

Supporting Information:
**Phosphonium tetraphenylborate: A Photocatalyst for
Visible-Light induced, Nucleophile-initiated Thiol-Michael
Addition Photopolymerization**

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Experimental Section

Materials:

Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) was purchased from Bruno Bock. Divinyl sulfone (DVS), polyethyleneglycol diacrylate ($M_n = 575$), butyl 3-mercaptopropionate, 1-hexanethiol, methyl thioglycolate, butyl acrylate, triethylamine (TEA), methyldiphenylphosphine (MDPP), 2-Isopropylthioxanthone (ITX), 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO), sodium tetraphenylborate (NaBH_4), were purchased from Sigma-Aldrich. All chemicals were used as received.

Characterization methods

Light source: 405 nm LED light (Thorlabs) was used as the induction light to initiate the photo reactions/ polymerizations. The light intensity was determined with a visible light profilometer. In model reaction experiment, Acticure 4000 mercury lamp with a 400-500 nm bandpass filter was used.

Ultraviolet-Visible Spectroscopy (UV-Vis): UV-Vis absorption experiments were performed on UV-Vis spectrophotometer (Thermo-Fischer Scientific) and PMMA cuvettes (1 cm light path lengths) were used during the measurements. Absorbance data was collected in absorbance mode with a bandwidth of 2 nm and a scan speed of 240 nm/min.

Real-time Fourier Transform Infrared Spectroscopy (FT-IR): All photopolymerization kinetics were measured on FT-IR, Nicolet 670. The polymer precursors were between two glass slides with 0.050 mm thickness spacers. The consumptions of the acrylate, vinyl sulfone and thiol moieties were measured by monitoring the corresponding IR peak area decreasing at 790 cm^{-1} , 3100 cm^{-1} , 2560 cm^{-1} , respectively. The real-time functional group conversion was calculated by the ratio of peak area to the peak area prior to the reaction.

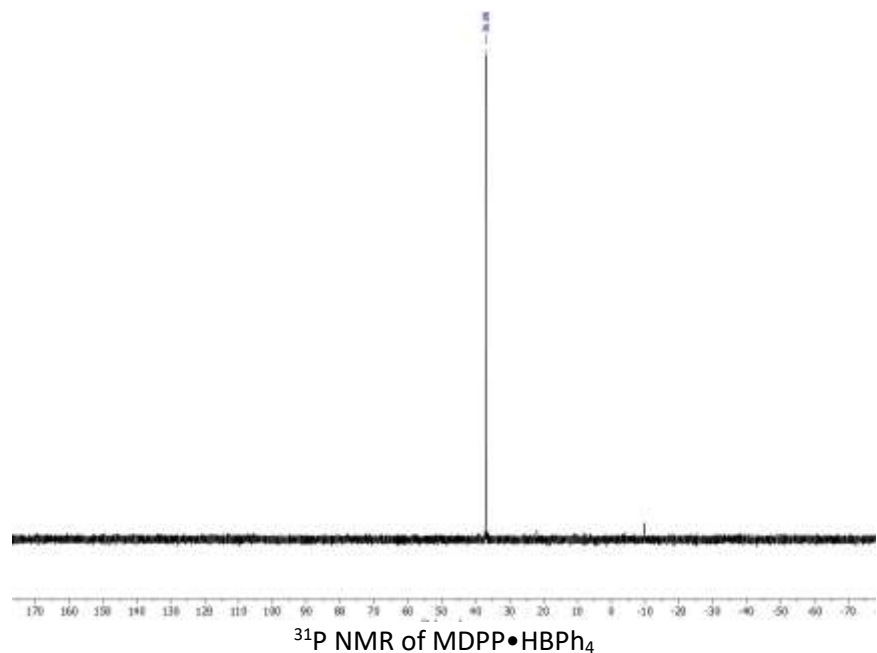
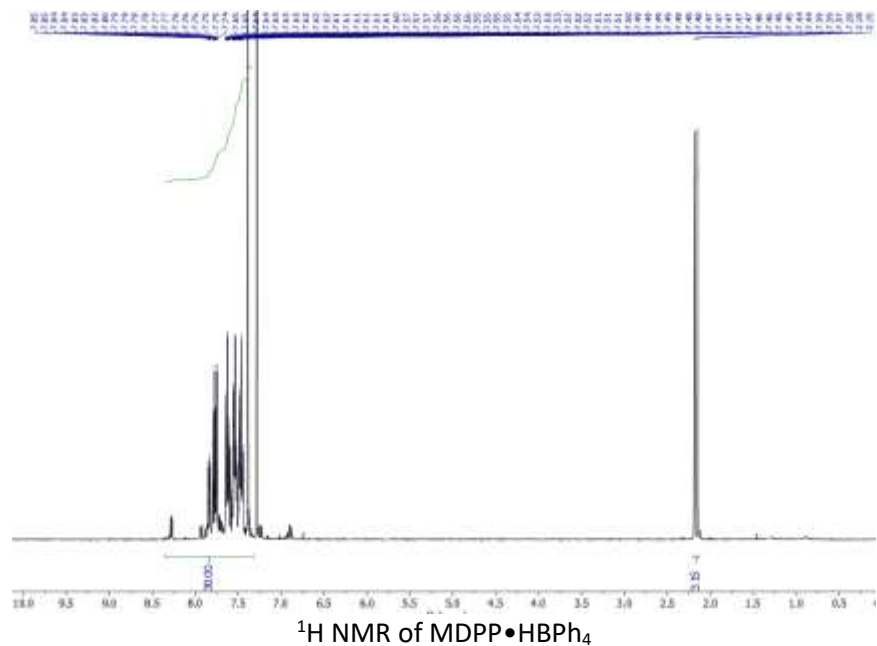
Dynamic Mechanical Analysis (DMA): thermomechanical property of the photocured polymer films were measured using TA Instruments Q800 dynamic mechanical analyzer. The PETMP/DVS resins were prepared by injecting between two glass sides with 0.45 mm thickness spacers. The sample was exposed to 400-500 nm light for 20 minutes, followed by post-curing at $80\text{ }^\circ\text{C}$ for one hour. For T_g and elastic modulus measurements, the temperature was ramped at $3\text{ }^\circ\text{C}/\text{min}$ with a frequency of 1 Hz. The glass transition temperature (T_g) was determined by the temperature at the peak of the $\tan \delta$ curve.

