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Alcohol-Mediated Controlled Cationic Photopolymerization of Vinyl Ethers for Programmable Additive Manufacturing

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Abstract:

Photopolymerization-based additive manufacturing has become a powerful platform for fabricating complex functional materials; however, the development of controlled cationic photopolymerization systems remains limited by the reliance on specialized chain-transfer agents and the lack of versatile resin-design strategies. Herein, we report an alcohol-mediated photoinduced controlled cationic polymerization of vinyl ethers and demonstrate its application in high-resolution digital light processing (DLP) 3D printing. Readily available alcohols function as chain-transfer regulators to control cationic chain growth through terminal acetal formation, enabling the synthesis of poly(vinyl ether)s with tunable molecular weights under mild photoirradiation. The resulting polymerization exhibits rapid curing while maintaining effective control over polymer network formation, allowing direct translation into DLP printing. By independently varying the crosslinking density, vinyl ether structures, and alcohol regulators, the mechanical properties of the printed materials can be programmed over a broad range while preserving excellent printing fidelity and fabrication efficiency. Furthermore, the compatibility of this strategy with structurally diverse, commercially available, and industrially accessible vinyl ethers and alcohols enables the preparation of degradable networks, polyurethane-like elastomeric materials, and other functional polymer systems through modular resin design. This work establishes alcohol-mediated controlled cationic photopolymerization as a general, cost-effective strategy for molecularly programming polymer networks and substantially expands the chemical space available for photopolymerization-based additive manufacturing.

Introduction

Three-dimensional (3D) printing, or additive manufacturing, has revolutionized the fabrication of complex architectures for applications ranging from biomedical devices to flexible electronics and soft robotics.¹⁻⁵ Among the various additive manufacturing technologies, photopolymerization-based 3D printing has emerged as one of the most powerful approaches because of its high spatial resolution, rapid fabrication speed, and excellent surface quality.⁶⁻⁹ Since the polymerization process directly dictates the network architecture, photopolymerization chemistry fundamentally determines the structural fidelity, mechanical performance, and functionality of printed objects. Consequently, the development of advanced photopolymerization strategies that enable precise control over polymer network formation has become a central research direction in additive manufacturing. Recent advances have demonstrated that rational molecular design of resin systems can significantly expand the capabilities of 3D printing. For example, Dove, Worch, and co-workers incorporated dynamic disulfide bonds into polymer networks through the polymerization of renewable lipoate-derived monomers, enabling closed-loop recycling and reprinting of photopolymerized materials.¹⁰ Xie, Zheng, and co-workers constructed circular 3D-printing resins by generating dynamic dithioacetal linkages through the photopolymerization of thiols and aldehydes.¹¹ Page and co-workers developed wavelength-selective hybrid epoxy–acrylate resins that orthogonally activate cationic and radical polymerizations, enabling rapid multimaterial printing with distinct mechanical properties.¹² More

recently, Commisso, Page, and co-workers reported a light-controlled strategy for programming the stereochemistry of polyolefins during photopolymerization, enabling grayscale lithographic printing of thermoplastics with continuously tunable mechanical properties.¹³ Collectively, these studies illustrate that innovations in photopolymerization chemistry provide powerful opportunities to regulate polymer network structures and endow printed materials with programmable properties.

Photopolymerization-based 3D printing primarily relies on radical and cationic polymerization mechanisms.¹⁴ Radical polymerization of (meth)acrylates dominates current commercial printing technologies because of its broad monomer compatibility, rapid curing kinetics, and excellent printing resolution. In contrast, cationic photopolymerization offers unique advantages, including oxygen tolerance, low volumetric shrinkage, and compatibility with diverse heteroatom-containing monomers,¹⁵ making it an attractive alternative for advanced additive manufacturing. Nevertheless, its broader implementation remains hindered by limited control over polymerization, which often results in overcuring, poor printing resolution, and restricted resin design. Consequently, cationic photopolymerization is frequently combined with radical polymerization to construct hybrid resin systems rather than being exploited as an independent printing strategy.¹⁶

Vinyl ethers are representative cationically polymerizable monomers that are readily accessible from both renewable and petrochemical feedstocks.¹⁷ Although they exhibit exceptionally high cationic polymerization activity, their applications remain largely confined

because conventional poly(vinyl ether)s are generally amorphous and exhibit limited practical utility.¹⁸ More importantly, the potential of vinyl ethers as versatile building blocks for photopolymerization-based additive manufacturing has been largely unexplored. The rapid propagation kinetics of vinyl ethers frequently lead to excessive curing and heat generation, thereby compromising printing resolution. Recently, we addressed this challenge by developing a controlled cationic polymerization strategy for high-resolution 3D printing.¹⁹⁻²¹ However, this system relied on specialized chain-transfer agents (CTAs), such as cationic RAFT agents and thioacetals, whose multistep synthesis and relatively high cost limit their practical implementation. Therefore, developing an inexpensive, readily accessible, and broadly applicable strategy for controlled cationic photopolymerization remains an important challenge.

Inspired by early studies demonstrating that alcohols can regulate living cationic polymerization through reversible chain-transfer processes,²²⁻²⁶ we envisioned that abundant and inexpensive alcohols could serve as molecular regulators for controlled cationic photopolymerization. However, previously reported alcohol-mediated systems generally require stringent reaction conditions and are incompatible with photopolymerization or additive manufacturing. Herein, we report an alcohol-mediated photoinduced controlled cationic polymerization of vinyl ethers and demonstrate its application in high-resolution digital light processing (DLP) 3D printing. Using diphenyliodonium hexafluorophosphate (DPI) and 2-isopropylthioxanthone (ITX) as the photoinitiating system,²⁷ readily available alcohols regulate

vinyl ether polymerization under mild irradiation conditions, enabling rapid curing together with controlled network formation. By varying the structures of vinyl ethers, alcohol regulators, and resin compositions, the mechanical properties of the printed materials can be programmed over a broad range while maintaining high printing resolution and fabrication efficiency. Furthermore, because many vinyl ether monomers can be readily synthesized from corresponding alcohol feedstocks, this strategy establishes a cost-effective, modular, and sustainable resin-design platform for additive manufacturing, expanding the scope of controlled cationic photopolymerization for programmable polymer materials.

