Supplementary Information (SI) for Polymer Chemistry.

Supporting Information

Bio-Based Cellulose-Supported Photocatalyst Enabling Reversible Complexation-Mediated Polymerization via Energy Transfer under White LED Irradiation

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Materials

All reagents and solvents were obtained from commercial outlets and used as received without further purification. Hydroxyethyl Cellulose (HEC, Mv~90000, viscosity (C=5%, H_2O at 25 °C): 136.0 cP, molar substitution (MS) = 2.97) was purchased from Shanghai Aladdin Biochemical Technology Co., LTD. N,N'-Carbonyldiimidazole (CDI, ≥98%) was purchased from RHAWN. Betaine (BET, ≥98%), 2-Iodo-2-phenylacetic acid ethyl ester (Eph-I), methyl methacrylate (MMA, 99%), benzyl methacrylate (BzMA, 99%), 2-methoxyethyl methacrylate (MEMA, 99%), butyl methacrylate (BMA, 99%), phenyl methacrylate (PhMA, > 97.0%), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) was purchased from Macklin. Dimethyl sulfoxide (DMSO) (>99.9%, Sunbio), tetrahydrofuran (THF) (>99%, Sunbio), methanol (>99.8%, Sunbio), hexane (>99%, Hushi), dichloromethane, and deuterated chloroform ($CDCl_3$) with 0.03% TMS (>99.8%D, Leyan) were purchased from Sinopharm. A light-emitting diode (LED) strip (White LED: 450 nm, 15 mW cm^{-2}) was purchased from Philips.

Characterization

Fourier transform infrared (FT-IR) spectra of HEC-QA were recorded by Thermo Scientific Nicolet is50 equipped with an attenuated total reflection (ATR) accessory. Proton and carbon nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded using a Bruker AVANCE NEO 600 spectrometer (14.1 T, 600 MHz). X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific ESCALAB QXi to analyze the elemental composition of the samples.The scanning electron microscopy (SEM, Verios G4) was used to analyze the morphology of HEC-QA. UV-vis diffused reflectance spectra were measured on PerkinElmer LAMBDA800 PE. Fluorescence spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer with an excitation wavelength of 365 nm. Fluorescence lifetime measurements were carried out using an Edinburgh Instruments FLS980 steady-state/transient fluorescence spectrometer. Photoelectrochemical characterization was carried out on CHI760E electrochemical workstation. The average molecular weight (M_n) and dispersity (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC). The GPC system consisted of a Shimadzu autosampler (SIL-20AC), a degasser unit (DGU-20A3R), and a differential refractive index detector (RID-20A). The GPC system was equipped with three Shodex columns in series: GPC KF-803, GPC KF-805, GPC KF-804, augmented by an additional guard column, the Shodex GPC KF-G 4A. The GPC system was calibrated using PMMA standards, with THF as the eluent, and operated at 40 °C. The organic elemental content of HEC-QA was determined using an Elementar Unicube elemental analyzer for the calculation of its degree of substitution (DS). Use the CEL-PCRD300-12 photochemical reactor to conduct the polymerization under different white light intensities.

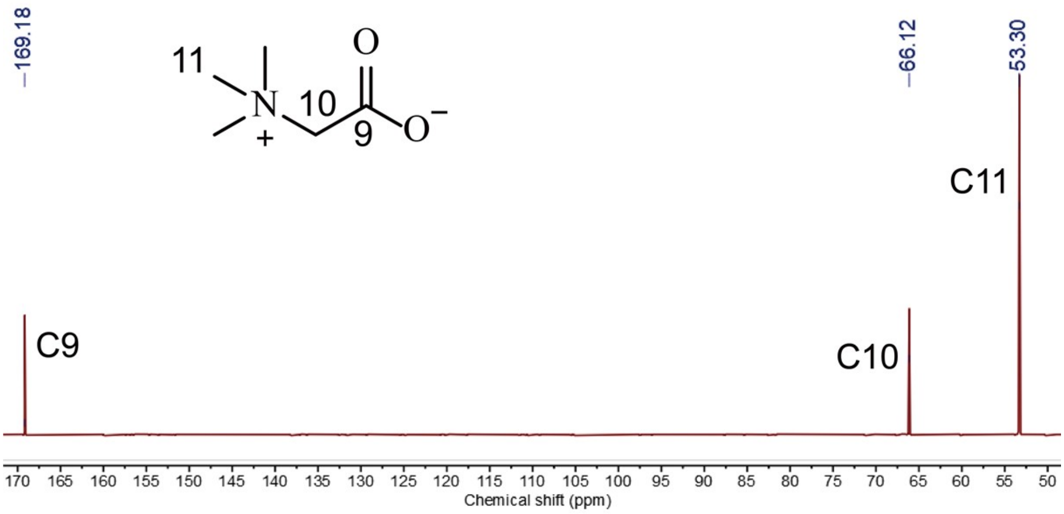

Figure S1. ^{13}C NMR spectrum of BET in deuterium oxide.

