

Electronic Supplementary Information (ESI) for Polymer Chemistry

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**Supramolecular Polymeric Photoinitiator with Enhanced Dispersion
in Photo-curing Systems**

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Experiment

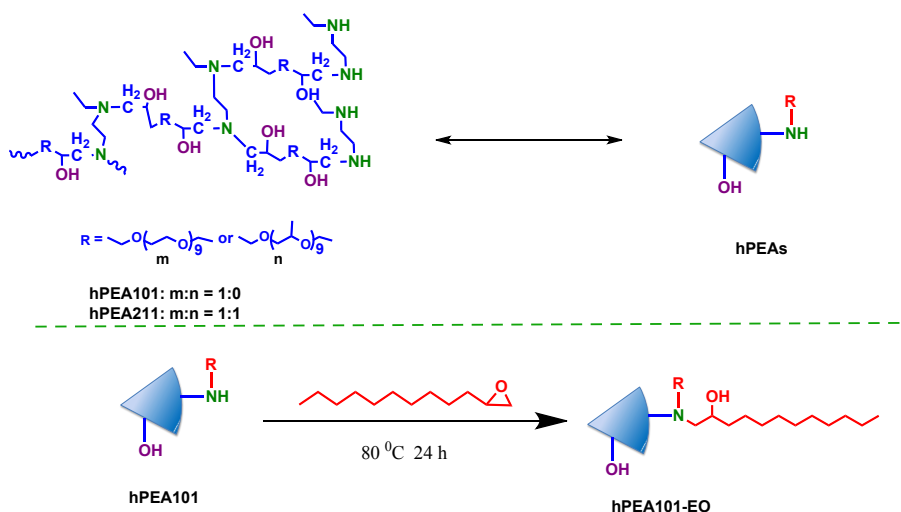
Materials

Hyperbranched poly(ether amine) (hPEA101 and hPEA211) were synthesized according to the previous reports.^{1, 2} Acrylamide (AM), triethanolamine (TEOA), ethanol, toluene and methyl methacrylate (MMA) (from Sinopharm Chemical Reagent), ethyl bromoacetate and poly(ethyleneimine) (PEI, Mw = 10000) (from Adamas), 1,2-Dodecylene Oxide (EO) and 1,6-Hexanediol diacrylate (HDDA) (from Alfa Aesar), 2-Hydroxy-4-(2-Hydroxyethoxy)-2-Methylpropiophenone (I2959) and trimethylolpropane triacrylate (TMPTA) (from Siegwerk Shanghai LTD). Jeffamine L100 (from Hustman Company), ethoxylated phenoxyl acrylate (EM2103) (from Changxing Chemical Company), 2-ethyl ester-thioxanthene (ETX), 9H-Thioxanthene-2-carboxylic acid (CTX), [(9-oxo-9H-thioxanthen-2-yl)oxy]acetic acid (ATX), 4-methyl-[(9-oxo-9H-thioxanthen-2-yl)oxy]acetic acid (MATX) and 3-(Carboxymethoxy)benzophenone (ABP) (Hitachi Chemical provided). All of the reagents were used as received.

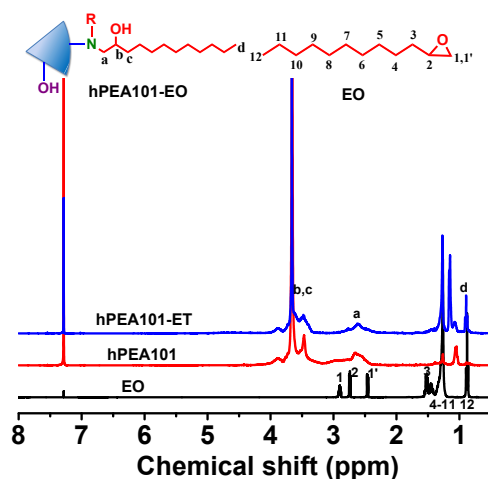
Synthesis of hyperbranched Poly (ether amine) hPEA101-EO.

hPEA-EO was synthesized according to **Scheme S1**. hPEA101 (5.88 g, 0.01

mol), 1,2-Dodecylene Oxide (EO) (2.76 g, 0.015 mol) and 100 ml ethanol was added into a 250 ml of three-necked flask under nitrogen atmosphere and stirred at 80 °C for 24 h. After cooling at the room temperature, the reaction system was precipitated for three times in hexane. After filtered and dried at 60 °C for 12 h at vacuum oven. The structure of hPEA101-EO was confirmed by both ¹H NMR and FT-IR spectra successfully in **Figure S1**.