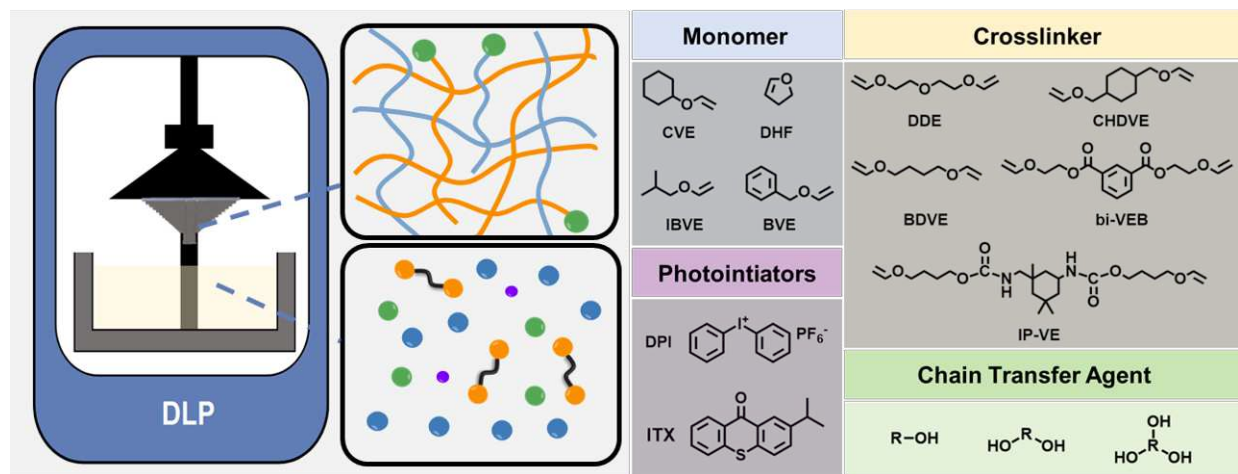


Figure 1. Alcohol-mediated cationic photopolymerization 3D printing.

Results and discussion

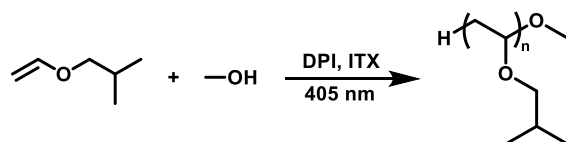
Alcohol-mediated photoinduced cationic polymerization of vinyl ethers

We first investigated whether alcohols could mediate photoinduced controlled cationic polymerization of vinyl ethers under conditions compatible with DLP printing. As summarized in

Table 1, poly(isobutyl vinyl ether) (PIBVE) with tunable molecular weights (2,300 to 25,000) was successfully prepared by varying the molar ratio of IBVE to methanol (Entries 1-7, **Table 1**), although the dispersities remained broader than those typically achieved in conventional living cationic polymerization. This behavior is likely attributable to the relatively inefficient degenerative chain-transfer process associated with acetal dormant species compared with thiocarbonate- or thioacetal-based systems.^{26, 27} In the absence of methanol, polymerization afforded polymers with substantially higher molecular weights and broader dispersities (Entry 8, **Table 1**), suggesting that methanol regulates chain growth through the formation of terminal acetal species via nucleophilic trapping of the propagating carbocation (**Figure S2**). To prove this proposed chain transfer process, a model reaction between IBVE and methanol (1:1 molar ratio) was carried out in the presence of DPI and ITX under photoirradiation. As shown in **Figure S2**, both IBVE and methanol were quantitatively consumed within 1 min, accompanied by the quantitative formation of the corresponding acetal. Consistent with this result, the characteristic resonance of the terminal acetal proton at 4.6 ppm was clearly observed in the ¹H NMR spectrum of PIBVE (**Figure S3**). More importantly, to distinguish reversible chain transfer from predominantly irreversible proton-transfer or termination pathways, we performed an in-situ chain-extension experiment (**Figure 2**). After polymerization to 96% monomer conversion, the isolated polymer had an M_n of approximately 3,900. Upon addition of a second portion of monomer under otherwise identical polymerization conditions, the SEC trace shifted clearly toward higher molecular weight, with M_n increasing to approximately 19,000 at similarly high monomer conversion (83%). These results

Table 1. Polymerization of IBVE in DCM with various conditions at 25 °C under a 405 nm LED

light, $[\text{IBVE}]_0 = 7.9 \text{ M}$, $V_{\text{DCM}} = 0.5 \text{ mL}$.



Entry	$[\text{IBVE}]_0:[\text{MeOH}]_0:[\text{DPI}]_0:[\text{ITX}]_0$	Time (min)	Conv. (%)	$M_{n,\text{th}}^{\text{a}}$	$M_{n,\text{SEC}}^{\text{b}}$	$\bar{D}$
1	100:1:0.005:0.005	60	20	2000	16200	1.71
2	100:1:0.01:0.01	2	99	10000	14400	1.75
3	10:1:0.001:0.001	2	97	1000	2300	1.57
4	20:1:0.002:0.002	2	99	2000	3600	1.73
5	30:1:0.003:0.003	2	99	3000	4800	1.82
6	50:1:0.005:0.005	3	97	4900	7500	1.71
7	200:1:0.03:0.03	10	98	19700	25000	1.76
8	100:0:0.01:0.01	1	99	-	22000	1.97

(a) Calculated based on conversion ($M_{n,\text{th}} = [\text{M}]_0/[\text{MeOH}]_0 \times M_{\text{IBVE}} \times \text{conversion} + M_{\text{MeOH}}$); (b)

determined by tetrahydrofuran (THF) SEC using polystyrene (PS) calibration.