BET: ^{13}C NMR (151 MHz, Deuterium Oxide) δ: 169.18, 66.12, 53.30.

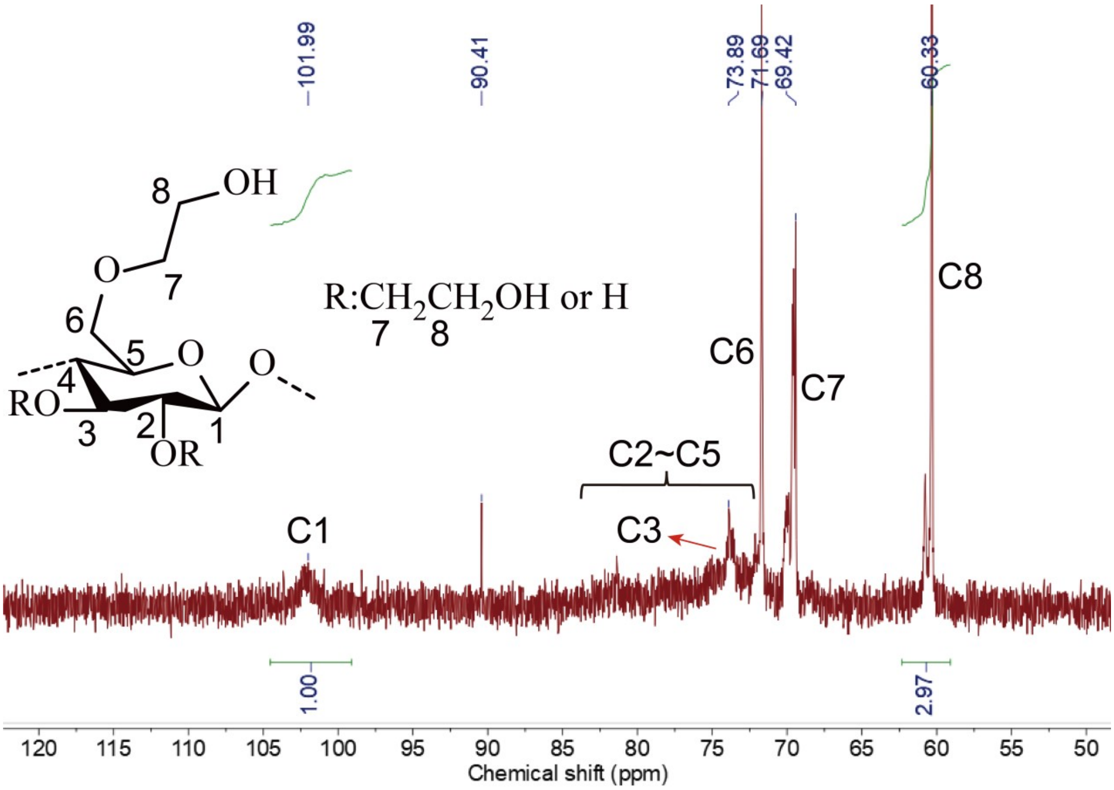

Figure S2. ^{13}C NMR spectrum of HEC in deuterium oxide.

HEC: ^{13}C NMR (151 MHz, Deuterium Oxide) δ: 101.99, 90.41, 73.89, 71.69, 69.42, 60.33.

Based on the peak area, the molar substitution degree of hydroxyethyl can be calculated, MS = 2.97.