Scheme S1. Synthesis process of hPEA101-EO



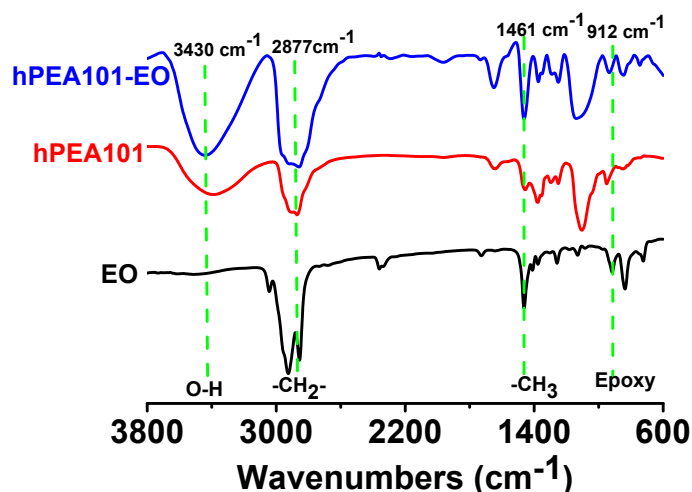


Fig. S1 ¹H NMR and FT-IR spectra of hPEA101, EO and hPEA101-EO.

Instruments and methods

Physicochemical measurements

The concentration of hyperbranched poly (ether amine) (hPEA)-based supramolecular photoinitiator system (hPEA@TX and hPEA@BP) are in terms of TX or BP moieties in all measurements. Nuclear magnetic resonance (¹H NMR) spectra were carried out on a Mercury Plus 400 MHz spectrometer with CDCl₃ as the solvent at room temperature. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by a Perkin–Elmer Paragon1000 FTIR spectrometer and the samples were prepared as KBr disc. UV-Visible Spectrophotometer (UV-*vis*) spectra were carried out by Shimadzu UV-2550 spectrophotometer in aqueous solution. Fluorescence spectra (FL) were conducted on Perkin–Elmer LS50B luminescence spectrophotometer and Fluorescence lifetime (FLT) was recorded by PTI(USA) QM/TM/IM Steady-State & Time-Resolved Fluorescence Spectrofluorometer. Electron spin resonance (ESR) were conducted on Magnetech's MiniScope MS-5000 with 365nm UV LED irradiation for 60 s at room temperature and the radicals were trapped by 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO). Steady state photolysis experiments is that photoinitiators were irradiated with the 365 nm UV LED bulb in aqueous solution, and the UV-*vis* spectra were carried out by the Shimadzu UV-2550 spectrophotometer at different irradiation times. Transmission Electron Microscopy

(TEM) images were checked using a JEM-2100 (JEOL Ltd., Japan) microscope operated at 200 kV and the samples were prepared by dropping the solution onto a copper grid and dried for 24h..

Results and discussion

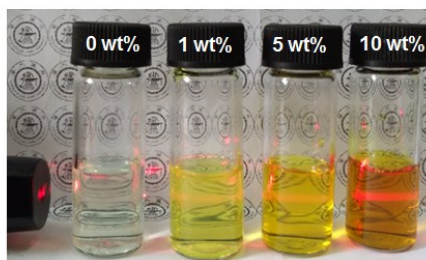


Fig.S2 color change and tyndall effect resulting from hPEA101@ATX by different concentration of hPEA101 from 0 wt%, 1 wt%, 5 wt% to 10 wt% in saturated photoinitiator (ATX) aqueous solution.