MDPP•HBPh₄ synthesis and purification

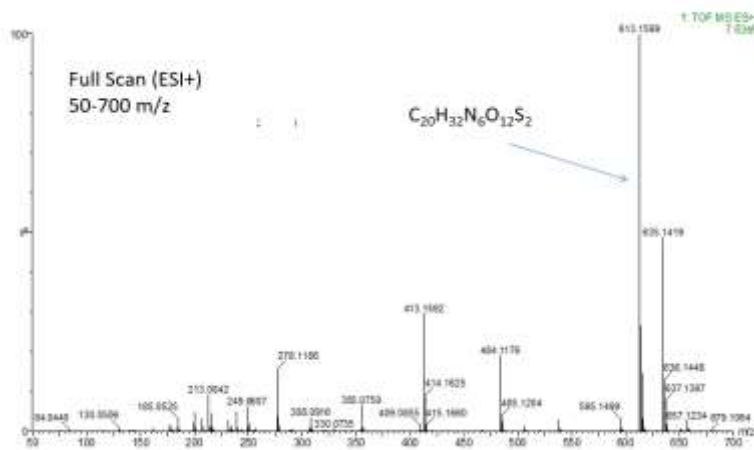
The methyldiphenylphosphine (10 mmol) was firstly dissolved in 10 mL 10% HCl (aq), and then, a slight excess of NaBPh_4 solution (12 mmol) in 10 mL water was slowly added. White precipitate appeared during the NaBPh_4 addition. After 2 hours of reaction, the precipitate of the salt was

filtered, and washed several times with water followed by last washing of trace amount of methanol. The product was then dried and kept under vacuum condition to avoid the potential oxidation.