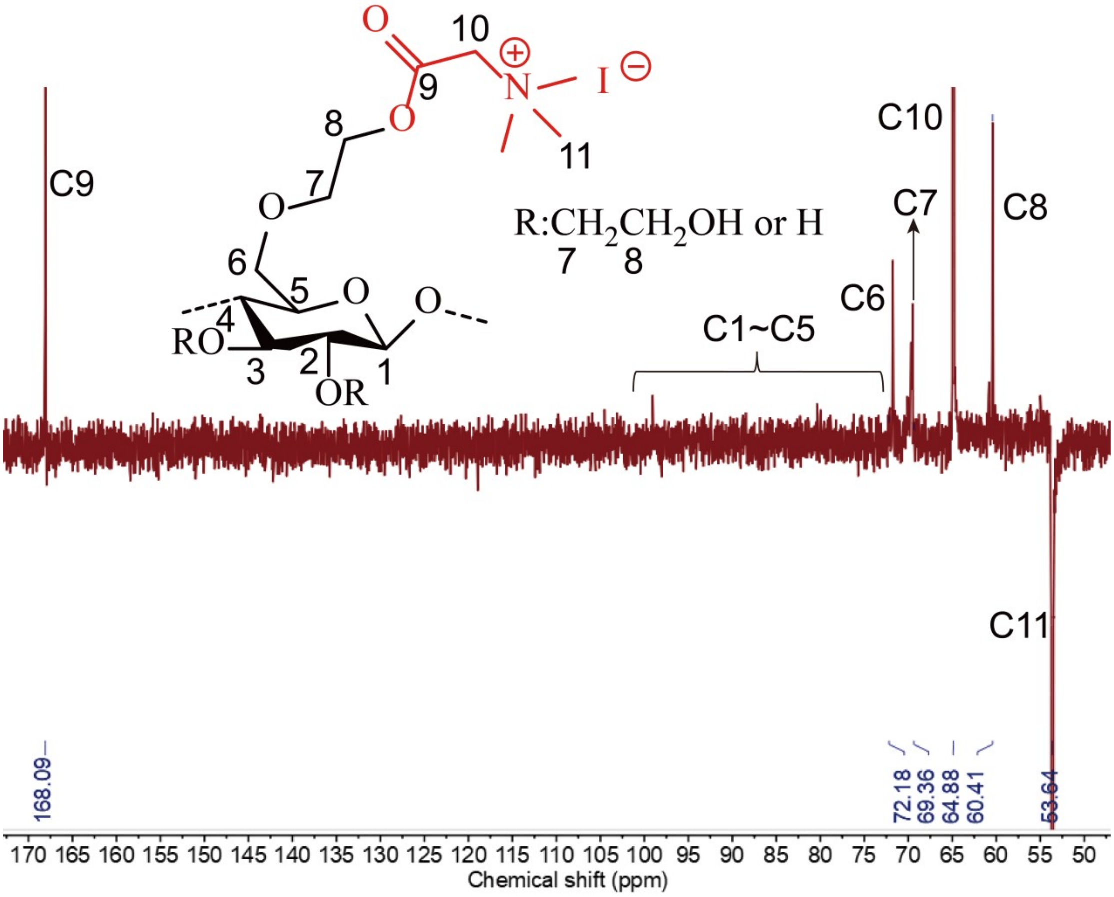

Figure S3. ^{13}C NMR spectrum of HEC-QA in deuterium oxide.

HEC-QA: ^{13}C NMR DEPTQ (151 MHz, Deuterium Oxide) δ: 168.09, 72.18, 69.36, 64.88, 60.41, 53.64.

Elemental analysis of HEC-QA

The degree of substitution (DS) of HEC-QA was determined by measuring the nitrogen content (N%) using an Elementar elemental analyzer. M_{HEC} represents the molar mass of an unsubstituted monomer unit (HEC, AGU=294.3 g/mol), M_N denotes the molar mass of nitrogen (14.01 g/mol), and M_{BET} corresponds to the molar mass of the betaine substituent excluding iodine (118.15 g/mol), which is incorporated into the backbone. $X_{organic}$ represents the mass fraction of the CHNO elements. Based on these values, the degree of substitution was calculated to be 2.46.

Table S1. Organic elemental composition and DS of HEC-QA.

Sample	N (%)	C (%)	H (%)	O (%)	DS[a]
HEC-QA	7.24	33.47	6.26	21.86	2.46

[a] $DS=M_{HEC}*X_N\% / (X_{organic}\%*M_N-(M_{BET}-M_{H_2O})*X_N\%)$

Elution curve of the polymer obtained by HEC-QA catalysis

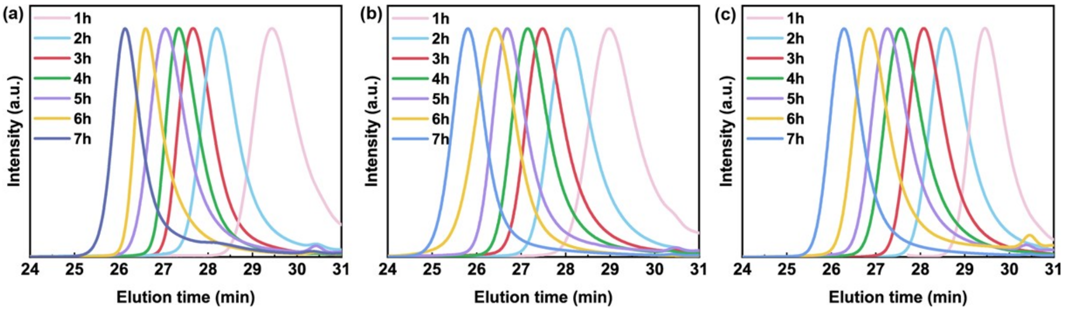

Figure S4. GPC traces of polymers synthesized with (a) 5 mg, (b) 10 mg, and (c) 15 mg of HEC-QA under white LED irradiation.