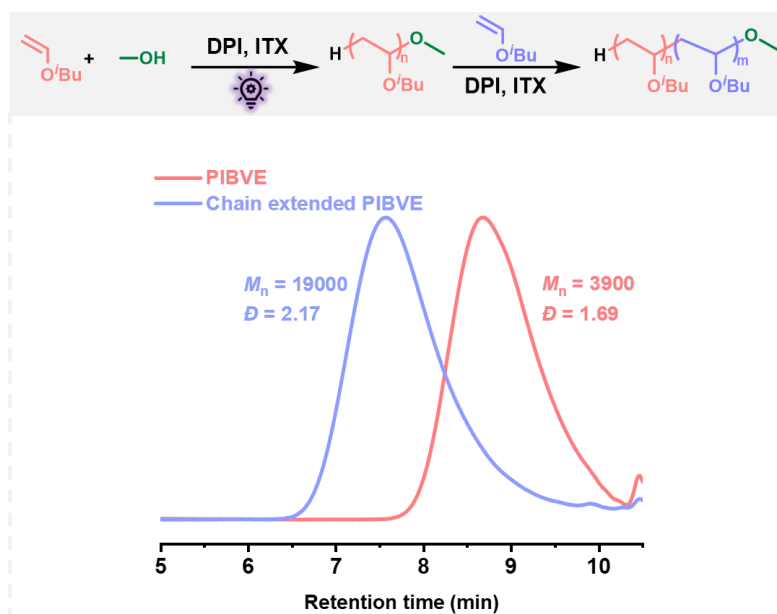


Figure 2. SEC traces of PIBVE before and after chain extension.

provide strong evidence for high chain-end fidelity and demonstrates that the polymer chains retain sufficient reactive chain ends to undergo further propagation. Furthermore, MALDI-TOF MS spectrum showed a single dominant series of peaks corresponding to PIBVE bearing an acetal chain end (**Figure S3**), providing additional evidence that alcohol-mediated chain transfer contributes to the formation of well-defined polymer chain ends. Together, these results support an alcohol-mediated chain-transfer mechanism that enables controlled cationic polymerization under photoirradiation. To further evaluate the generality of this strategy, the polymerization of IBVE was investigated in the presence of a series of structurally diverse alcohols. In all cases, polymers with tunable molecular weights were successfully obtained (**Table S1**), demonstrating the broad applicability of alcohols as regulators for photoinduced controlled cationic polymerization. However, higher experimental molecular weights and broader dispersities were observed, indicating the methanol is the best CTA for this system.

Tuning mechanical properties of 3D-printed materials via alcohol concentration

The rapid polymerization kinetics (>90% monomer conversion within 2 minutes) prompted us to translate this chemistry into DLP-based 3D printing. A resin formulation comprising the divinyl ether crosslinker, diethylene glycol divinyl ether (DDE), the high-boiling-point reactive diluent, cyclohexyl vinyl ether (CVE), methanol, DPI, and ITX was developed for printing using a commercial DLP printer ($\lambda_{\text{max}} = 405 \text{ nm}$, $I_0 = 1.0 \text{ mW cm}^{-2}$, **Figure 1**). The photopolymerization kinetics were first evaluated by attenuated total reflectance Fourier transform infrared (ATR-FTIR)

spectroscopy to optimize the curing conditions. As shown in **Figure 3A**, increasing the photoinitiator concentration accelerated the polymerization, whereas varying the methanol concentration had a negligible effect on the polymerization rate (**Figure 3B**). All formulations reached >90% monomer conversion within 1 min, highlighting the excellent curing efficiency of this alcohol-mediated controlled cationic photopolymerization system. A Jacobs working curve was subsequently established to determine the optimal exposure conditions for layer-by-layer fabrication (**Equation S1** and **Figure S11**)²⁸. Based on this analysis, a layer thickness of 100 μm and an exposure time of 11 s per layer were selected for subsequent printing experiments.

The effect of alcohol-mediated chain transfer on the mechanical properties of the printed networks was then investigated using dumbbell-shaped tensile specimens prepared with different methanol concentrations. As shown in **Figure 3C** and **Table S2**, increasing the methanol content progressively decreased the Young's modulus of the printed materials. This behavior is attributed to alcohol-mediated chain transfer, which delays gelation during network formation and consequently reduces the effective crosslink density while promoting a more homogeneous network structure.^{29, 30} Consistent with this interpretation, dynamic mechanical analysis (DMA) revealed progressively narrower full widths at half-maximum (FWHM) of the $\tan \delta$ peaks with increasing methanol concentration (**Figures 3D** and **3E**), indicating a narrower network relaxation distribution and enhanced network homogeneity. Together, these results demonstrate that alcohol-mediated controlled cationic polymerization not only enables rapid photoprinting but also

provides an effective molecular strategy for regulating polymer network architecture and, consequently, the mechanical properties of the printed materials.

