron catalyst.

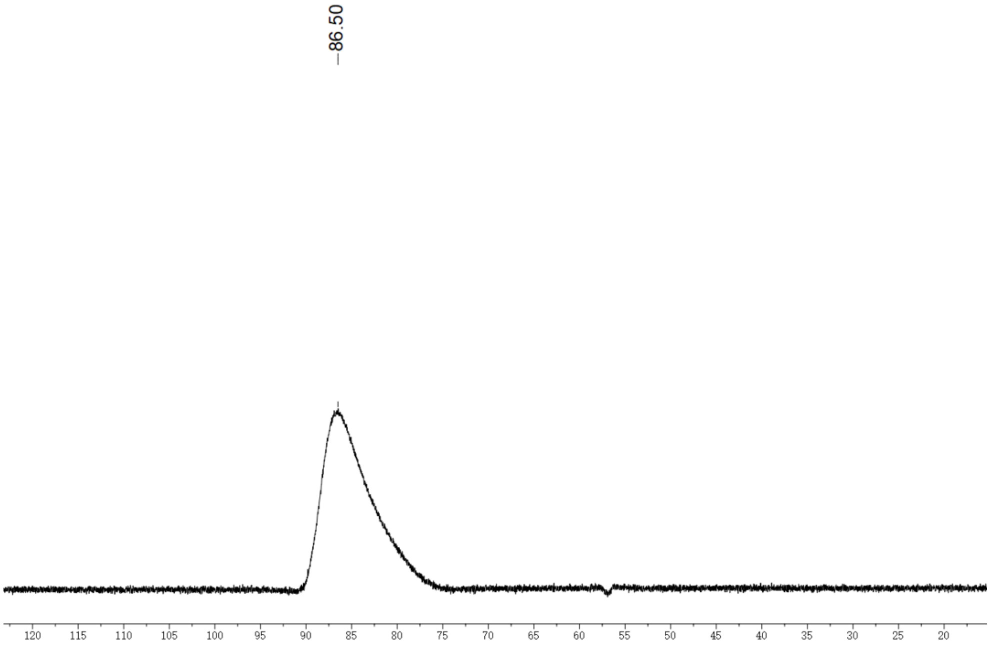


Figure S5. ^{11}B NMR spectrum of the bifunctional organoboron catalyst.

Synthesis of Catalyst

Ring-opening copolymerization of PA and AGE by using bifunctional organoboron as catalyst and BA as chain-transfer agents

In an Ar-filled glovebox, PA (1.48 g, 10 mmol), catalyst (0.0492 g, 100 μmol), BA (0.108 g, 1 mmol) and AGE (8 mL, 70 mmol) were weighed into a flame-dried Schlenk tube equipped with magnetic stirrer. The tube was sealed with a teflon-coated screw cap and immediately taken out of the glove box, then the reaction solution was heated at 120 °C. The reaction was cooling to ambient temperature and opened to air to quench the reaction diluted with CH_2Cl_2. A small aliquot of the polymerization mixture was taken out for the analysis of the conversion of PA by ^{1}H NMR spectroscopy. When the completion of polymerization, the resulting polymer was obtained by precipitation from n-hexane and cyclohexane. Then the polymer was dried under vacuum at 50 °C overnight.