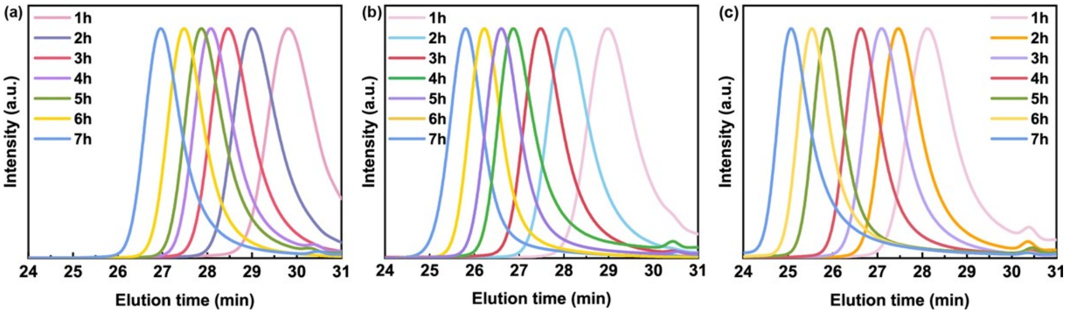

Figure S5. GPC traces of polymers with target degrees of polymerization of (a) 100, (b) 200, and (c) 400, synthesized using HEC-QA under white LED irradiation.

Catalyst Recyclability Experiment

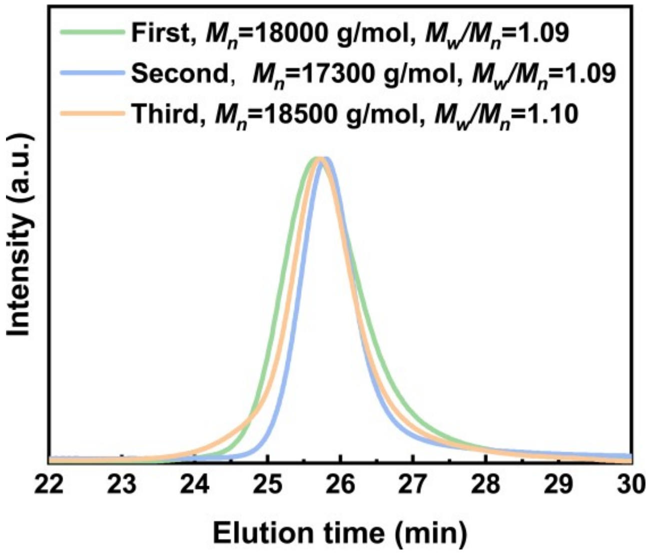

Figure S6. GPC traces of polymers collected from successive catalytic cycles.

Table S2. Bulk polymerization of methyl methacrylate (MMA) using recycled HEC-QA.

Cycle	Catalyst mass (mg)	Conv. (%)	M_n ($M_{n,theo}{}^b$)	*Đ*	K_p^{app} (h^{-1})	Catalyst recovery yield (%)
1	10	86.15	18000(17300)	1.09	0.282	89.98
2	10	84.67	17300(16900)	1.09	0.269	87.14
3	10	85.31	18000(17100)	1.11	0.274	87.61