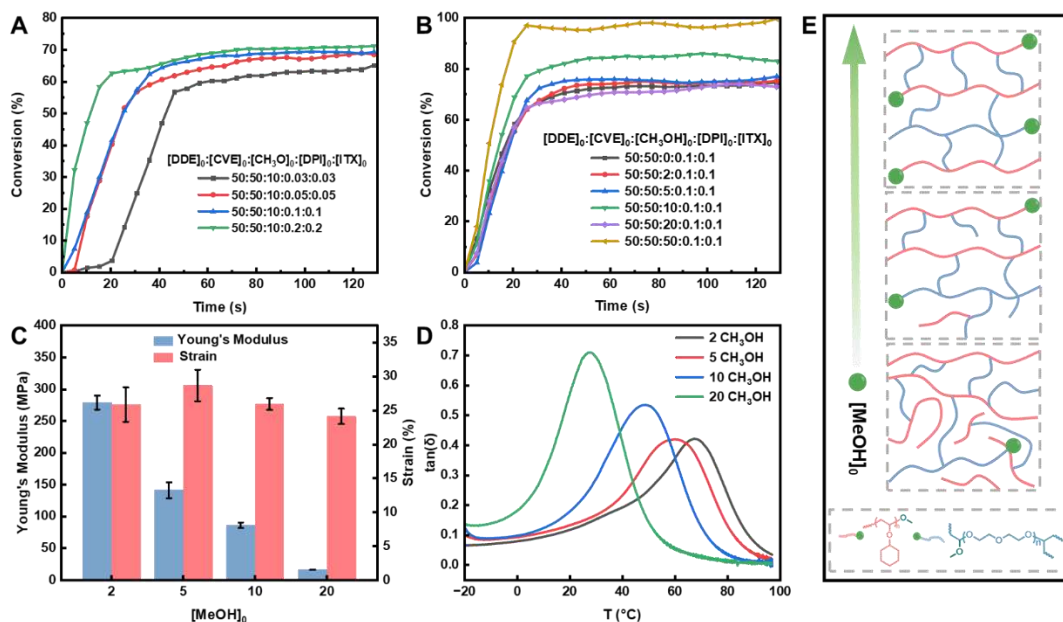


Figure 3. (A, B) Conversion versus time of different resin formulation under 405 nm LED light (1.0 mW cm^{-2}) at room temperature and open to air. (C) Mechanical properties obtained from tensile testing. (D) DMA results of the printed samples obtained by printing resins consisting $[\text{DDE}]_0:[\text{CVE}]_0:[\text{MeOH}]_0:[\text{DPI}]_0:[\text{ITX}]_0 = 50:50:x:0.1:0.1$. (E) Schematic illustration of the crosslinking network with varying methanol content.

Programmable mechanical properties of printed materials through molecular design

Furthermore, the mechanical properties of the printed networks could be readily programmed by varying the crosslinking density through adjustment of the DDE/CVE ratio. As shown in **Figure**

4A, decreasing the DDE content progressively reduced the Young's modulus from 479.56 to 3.14 MPa while simultaneously increasing the elongation at break (ϵ_b) from 10.43% to 90.90%. This behavior is attributed to the reduced crosslinking density of the polymer networks (**Figure 4B**). These results demonstrate that simple modulation of the resin composition enables precise control over network architecture and mechanical performance.

Having established control through network architecture, we next explored whether molecular diversity could further expand the accessible mechanical property space. A broad range of commercially available mono- and divinyl ethers, including CVE, 2,3-dihydrofuran (DHF), isobutyl vinyl ether (IBVE), butyl vinyl ether (BVE), 1,4-butanediol divinyl ether (DVBE), and 1,4-cyclohexanedimethanol divinyl ether (CHDVE), proved compatible with this printing platform, affording polymer networks with widely tunable mechanical properties (**Figures 4C and 4D**). Notably, DHF is a commercially available bio-derived vinyl ether that has recently attracted considerable interest as a building block for degradable thermosets.³¹ More broadly, most vinyl ether monomers are either commercially available or can be readily synthesized from the corresponding alcohols on an industrial scale,^{32, 33} providing a sustainable and economically attractive feedstock platform for resin design.

We next investigated the scope of alcohol regulators by evaluating structurally diverse alcohols as chain-transfer agents for DLP printing (**Figure 4E**). Monofunctional alcohols primarily functioned as chain-end regulators, whereas multifunctional alcohols became covalently incorporated into the crosslinked polymer network. Consequently, the chemical structure of the