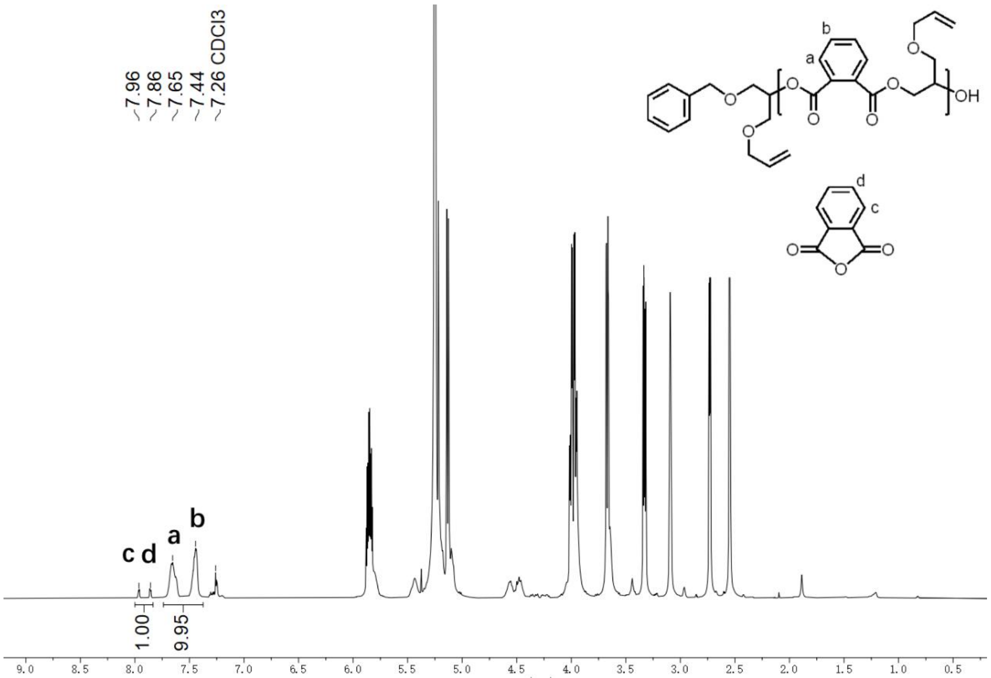


Figure S6. ^{1}H NMR spectrum of the crude reaction mixture that BA as chain-transferagent diluted with CH_2Cl_2 ($CDCl_3$, 25 °C, 700 MHz). The conversion of PA was determined to be 90.9% (aromatic unit in polymer at 7.56 and 7.39 ppm vs residual PA at 7.98 and 7.86 ppm). PA/ BA/ NB_2-Br =10 / 1 / 0.1, 120 °C, 40 min.

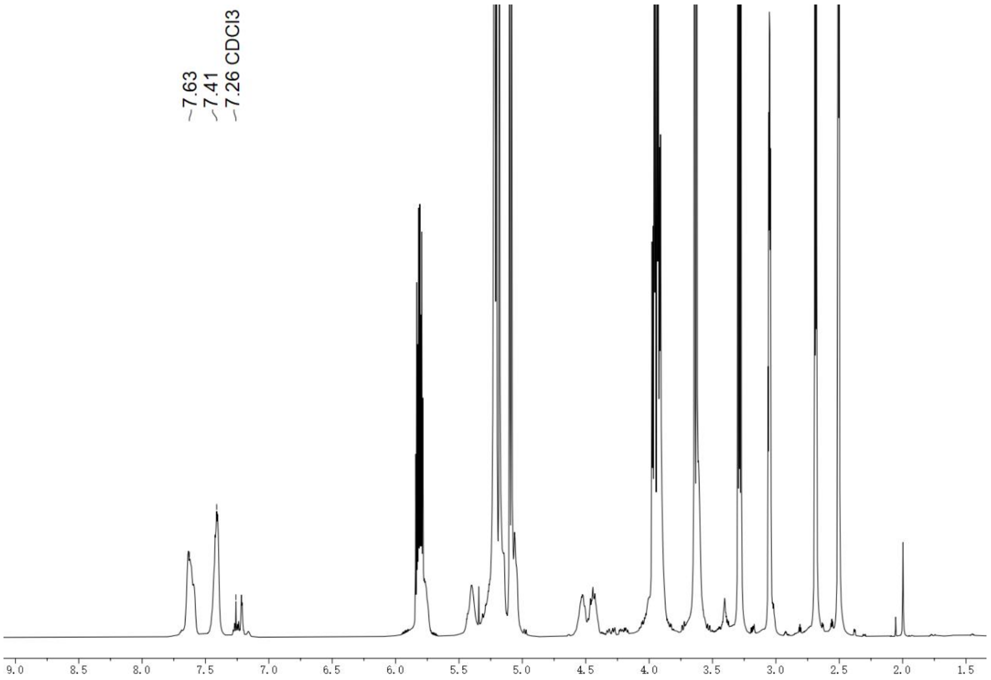


Figure S7. ^{1}H NMR spectrum of the crude reaction mixture that BA as chain-transferagent diluted with CH_2Cl_2 ($CDCl_3$, 25 °C, 700 MHz). The conversion of PA was determined to be 99.9 % (aromatic unit in polymer at 7.56

and 7.39 ppm vs residual PA at 7.98 and 7.86 ppm). PA/ BA/ NB$_2$-Br =10/1/0.1, 120 °C, 55 min (entry 1 in Table 1).