Monomer Scope Exploration

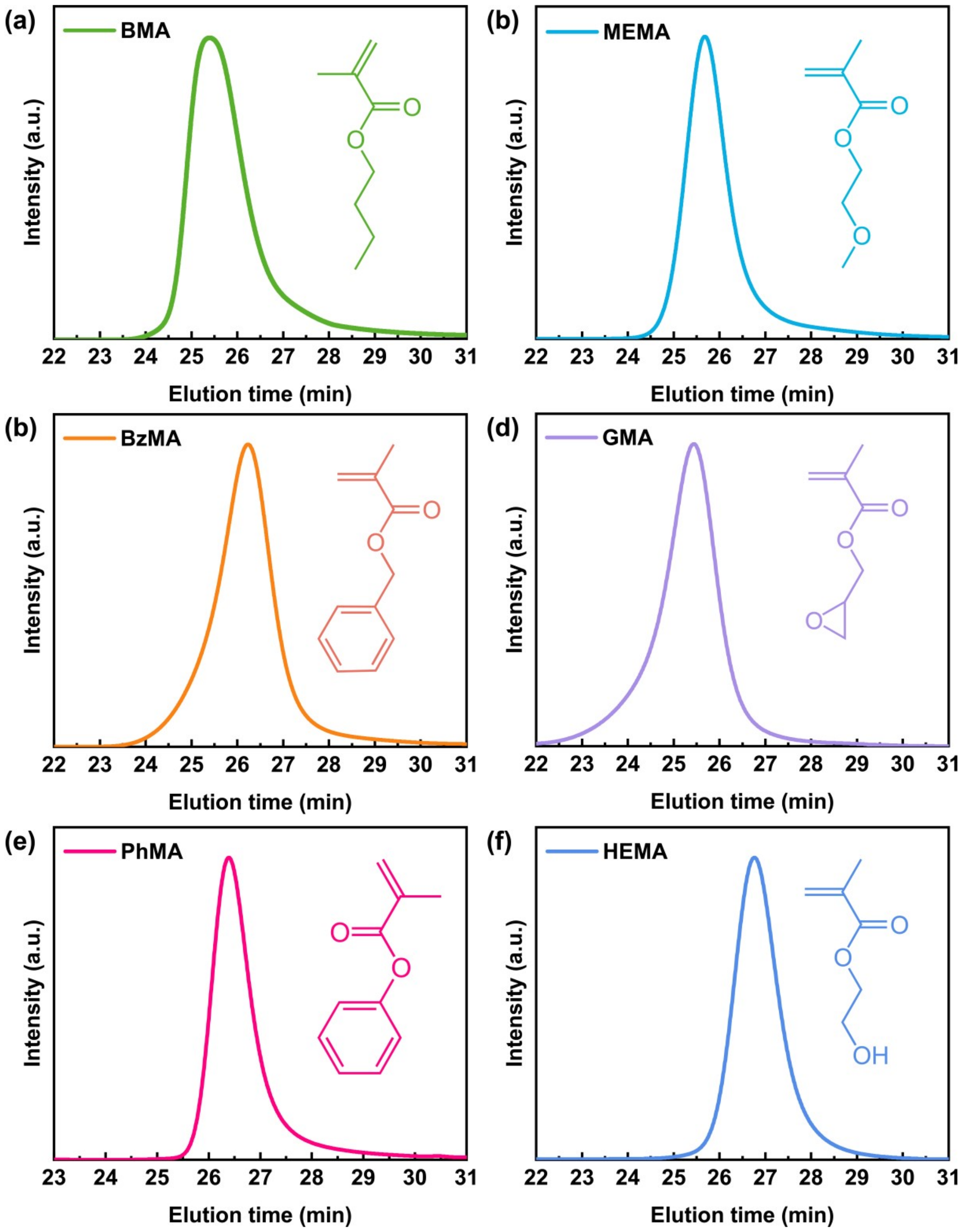

Figure S7. GPC molecular weight distribution curves of polymers obtained from reversible complexation-mediated polymerizations with different monome