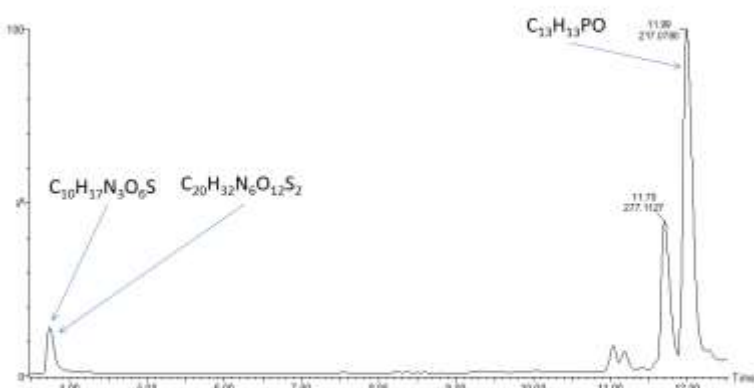
Methyldiphenylphosphium tetraphenylborate (DMPP·HBPh₄): white solid (yield 87%); ¹H NMR (300 MHz, CDCl₃) δ 2.17 (d, 3H), 7.17 (m, 30H); ¹³P NMR (300 MHz, CDCl₃) δ 36.88.



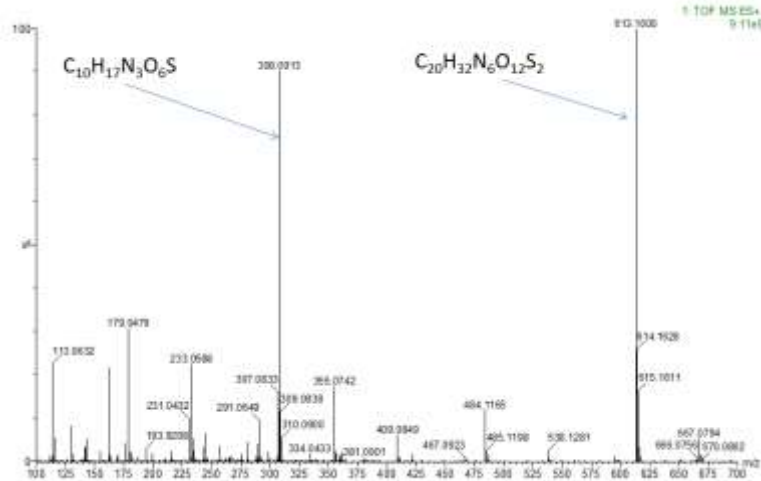
Supporting Data



MS (ESI+) of glutathione disulfide (GSSG)