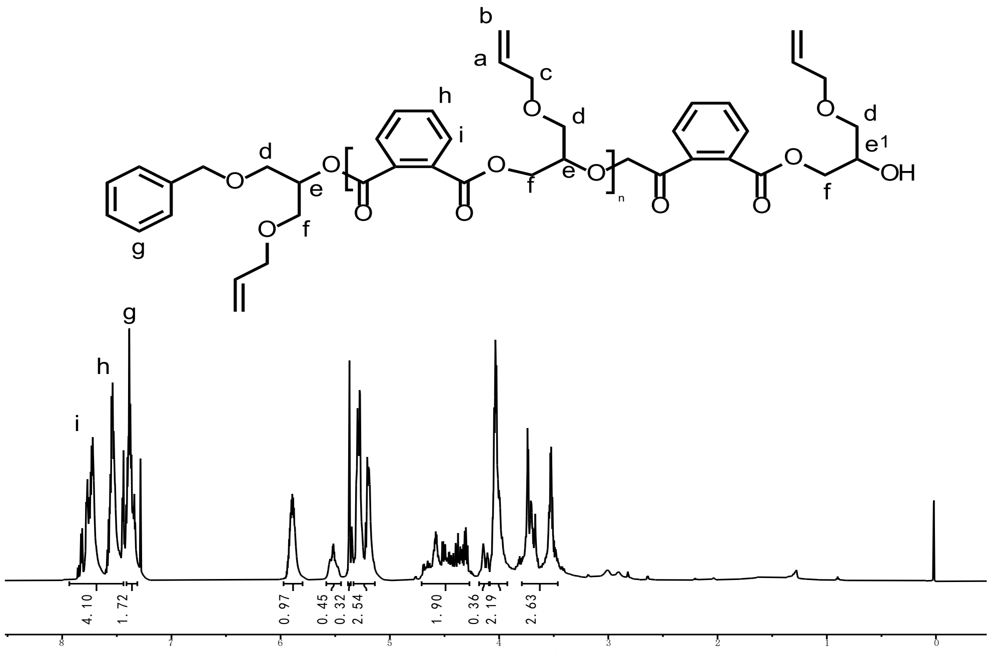


Figure S8. ^{1}H NMR spectra (CDCl$_3$, 25 °C, 700 MHz) of neat PAGEP.

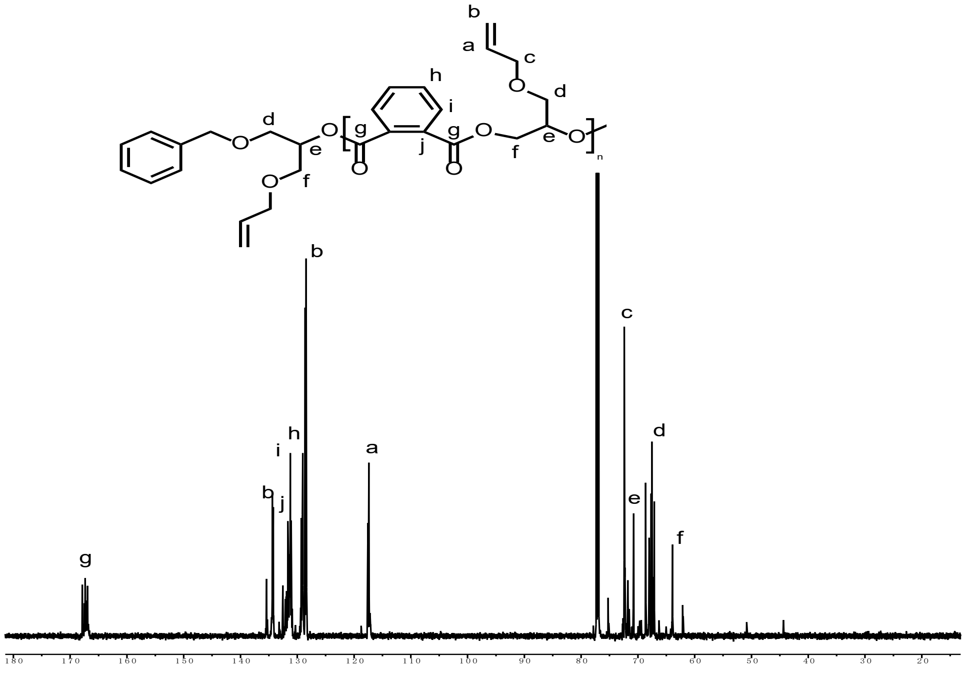


Figure S9. ^{13}C NMR spectra (CDCl$_3$, 25 °C, 600 MHz) of neat PAGEP.