Polymerization under monochromatic LEDs

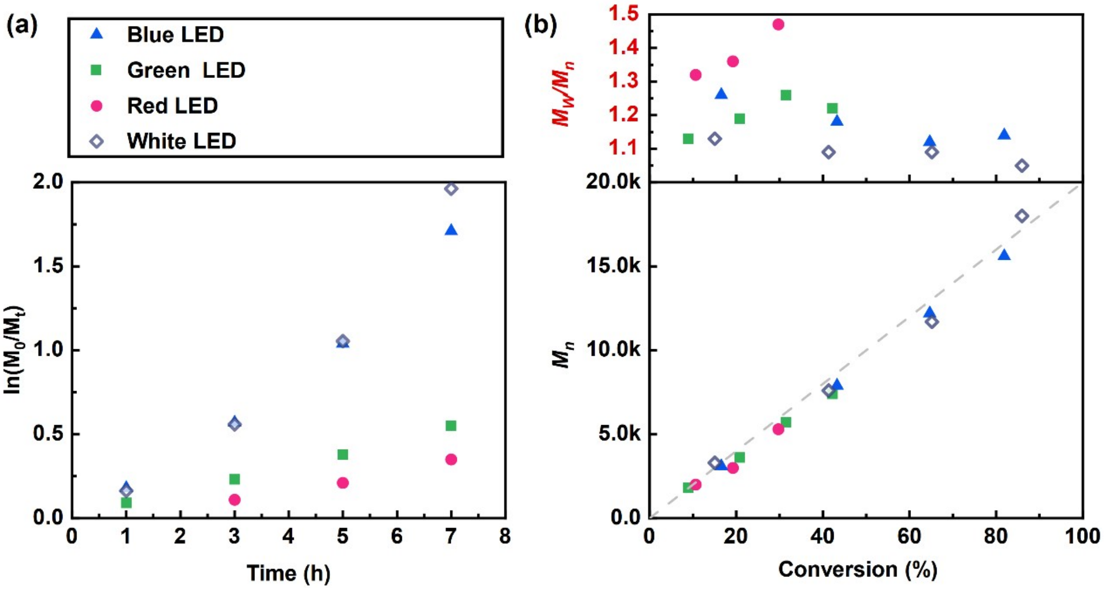

Figure S8. Red, green, and blue LED-mediated polymerization of MMA/Eph-I/HEC-QA ($[MMA]_0$ = 18.9 mmol; $[Eph\text{-}I]_0$ = 0.0945 mmol; $[HEC\text{-}QA]_0$ = 10 mg) at a light intensity of 15 mW/cm^2: (a) Kinetic plots of $\ln([M]_0/[M]_t)$ vs time; (b) Evolution of M_n and $Đ$ with conversion.

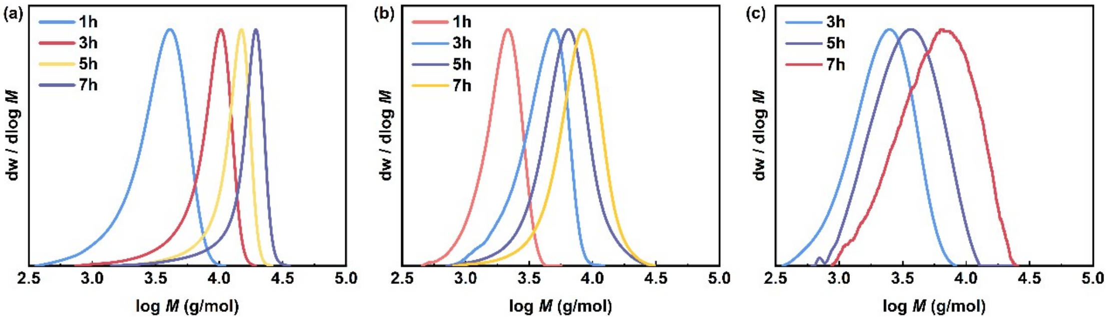

Figure S9. GPC normalized molecular weight distribution trace of polymers obtained from HEC-QA-mediated MMA polymerizations under different monochromatic LEDs (15 mW cm^{-2}): (a) blue light, (b) green light, (c) red light.

Polymerization under different white light intensities.

To study the effect of white light intensity on the catalytic polymerization kinetics of MMA by HEC-QA, we further employed a CEL-PCRD300-12 photochemical reactor, enabling precise control of light intensity at 65, 132, and 258 mW/cm², with the current adjusted to 175, 350, and 700 mA accordingly. Our initial polymerization experiments were performed using a 15 mW/cm^2 LED strip wrapped around the reaction vessel, which provided efficient and scalable photocatalytic polymerization. It should be noted that due to differences in light source geometry and irradiation area between the two setups, the power values are not directly comparable across the two systems. Nevertheless, both sets of experiments consistently demonstrate that the HEC-QA catalyst remains effective across a broad range of light intensities.

Results and Discussion:

As shown in Figure S10 and 11, increasing light intensity significantly accelerated the polymerization rate. At all three light intensities, the polymerizations exhibited controlled characteristics: molecular weights increased linearly with monomer conversion, and dispersities remained narrow ($Đ < 1.2$), indicating that polymerization controllability is well maintained across the investigated light intensity range.

These results demonstrate that the HEC-QA catalyst effectively catalyzes polymerization across a broad range of light intensities, with polymerization rates increasing as a function of light intensity, underscoring the robustness of the system.