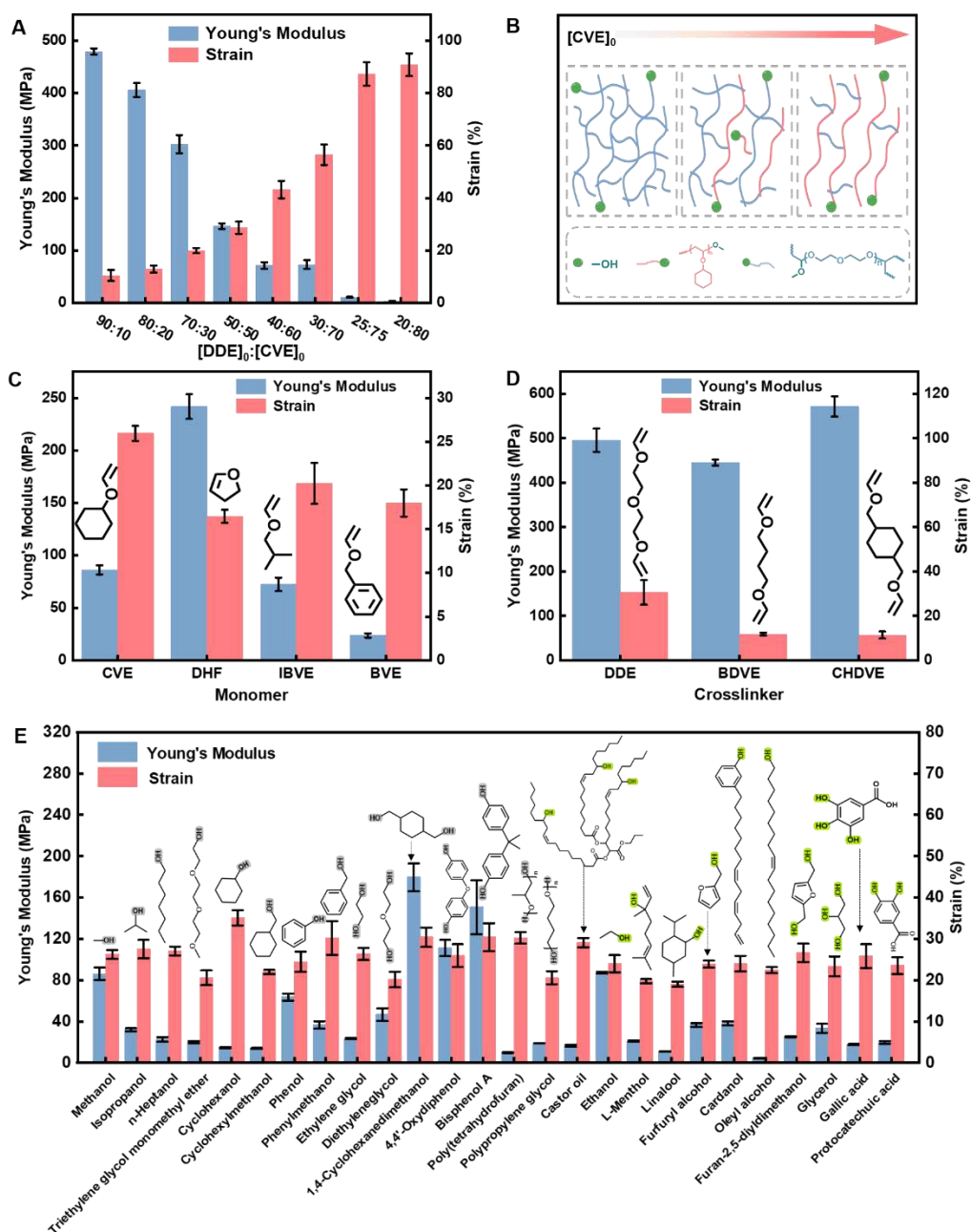


Figure 4. (A) Tensile testing results of the printed samples obtained by printing resins consisting

$[DDE]_0:[CVE]_0:[MeOH]_0:[DPI]_0:[ITX]_0 = x:y:5:0.1:0.1$ ($x + y = 100$). (B) Schematic illustration of the

crosslinking network with varying monomer content. (C) Tensile testing results of the printed samples with different monomers at a molar ratio of $[DDE]_0:[Monomer]_0:[MeOH]_0:[DPI]_0:[ITX]_0 = 50:50:10:0.1:0.1$. (D) Tensile testing results of the printed samples with different crosslinkers at a molar ratio of $[Crosslinker]_0:[DHF]_0:[MeOH]_0:[DPI]_0:[ITX]_0 = 20:80:5:0.1:0.1$. (E) Tensile testing results of the printed samples obtained by printing resins with different alcohols at a molar ratio of $[DDE]_0:[CVE]_0:[Alcohol]_0:[DPI]_0:[ITX]_0 = 50:50:10:0.1:0.1$.

alcohol regulator directly influenced the mechanical properties of the resulting materials. In particular, networks prepared from rigid alcohols, such as 1,4-cyclohexanedimethanol, 4,4'-oxydiphenol, and bisphenol A, exhibited substantially higher Young's moduli than those prepared from flexible aliphatic alcohols, demonstrating that incorporation of rigid molecular segments into the network backbone provides an effective strategy for enhancing mechanical stiffness. Because these alcohols are likewise derived from abundant renewable and petrochemical feedstocks, they further expand the molecular design space of this resin platform. Collectively, these results demonstrate that the mechanical properties of the printed materials can be independently programmed through two orthogonal molecular design parameters: the chemical structures of the polymerizable vinyl ether monomers and the alcohol-mediated chain-transfer regulators. This modular strategy greatly expands the compositional flexibility of controlled cationic photopolymerization and provides a versatile platform for designing mechanically programmable materials through additive manufacturing.

Expanding functional and mechanical space through modular molecular design

Having established that the mechanical properties of the printed networks can be programmed through molecular design, we next investigated whether this platform could be extended to incorporate additional functionalities. As shown in **Figure 5**, bifunctional vinyl ether monomers containing either ester or urethane linkages were synthesized and incorporated into the printing formulations. Networks prepared from ester-containing vinyl ethers exhibited hydrolytic degradability, enabling their potential use as sacrificial molds (**Figure 5A**). In contrast, incorporation of urethane-containing vinyl ethers produced polymer networks with polyurethane-like elastomeric behavior (**Figure 5B**). These results demonstrate that the molecular structure of vinyl ether monomers can be rationally engineered to introduce functionalities beyond mechanical regulation. The versatility of this strategy is further enhanced by the broad structural diversity of both vinyl ether monomers and alcohol regulators. As demonstrated in **Figures 5C** and **5D**, molecular-level variation of these two components enables access to printed materials spanning a wide range of mechanical properties, comparable to those of silicone elastomers, polyurethane foams, polyimide foams, and epoxy resins. Unlike conventional photopolymerization systems, this alcohol-mediated controlled cationic photopolymerization strategy enables independent molecular engineering of both polymerizable monomers and chain-transfer regulators. Consequently, it establishes a modular resin-design platform that integrates broad compositional

diversity with programmable network structures and material functions, thereby substantially expanding the chemical space accessible for photopolymerization-based additive manufacturing.