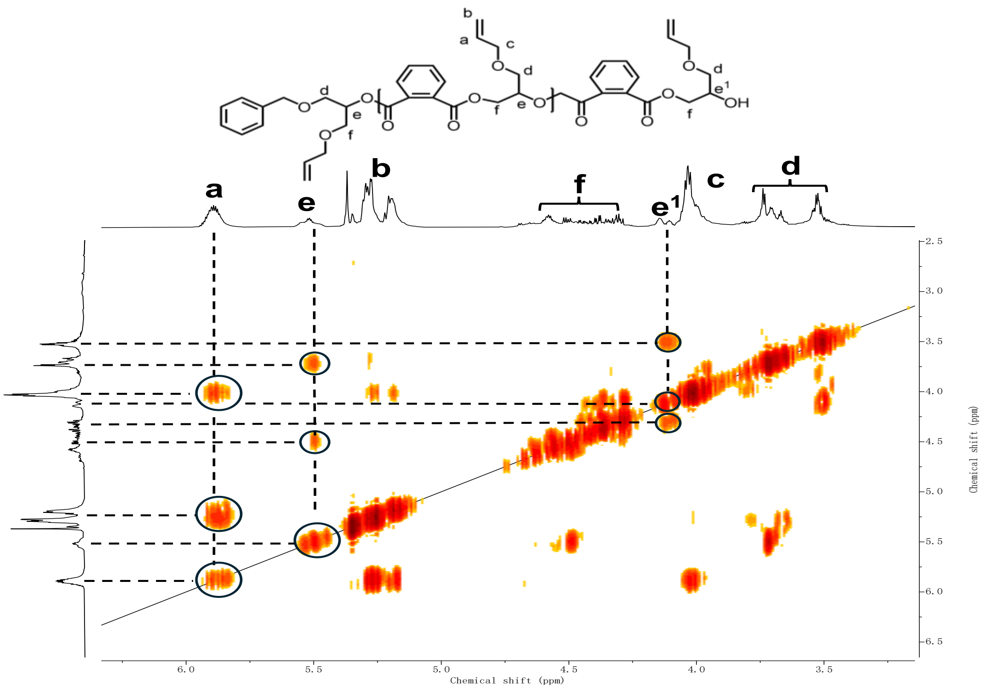


Figure S10. The DOSY NMR spectra ($CDCl_3$, 25 °C, 600 MHz) of neat PAGEP.

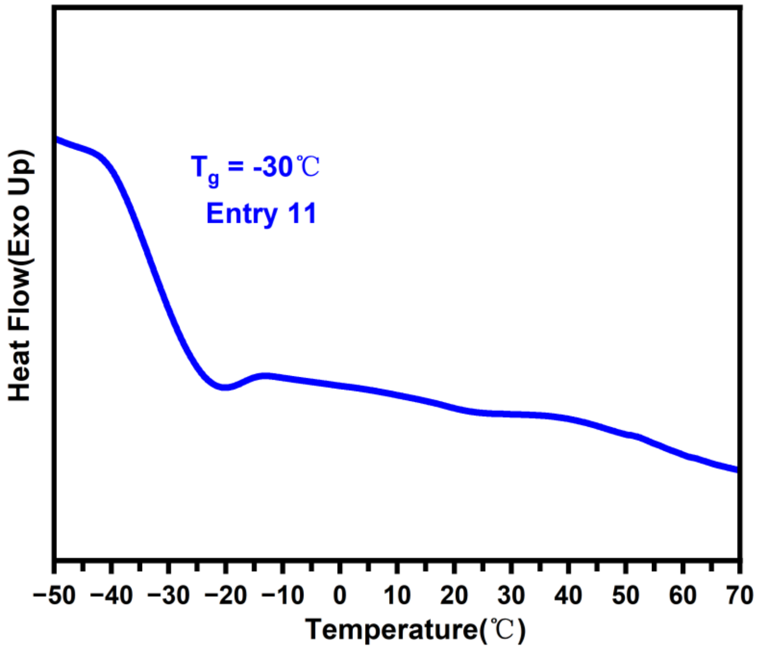


Figure S11. Differential scanning calorimetry (DSC) curve of PAGEP (Table1, Entry 11, full temperature sweep)