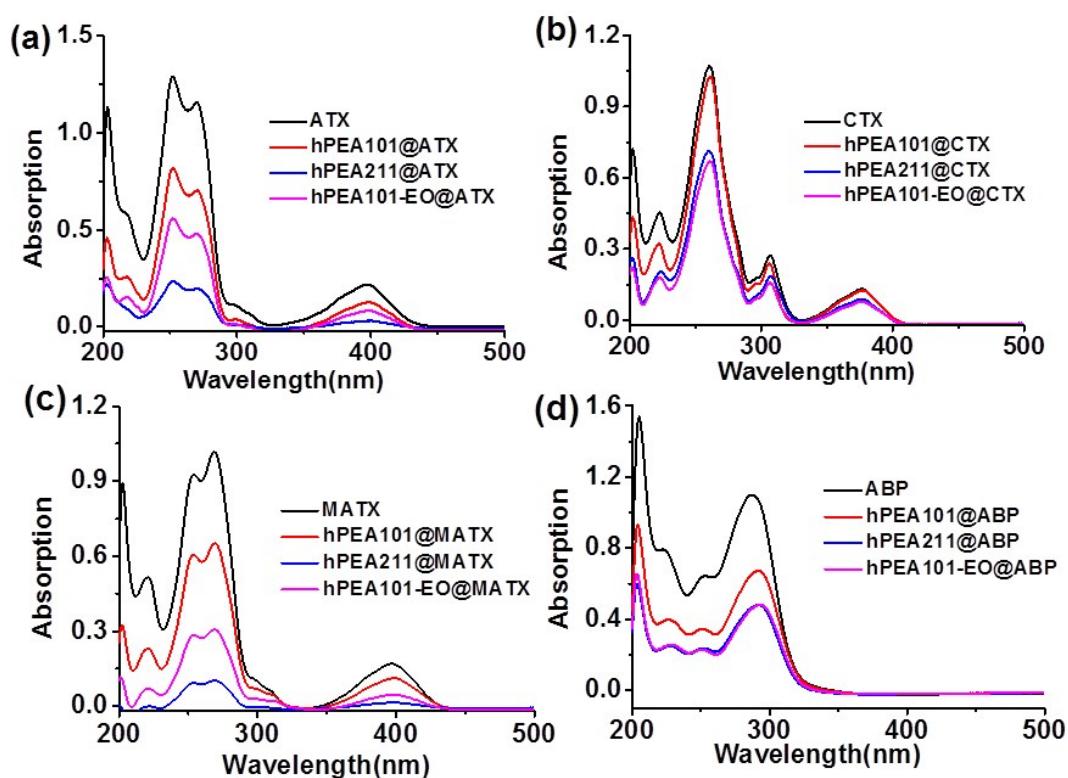


Fig.S3 UV-*vis* spectra of hPEA@PI saturated aqueous solution after being diluted 500 times by ethanol. Standard sample concentration: [ATX] = 0.01 mg/ml, [ABP] = 0.01mg/ml, [CTX] = 0.005 mg/ml and [MATX] = 0.02 mg/ml in ethanol solution.

Table S1 The solubility of ATX, CTX, MATX and ABP in aqueous solution.

Photoinitiators	ATX	CTX	MATX	ABP
Solubility(mg/ml)	0.05	0.004	0.06	0.10

Table S2 Encapsulation efficiency of hPEA101(1wt%), hPEA101(5 wt%) and hPEA101(10 wt%) for ATX in saturated aqueous solution.