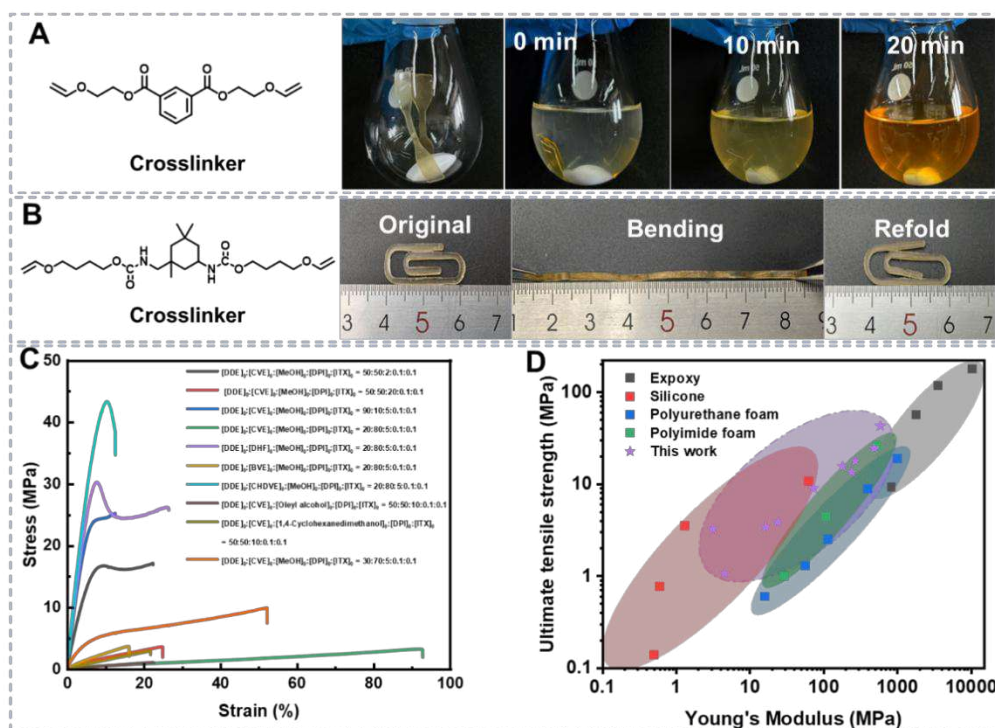


Figure 5. (A) Images of the degradation process of the printed objects ([bi-VEB]₀: [DHF]₀: [MeOH]₀: [DPI]₀: [ITX]₀ = 20:80:5:0.1:0.1) in a THF/MeOH solution (1/1 v/v) containing 5 wt % KOH. (B) Images of the flexing process of the printed objects at a molar ratio of [IP-VE]₀: [CVE]₀: [MeOH]₀: [PAG-SbF₆]₀: [ITX]₀ = 20:80:5:0.5:0.5. (C) Stress and strain curves of the printed samples of different resin formulations. (D) The printed materials in this work show comparable properties to commercial thermosets (all values used to make the graph can be found in **Table S10**).

High-fidelity, rapid, and cost-effective DLP printing enabled by alcohol-mediated cationic photopolymerization

Using an optimized resin formulation ([DDE]₀:[CVE]₀:[MeOH]₀:[DPI]₀:[ITX]₀=70:30:5:0.1:0.1), scanning electron microscopy (SEM) images revealed well-defined features and smooth surfaces with a minimum feature size of 200 μm (**Figure 6A**), demonstrating the excellent fidelity of the printing process. The fabrication efficiency was further evaluated by measuring the build rate under different printing conditions, affording printing speeds ranging from 2.10 to 8.21 cm h⁻¹ with layer thicknesses of 0.05-0.20 mm (**Figure S12** and **Table S11**). These build rates are comparable to those achieved with commercial radical-based photopolymerization resins (~2 cm h⁻¹), despite the fundamentally different polymerization mechanism. To further improve the fabrication of complex architectures, a small amount of curcumin (0.05 wt%) was incorporated as a UV absorber to reduce light penetration and suppress undesired curing beyond the irradiated regions. Under these conditions, a series of complex structures, including a grid, a Mayan pyramid, and a lizard, were successfully fabricated with excellent structural fidelity (**Figures 6B-6D**). To evaluate the potential effects of the residual acidic species generated from the photodecomposition of the DPI salt, we monitored the stability of the printed samples over a period of one week. As shown in **Figures S13-S14**, no obvious change in the appearance or coloration of the printed samples was observed during the testing period. In addition, the tensile properties remained essentially unchanged after one week, indicating that the residual acidic species did

not cause an appreciable deterioration of the mechanical properties under the conditions examined. These results demonstrate that alcohol-mediated controlled cationic photopolymerization simultaneously enables rapid curing, high printing resolution, and precise structural control. The practical potential of this platform was further evaluated through an analysis of the resin cost (**Tables S8** and **S9**). The estimated material cost was approximately 2880 USD t⁻¹, substantially lower than that of commercially available photopolymerization resins (8500-206000 USD t⁻¹). This economic advantage arises from the use of inexpensive, readily available alcohols as chain-transfer regulators and industrially accessible vinyl ether monomers, eliminating the need for synthetically elaborate chain-transfer agents. Collectively, these results demonstrate that alcohol-mediated controlled cationic photopolymerization provides a general and cost-effective strategy for molecularly programming polymer network formation while maintaining the processing efficiency required for high-performance additive manufacturing. By integrating controlled polymerization, modular resin design, and rapid DLP printing within a single platform, this approach substantially expands the scope of cationic photopolymerization for advanced functional materials.