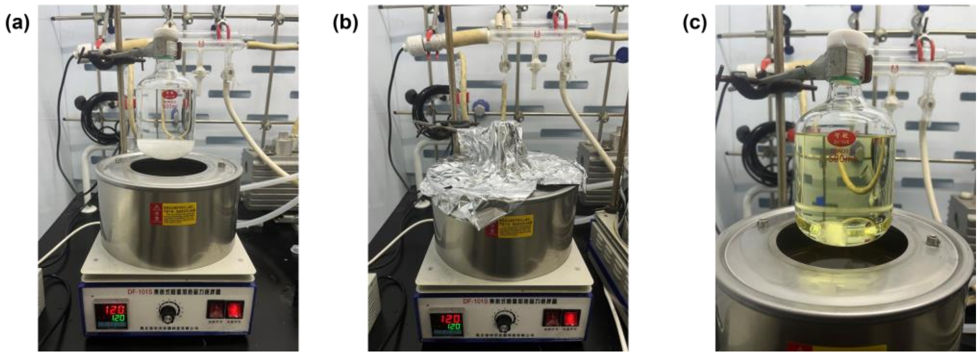
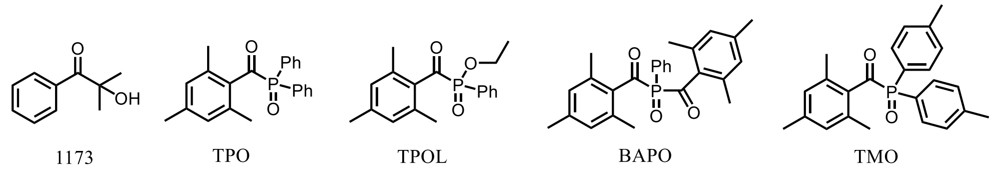


Figure S12. Digital pictures for large production of PAGEP.

Figure S13. The kilogram scale neat PAGEP.



Scheme S1. Five common photoinitiators.

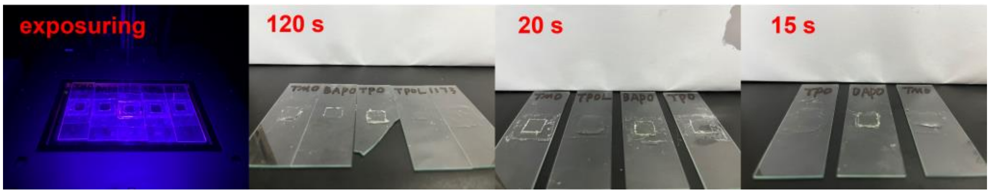


Figure S14. Photopolymer resin with five common photoinitiators was exposed for 120 s, 20 s, and 15 s.

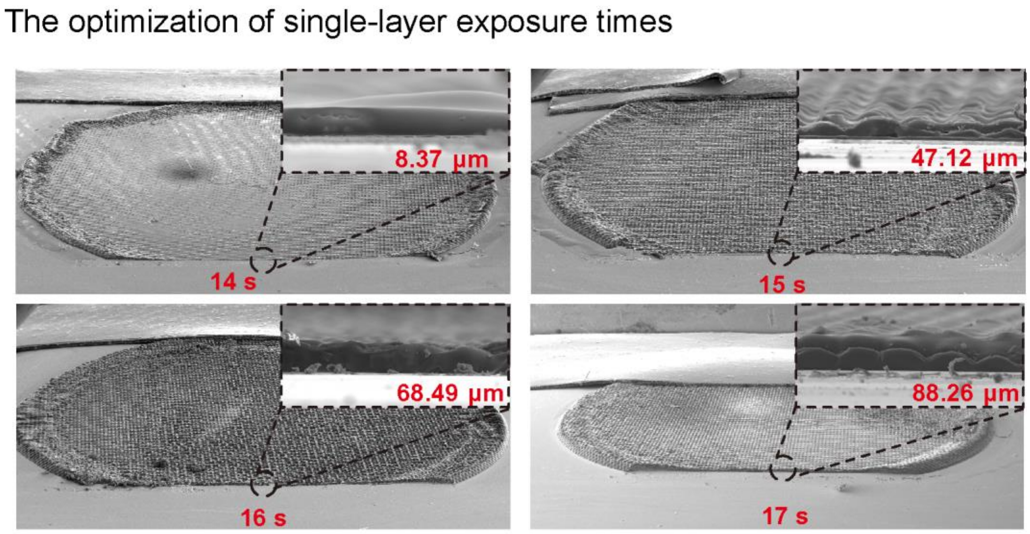


Figure S15. SEM images of the UV resin thickness at varying durations.