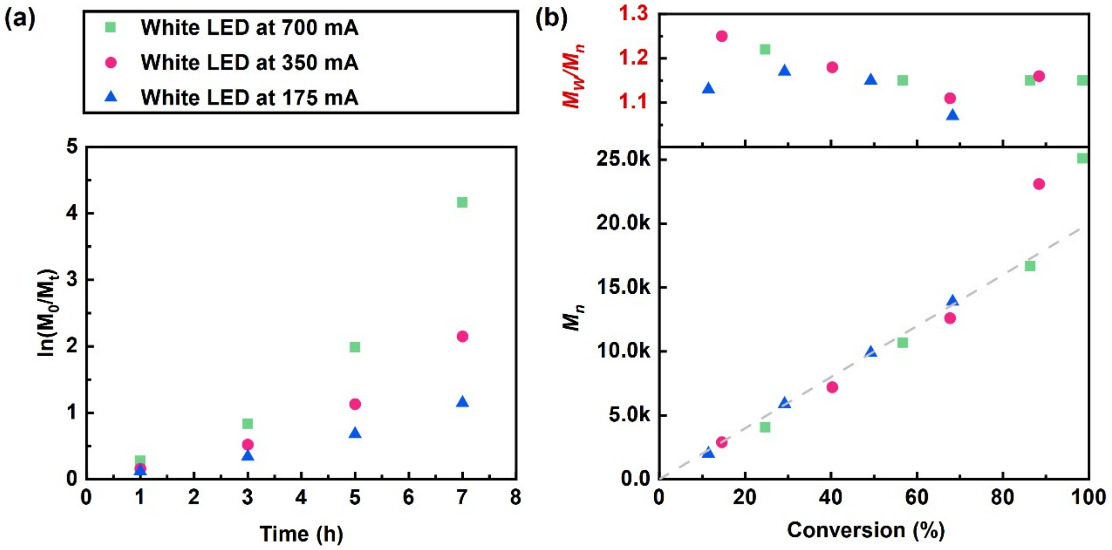

Figure S10. Polymerization of MMA/Eph-I/HEC-QA ($[MMA]_0$ = 18.9 mmol; $[Eph\text{-}I]_0$ = 0.0945 mmol; $[HEC\text{-}QA]_0$ = 10 mg) under different white light intensities: (a) Kinetic plots of $\ln([M]_0/[M]_t)$ vs time; (b) Evolution of M_n and $Đ$ with conversion.

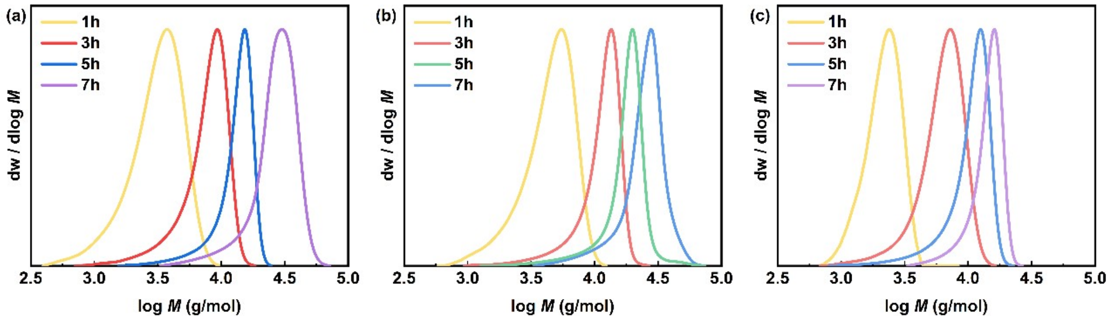

Figure S11. GPC normalized molecular weight distribution trace of polymers prepared by HEC-QA mediated MMA polymerization under different light intensities: (a) 175 mA, (b) 350 mA, (c) 700 mA.

Blank Control Experiments for RCMP of MMA Using HEC-QA as Photocatalys.

As shown in Table S3, in the absence of the alkyl iodide initiator (Entry 1), negligible monomer conversion (<1%) was observed, confirming that the initiator is essential for radical generation. In the absence of the HEC-QA photocatalyst (Entry 2), only trace polymerization occurred after 7 h, yielding a low molecular weight polymer (M_n = 820 g/mol) with a broad dispersity ($Đ$ =2.7). This indicates that without the catalyst, the polymerization is uncontrolled and inefficient, consistent with background thermal polymerization or direct light-induced initiation.

Table S3. Blank Control Experiments for HEC-QA-Catalyzed RCMP of MMA.[a]

Entry	HEC-QA (mg)	Eph-I (mmol)	Time (h)	Conversion (%)	M_n (g/mol)	$Đ$
1	10	0	7	< 1	n.d.[b]	n.d.
2	0	0.0945	7	< 5	820	2.7

[a] Reaction conditions: $[MMA]_0$ = 18.9 mmol, white LED (15 mW/cm^2).

[b] n.d. = not determined due to very low conversion.

Reaction Conditions for MMA Polymerization under Sunlight Irradiation.

The experiment was conducted on July 19, 2024, at the coordinates 26°4'2" N, 119°11'31" E (Fuzhou, China), with solar radiation data obtained from a publicly accessible historical weather database for the Fuzhou region. These data provide a quantitative reference for the sunlight-driven polymerization conditions and further demonstrate the practical applicability of our HEC-QA catalyst under natural sunlight.