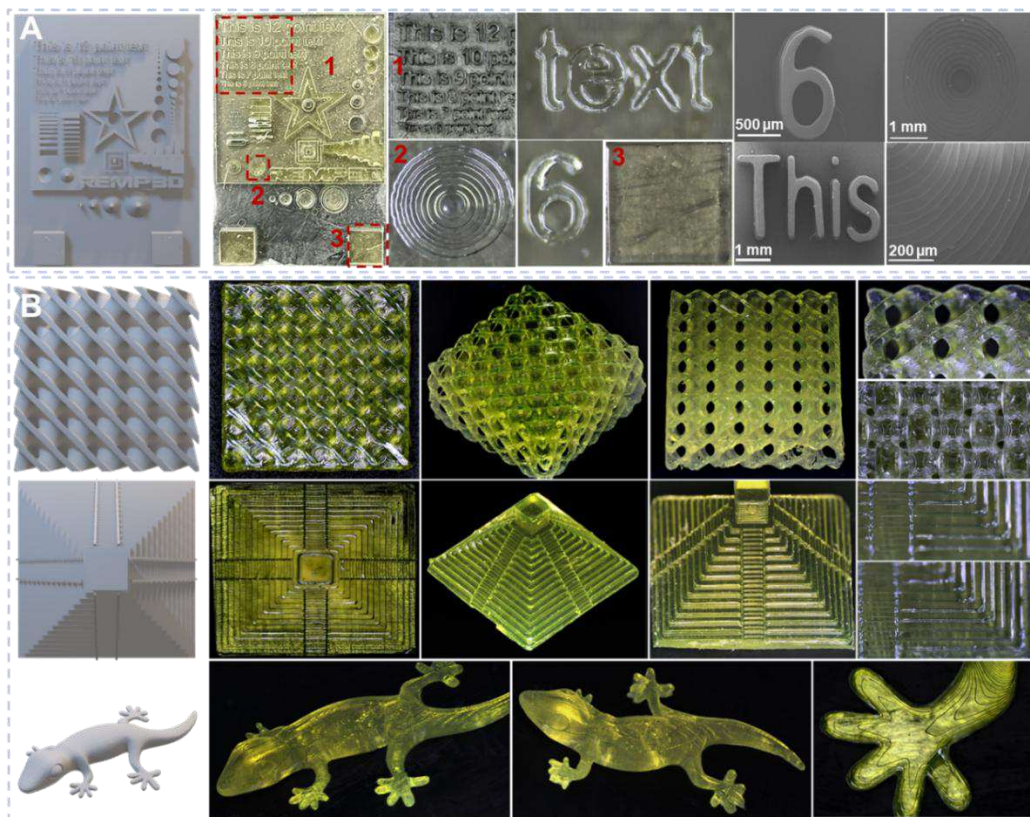


Figure 6. (A) Digital and SEM images of the printed precision model under a fixed molar ratio of $[DDE]_0:[CVE]_0:[MeOH]_0:[DPI]_0:[ITX]_0 = 70:30:5:0.1:0.1$. (B) Other printed objects (containing 0.05 wt% curcumin).

Conclusion

In summary, we have developed an alcohol-mediated photoinduced controlled cationic polymerization of vinyl ethers and demonstrated its application as a versatile platform for digital light processing (DLP) 3D printing. Readily available alcohols regulate cationic chain growth through terminal acetal formation, providing an inexpensive alternative to conventional specialized chain-transfer agents while enabling controlled polymerization under mild photochemical conditions. The resulting polymerization combines rapid curing with effective

control over network formation, allowing efficient translation from molecular design to high-resolution additive manufacturing. More importantly, this strategy establishes a modular molecular design framework for programming the properties of printed polymer networks. Independent regulation of crosslinking density, vinyl ether monomers, and alcohol-mediated chain-transfer regulators enables systematic control over network architecture and mechanical performance, while tailor-designed monomers further introduce functionalities such as hydrolytic degradability and polyurethane-like elastomeric behavior. The compatibility of this platform with structurally diverse and industrially accessible feedstocks substantially broadens the compositional space of cationic photopolymerization resins. Beyond providing a practical resin formulation for additive manufacturing, this work demonstrates that alcohol-mediated controlled cationic photopolymerization is a general synthetic strategy for engineering polymer networks through molecular-level regulation of chain growth and network formation. We anticipate that this concept will stimulate the development of new cationic photopolymerization methodologies and expand the application of controlled polymerization in advanced manufacturing, functional materials, and sustainable polymer synthesis.

Methods

Synthesis of bis(2-(vinylloxy)ethyl) isophthalate (bi-VEB)

Trimethylamine (29.91 g, 295.5 mmol) and 2-(vinylloxy) ethanol (26.04g, 295.5 mmol) were dissolved in 200 mL of dichloromethane by stirring in a 500 mL flask in an ice water bath. A

solution of isophthaloyl chloride (20 g, 98.5mmol) in dichloromethane (100 mL) was added dropwise and allowed to react for 30 minutes. Then the mixture was stirred under room temperature for 12 hours. After the filtration, the solution was concentrated by rotary evaporator. Next, the concentrated mixture was washed with deionized water and saturated brine and extracted by dichloromethane for twice. The organic phase was dried over Na_2SO_4 and evaporated to dryness to obtain a pale yellow-green and transparent liquid(82% yield). ^1H NMR (**Figure S10**, CDCl_3 , 300 MHz), δ : 8.72 (t, 1H), 8.26(m, 2H), 7.54 (m, 1H), 6.52 (dd, 2H), 4.59 (dd, 4H), 4.25 (dd, 2H), 4.06 (m, 6H).

Synthesis of the Difunctional Vinyl Ether Monomer (IP-VE)

Isophorone diisocyanate (IPDI) (0.2 mol) was charged into a 500 mL three-neck round-bottom flask. 4-hydroxybutyl vinyl ether (HBVE) (0.4 mol) was placed in a pressure-equalizing addition funnel, and dibutyltin dilaurate (DBTDL) (0.05 wt %) was added as a catalyst. HBVE was added dropwise to the IPDI solution under argon with vigorous stirring at 50 °C. After the addition was complete, the reaction was maintained at 50 °C for 2 h. ^1H NMR (**Figure S11**, $\text{DMSO}-d_6$, 300MHz), 7.18-6.84(m, 2H), 6.49(q, 2H), 4.18(d, 2H), 3.96(m, 6H), 3.68(t, 4H), 3.57(m, 1H), 2.72(m, 2H), 1.62(m, 8H), 1.45(m, 2H), 1.16-0.80(m, 13H).