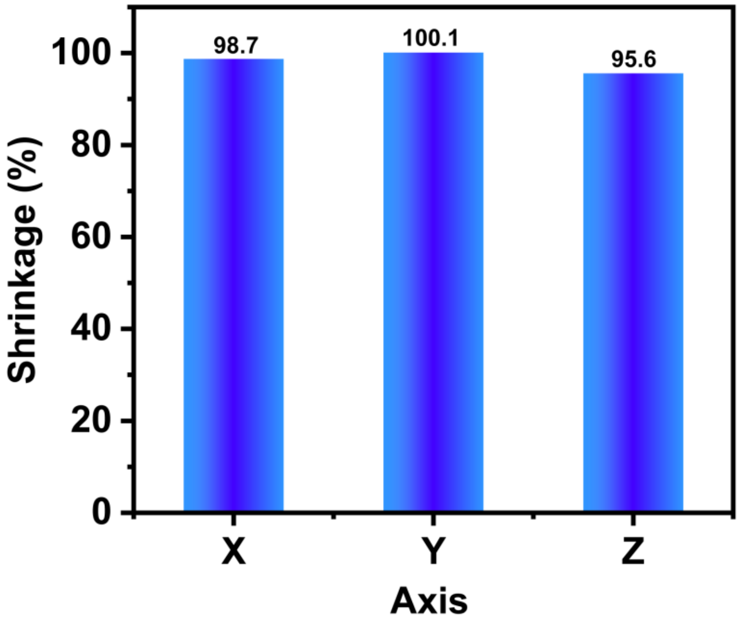


Figure S16. Three-dimensional shrinkage (along the X, Y, and Z axes) of ASTM D638 Type V tensile dogbone specimens, demonstrating the deviation between the printed parts and their as-designed dimensions based on the original .stl file (n = 5).

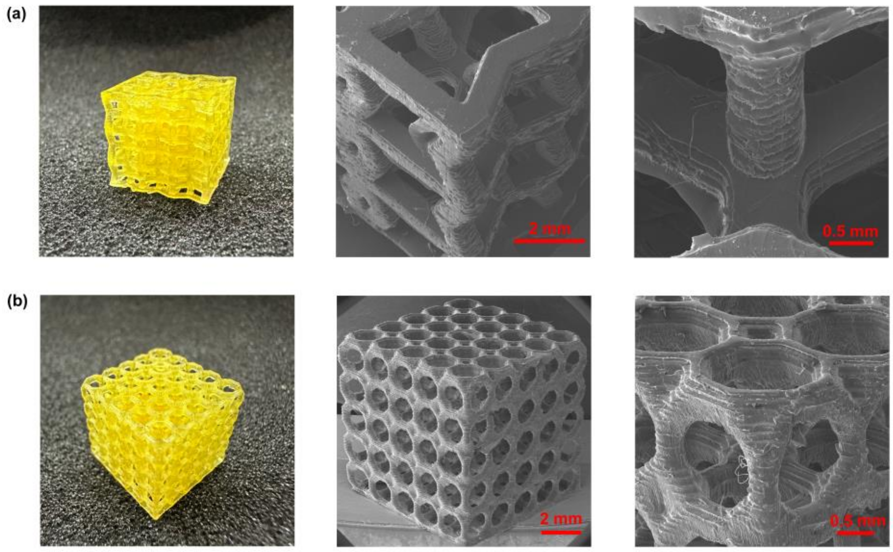


Figure S17. The high-resolution gyroid and cubic lattice structures fabricated via DLP 3D printing.

[1] M. I. Segal, A. J. Bahnick, N. G. Judge, M. L. Becker, *Angewandte Chemie International Edition* **2024**, *64*.