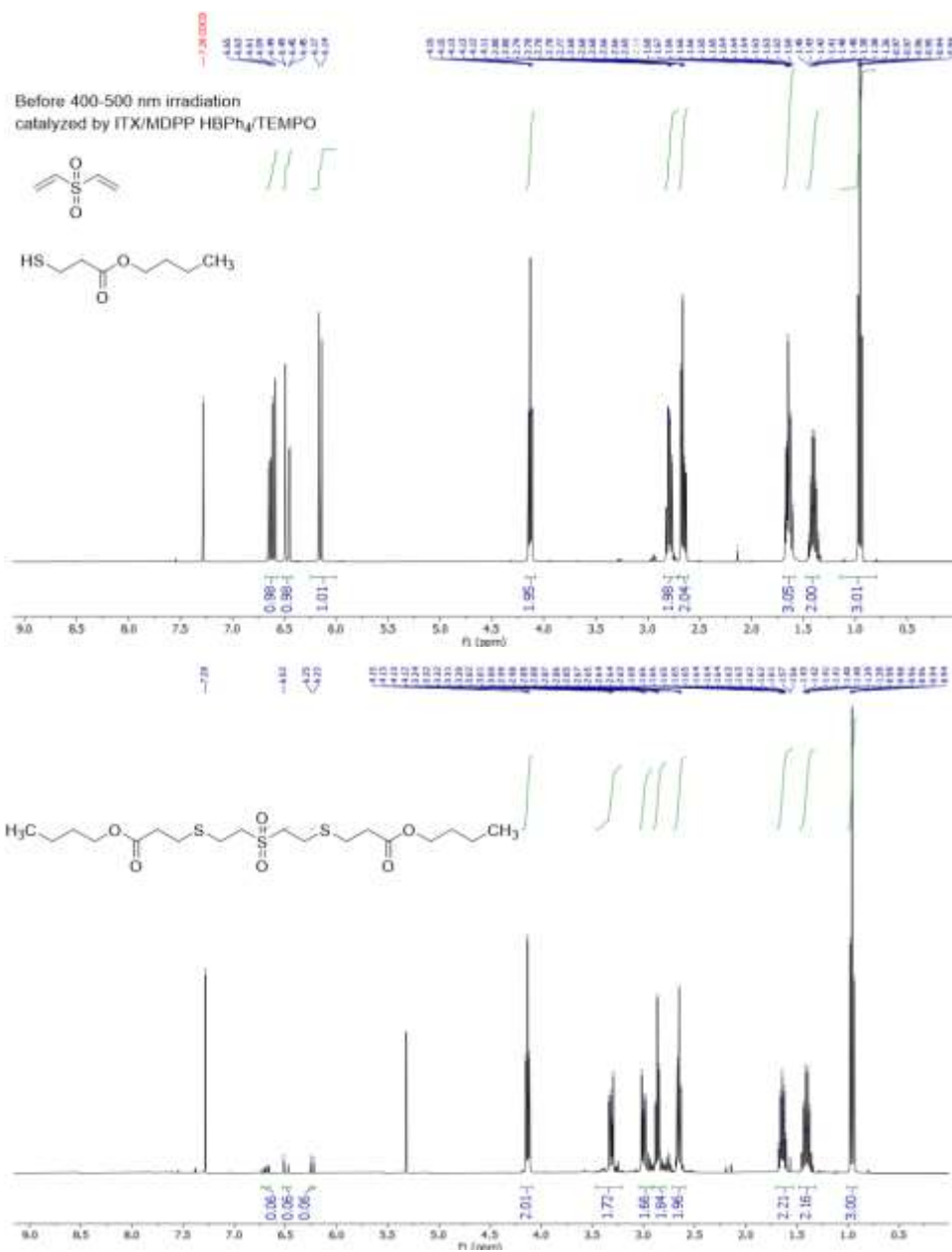
Chromatogram of oxidized glutathione (GSSG) reduced by ITX/MDPP•HBPh₄