General procedure for photopolymerization of IBVE

All polymerizations were conducted in a nitrogen-filled glovebox. Monomers were dried over CaH_2 for at least 12 hours, distilled under nitrogen, subjected to three freeze–pump–thaw cycles, and

stored in the glovebox. In a typical experiment, IBVE (1.00 g, 10 mmol), CH₃OH (3.20 mg, 0.1 mmol), DPI (0.426 mg, 1.0×10^{-3} mmol), ITX (0.254 mg, 1.0×10^{-3} mmol) and DCM (0.5 mL) were added to a 4 mL Teflon vial ([IBVE]₀: [CH₃OH]₀: [DPI]₀: [ITX]₀ = 100:1:0.01:0.01). The mixture was irradiated with a 405 nm LED (3.0 mW cm⁻²) at 25 °C under stirring for the desired time. The reaction was quenched by dilution with THF and addition of trace triethylamine. Monomer conversion was determined gravimetrically.

Chain extension of IBVE *in situ*

The first stage of polymerization was carried out according to the above steps with a molar ratio of [IBVE]₀: [CH₃OH]₀: [DPI]₀: [ITX]₀ = 20:1:0.002:0.002. After a predetermined time (2 min), a small amount of the polymer was taken for SEC testing, and 0.5 mL of the purified monomer was added into the reaction mixture. The polymerization was continued for 30 min, and then a small amount of the polymer was taken for SEC testing.

Photopolymerization of Printing printing Resins resins for Online online Infrared infrared

Analysis analysis

Printing resins for online infrared analysis were prepared by mixing different proportions of DDE, CVE, CH₃OH, DPI and ITX. The mixture was uniformly mixed and dissolved by an oscillator for online infrared analysis under 405 nm LED light irradiation of the DLP 3D printer (1.0 mW cm⁻²) and open to air.

3D printing procedure

A resin mixture (≈ 30 mL) containing DDE, CVE, CH₃OH, DPI and ITX with a molar ratio of [DDE]₀: [CVE]₀: [CH₃OH]₀: [DPI]₀: [ITX]₀ = 50:50:5:0.1:0.1 was poured into the sink of the DLP 3D printer. Then, the mold.stl file was imported into the printer. The printing parameters were set as follow: exposure time per layer: 6 s; target per layer thickness: 0.1 mm; 1 bottom layer and 8 s exposure time for bottom layer; 2 for anti-alias; 5 mm Z lift height; 2 mm s⁻¹ Z lift speed; 2 mm s⁻¹ Z retract step speed. Then the printing process was started. Printed objects were washed with ethyl acetate and post-cured under 405 nm irradiation (60 mW cm⁻²) for 2 hour.

Conduction of Jacob test

To determine the exposure time per layer in the printing process, a Jacob test was conducted, which involved printing elements in the form of 1 × 1 mm discs at various exposure times, each at the same light intensity specific to each compound. After printing, the discs were initially cleaned of uncured material using ethyl acetate, and their thickness was measured at five different points using a micrometre screw. This allowed for the determination of the average thickness. Next, based on the ratio of the curing time of each disc to the intensity of light irradiating the printed disc, the values of E_0 (the light energy per unit area expressed in mJ/cm³) were calculated. The averaged value of C_d (Equation 1) was then plotted on a logarithmic graph as a function of $C_d = f(E_0)$, which enabled the determination of D_p as the slope of the curve and E_c as the intersection point with the x- axis.

$$C_d = D_p * \ln \left(\frac{E}{E_c} \right) \quad (\text{Equation S1})$$

Dumbbell-shaped mold samples for tensile testing

Printing resin (≈ 30 mL) containing DDE/DVBE/CHDVE, IBVE/DHF/CHVE/BVE, Alcohol, DPI and ITX at various molar ratios was prepared and poured into the sink of the DLP 3D printer. A dumbbell-shaped mold (.stl file) was imported into the printer. The printing parameters were set as follow, the exposure time per layer was adjusted according to the minimum curing time required to obtain well-defined objects; target per layer thickness: 0.1 mm; one bottom layer and exposure time (same exposure time for per layer) for bottom layer; 2 for anti-alias; 5 mm Z lift height; 2 mm s^{-1} Z lift speed; 2 mm s^{-1} Z retract step speed. After printing, the specimens were removed, washed with ethyl acetate, and post-cured under 405 nm LED irradiation (60 mW cm^{-2}) for 2 hour.

Data availability

The authors declare that the data supporting the findings of this study are provided within the article and its Supplementary Information file. Additional data are available upon request from the corresponding author.

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Author contribution

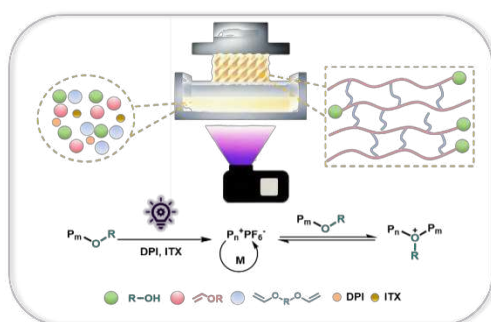
Yuan Wang: Writing-original draft, Data curation, Investigation; Xiaofeng Pan: Data curation, Investigation; Juntao Hu: Investigation, Data curation; Wenhui Li: Data curation; Xiangqiang Pan: Writing-review and editing; Jiajia Li: Conceptualization, Supervision, Writing- original draft, review and

editing, Funding acquisition; Jian Zhu: Conceptualization, Supervision, Funding acquisition, Writing-review and editing, Project administration.

Competing interests statement

The authors declare no competing interests.

Table of Contents



Alcohol-mediated controlled cationic photopolymerization of vinyl ethers enables molecular programming of polymer networks through inexpensive chain transfer agents, providing a modular resin-design platform for high-resolution additive manufacturing with broadly tunable mechanical properties.

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