hPEA101	1 wt%	5 wt%	10 wt%
ATX(%)	28.3	32.7	58.8

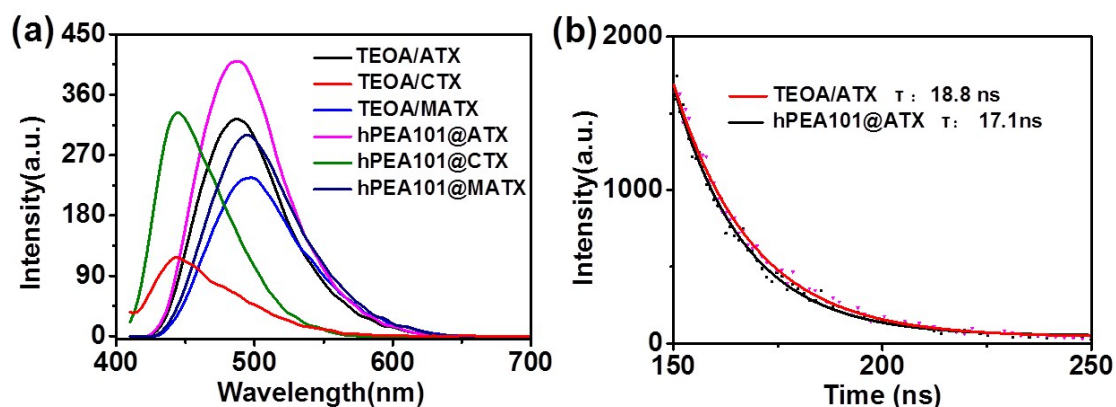


Fig.S4 (a) fluorescence spectra of photoinitiators and (b) fluorescence lifetime of hPEA101@ATX and TEOA/ATX in aqueous solution. (the concentration is 2.5×10^{-5} mol/L in terms of TX moiety).

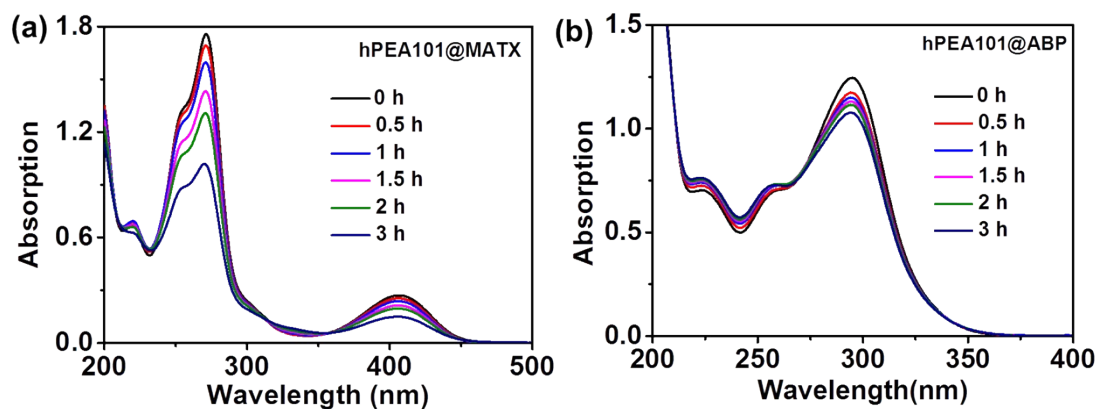


Fig.S5 The dependence of UV-vis spectra of (a) hPEA101@MATX and (b) hPEA101@ABP aqueous solution on 365 nm UV irradiation time.

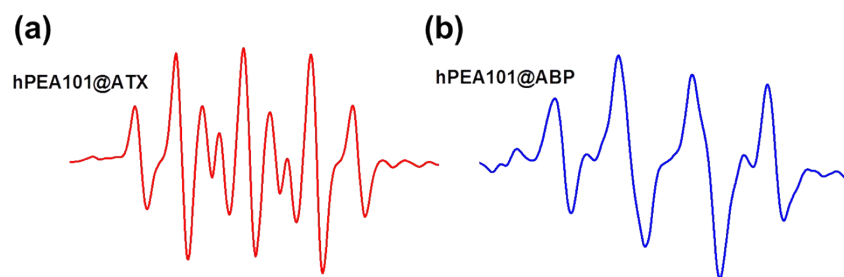


Fig.S6 ESR spectra of hPEA101@ATX (a) and hPEA101@ABP (b) in aqueous solution, photolysis time 1 min under the UV lamp of 365 nm. [PI] is 1.0×10^{-3} M in terms of TX or BP moiety.

References

1. B. Yu, X. Jiang, R. Wang and J. Yin, *Macromolecules*, 2010, **43**, 10457-10465.
2. B. Yu, X. Jiang, G. Yin and J. Yin, *J. Polym. Sci. Pol. Chem.*, 2010, **48**, 4252-4261.