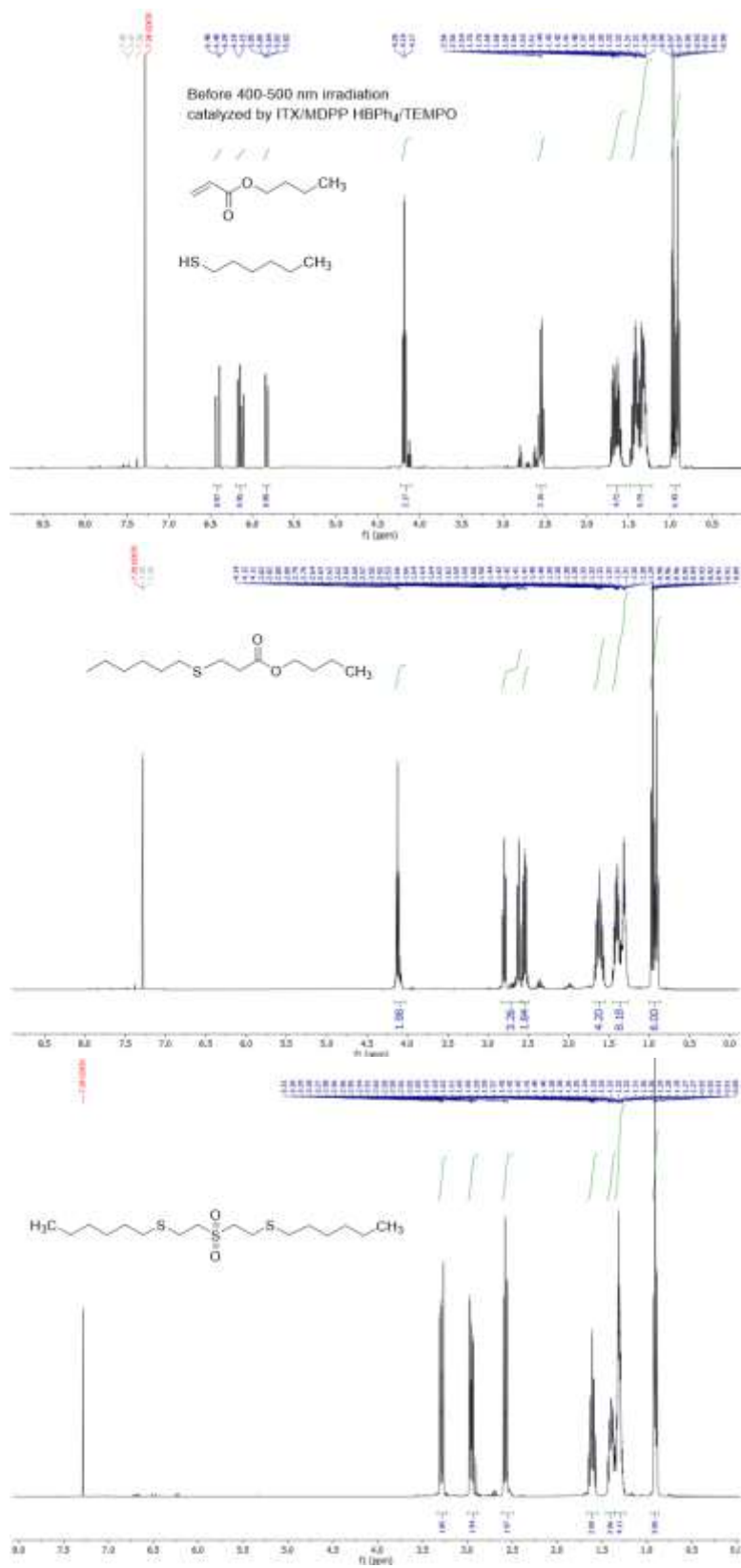


MS (ESI+) measured at 3.7 minute retention time in LC-MS

Figure S1. Chromatogram of glutathione disulfide (GSSG, red trace) reduction using ITX/MDPP•HBPh₄. After 405 nm LED light exposure, the generation of reduced glutathione (C₁₀H₁₇N₃O₆S, GSH) was observed in the LC-MS experiment. **Experiment procedure:** All GSSG reduction reactions were performed in N₂ glove box. 0.3 mM solution of GSSG in water. 0.15 mM ITX and 0.3mM MDPP•HBPh₄ in methanol was added into GSSG solution. The mixture was then stirred and irradiated with a 405 nm LED (10 minutes,

20 mW/cm²). After the reaction, the mixture was extracted with dichloromethane and aqueous phase was analyzed by analytical LC-MS (C18 reversed phase column). (eluting solvent: 0-15 min: 95% water, 5% methanol; 15 min: 50% water, 50% methanol).





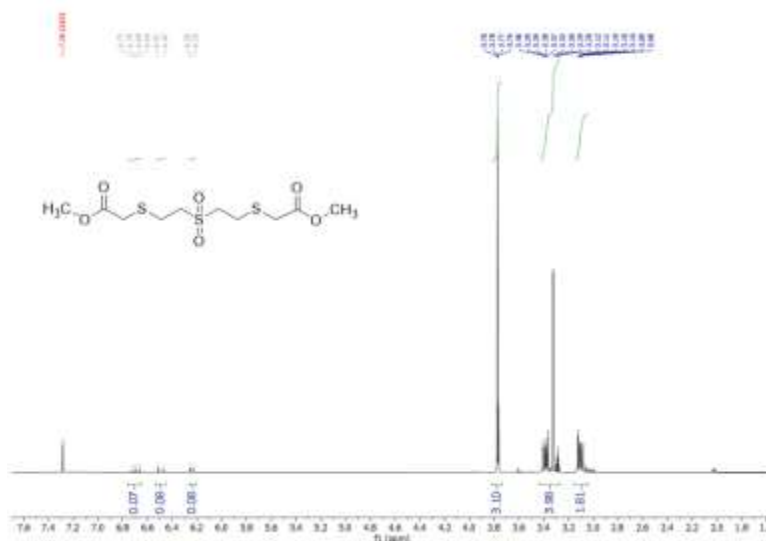


Figure S2. ^1H -NMR results measured for thiol-Michael model reaction. **Experiment procedure:** butyl acrylate, divinyl sulfone, mono-functional thiols and the photoinitiator, ITX/MDPP•HBPh₄/TEMPO were well mixed. After injecting the mixture between two glass slides, the sample was irradiated with 400-500 nm, 40 mW/cm² light. After the photoreaction, the mixture was dissolved in CDCl₃ to do ^1H -NMR. The amount of vinyl residue can be determined by integrating the corresponding peak (around 6.2-6.7 ppm) and calculating the ratio. (**Table 1**)