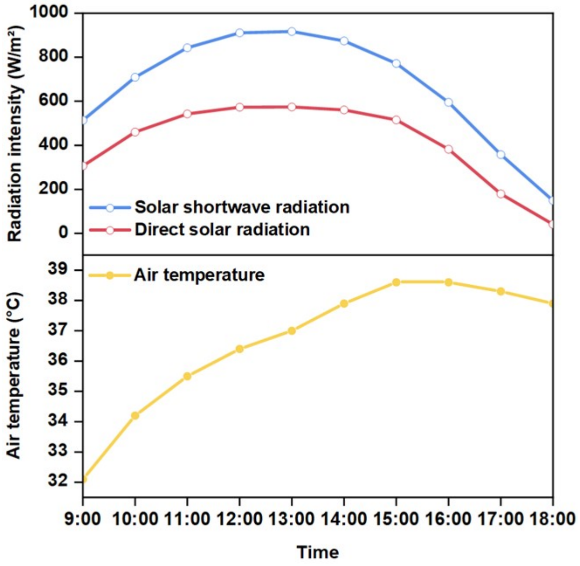

Figure S12. Air mbient temperature and solar radiation intensity recorded during the sunlight polymerization experiment (10:00 – 18:00).

^{1}H NMR spectrum (in $CDCl_3$) of iodine capped polymethyl methacrylate (PMMA-I)

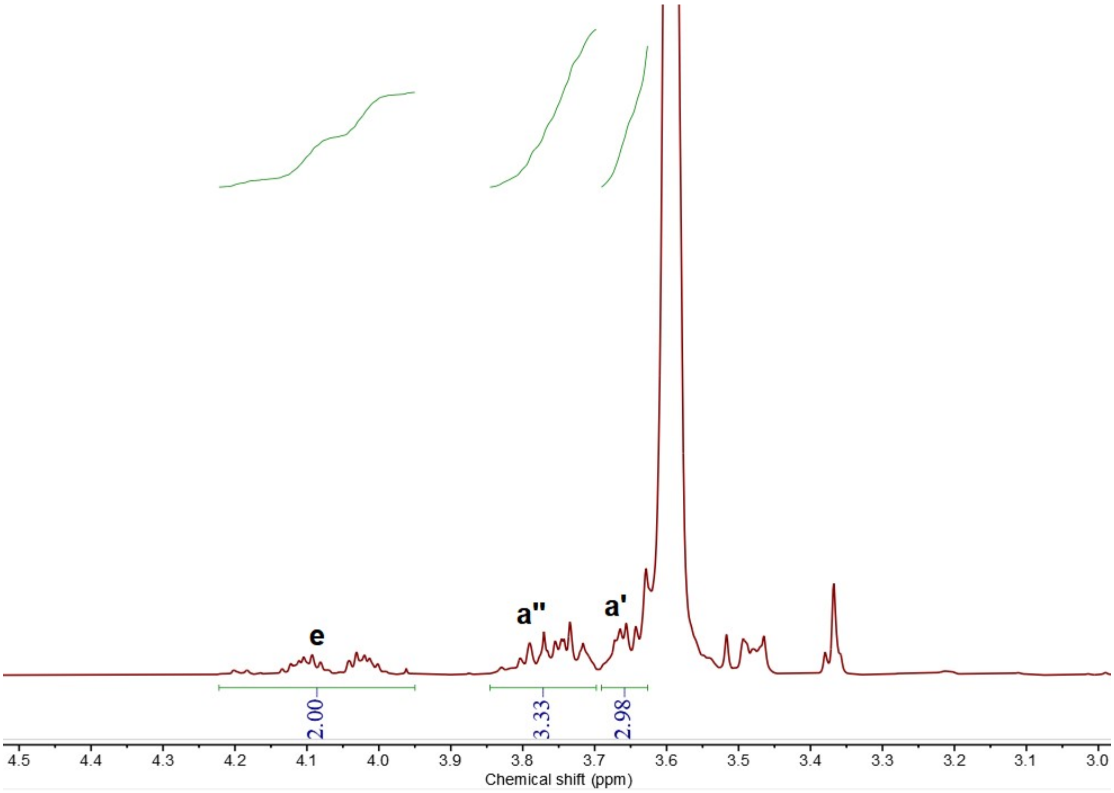

Figure S13. ^{1}H NMR spectrum (in $CDCl_3$) of iodine capped polymethyl methacrylate (PMMA-I)

The chain-end fidelity was calculated based on the integral of the ω-terminal methyl proton signal (a′), using the equation: chain-end fidelity = $(I_a'/3) \times 100\% = 2.98/3 = 99.3\%$, as detailed in Figure S13.