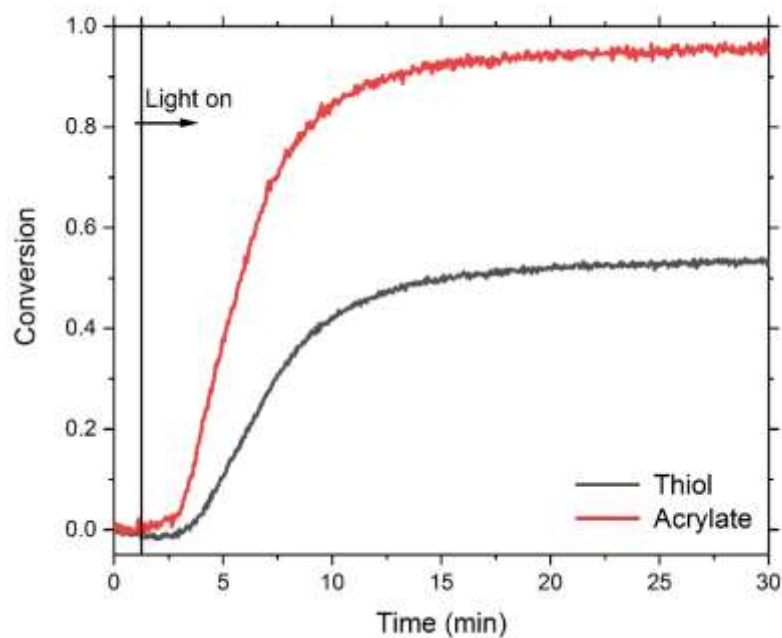


Figure S3. Conversions of thiol and vinyl moieties as a function of reaction time in TEA ITX/TEA·HBPh₄/TEMPO (1/2/2 wt %) catalyzed thiol-acrylate reaction in PETMP and PEGDA (M_n=575). The sample was irradiated with 405 nm, 40 mW/cm² LED light. A relatively slow polymerization kinetics and off-stoichiometric thiol-acrylate reaction was observed, indicating the photocaged weak nucleophiles are less reactive towards the thiol-Michael photopolymerization.

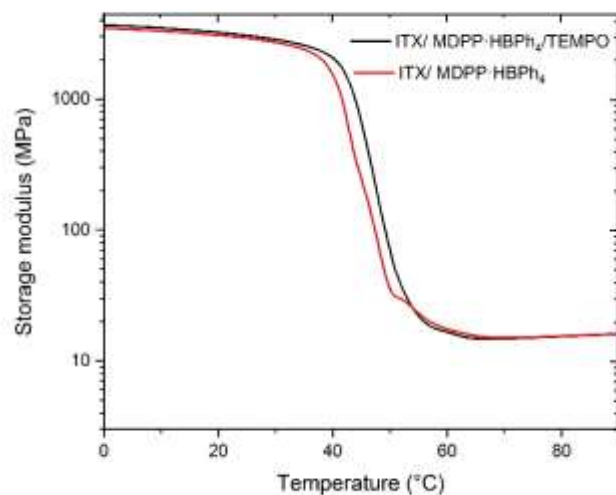


Figure S4. The storage modulus of PETMP/DVS polymer film photocured by ITX/MDPP·HBPh₄ and ITX/MDPP·HBPh₄/ TEMPO. The sample was irradiated with 405 nm, 40 mW/cm² LED light. The storage modulus of the polymer materials photocured by ITX/MDPP·HBPh₄ and ITX/MDPP·HBPh₄ TEMPO was similar. However, one major issues of the off-stoichiometric reaction and heterogeneous polymer is the reduced long-time stability and the biocompatibility.