Efficient Preparation of Polyoxometalate-Junctional Cross-Linking Hybrid Nanocomposites by Polymerization-Induced Self-Assembly

Zhibo Zheng,‡[ab] Peiyao Yu,‡[a] Rong Wang,[a] Junyan Tan,[a] Jie Zhang*[a] and Xinhua Wan[a]

[a] Beijing National Laboratory for Molecular Science, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.
[b] School of Chemistry and Chemical Engineering, Ankang Research Centre of New Nano-materials Science and Technology, Ankang University, Shaanxi Ankang 725000, China.

*To whom correspondence should be addressed.
E-mail: jz10@pku.edu.cn (J. Z.)

1. Material and methods

All chemicals were used as received unless otherwise noted. 2-Hydroxypropyl methacrylate (HPMA) was purchased from J&K Scientific Ltd. This monomer comprises an isomeric mixture of 75 mol% HPMA and 25 mol% 2-hydroxyisopropyl methacrylate. 2,2'-Azobis(2-methylpropionamide) dihydrochloride (V-50) was also purchased from J&K Scientific Ltd. Methoxypolyethylene glycols (Mn∼2000 or 5000) were purchased from Sigma-Aldrich. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP) was synthesized according to a literature protocol.[1]

1.1 Synthesis of *N*-ethyl-2-(methacryloyloxy)-*N,N*-dimethylethan-1-aminium bromide (EMDA)

In a flask equipped with a stirrer, thermometer, and reflux condenser, 3.14 g (0.02 mol) freshly distilled dimethylaminoethyl methacrylate containing a little hydroquinone was reacted with 2.18 g (0.02 mol) ethane bromide in 40 mL acetone at 40°C for 20 h. After removal of acetone, anhydrous ether was added, and the precipitated solid was filtered and recrystallized repeatedly in dry ethyl acetate. Yield was 60%. [1] H NMR (CDCl$_3$, ppm): 6.15 (s, 1H, C*H*=C), 5.68 (s, 1H, C*H*=C), 1.95 (s, 3H, C=CC*H$_3$*), 4.66 (s, 2H, COOC*H$_2$*), 4.16 (s, 2H, COOCH$_2$C*H$_2$*), 3.51 (s, 6H,

N(C*H₃*)₂), 3.83 (t, 2H, NC*H₂*), 1.47 (t, 3H, NCH₂C*H₃*).
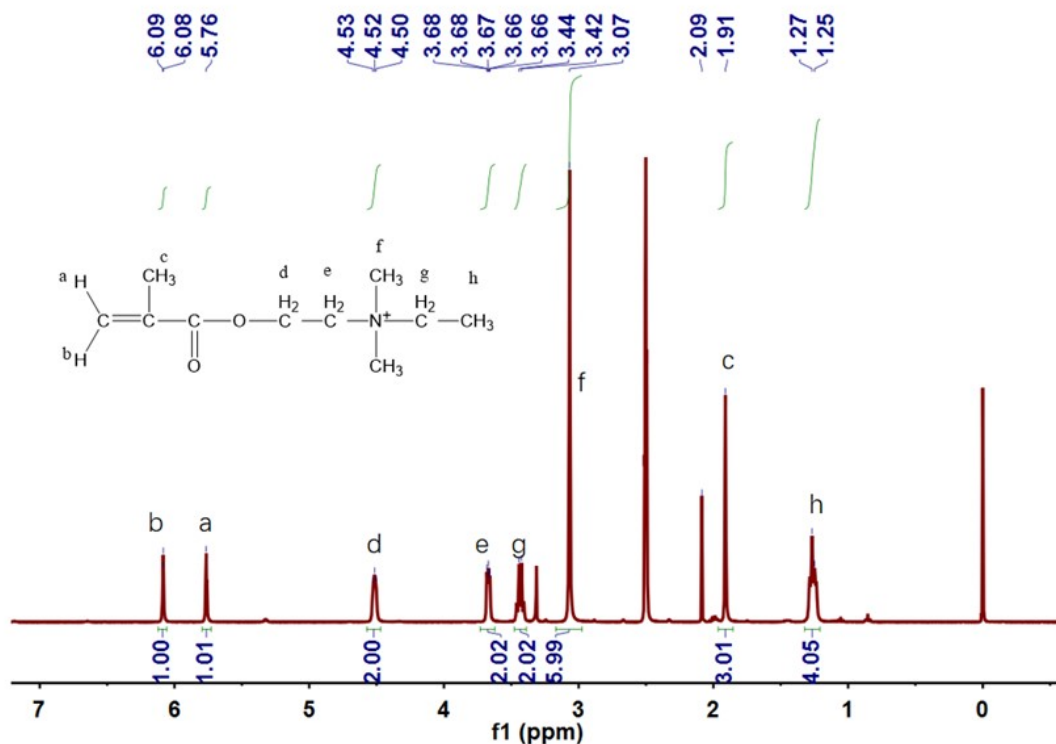
Figure S1. 400 MHz ^{1}H NMR spectra of EMDA recorded in DMSO-d_6.

1.2 Synthesis of PEG macro-CTAs

PEG macro-CTAs were prepared by the condensation of DMP and methoxypolyethylene glycols (Mn∼2000 or 5000). For the synthesis of PEG$_{113}$-DMP, methoxypolyethylene glycols (PEG$_{113}$, Mn∼5000, 5.0 g, 1 mmol), 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 1.2 g, 6 mmol)，4-dimethylaminopyridine (DMAP, 74 mg, 0.6 mmol) was dissolved in 100 mL dichloromethane. The mixture solution was cooled by ice bath andand stirred for 30 min, protected with nitrogen. And then, the DMP (0.73g, 2 mmol) in dichloromethane (20 mL) was added dropwise. The ice bath was removed after the addition of DMP. The mixed solution was stirred at room temperature for 3 days. Then, the solvent was removed by rotary evaporation. The raw product was purified by silica gel column chromatography (dichloromethane : methanol = 20 : 1). The obtained product was dissolved in THF and then precipitated in ethyl ether. After filtration and vacuum drying, pale yellow solid (2 g, yield: 37.3%) was obtained. ^{1}H NMR (400 MHz, CDCl₃)

δppm: 4.33 (2H, t, COOCH_2); 3.65 (452H, s, (OCH_2CH_2O)$_{113}$); 3.26 (2H, t, SCH_2); 1.70 (6H, s, SC(CH_3)$_2$); 1.65 (2H, m, SCH$_2$CH_2); 1.36 (2H, m, SCH$_2$CH$_2$CH_2); 1.23 (16H, m, CH$_3$(CH_2)$_8$); 0.86 (3H, t, CH_3).
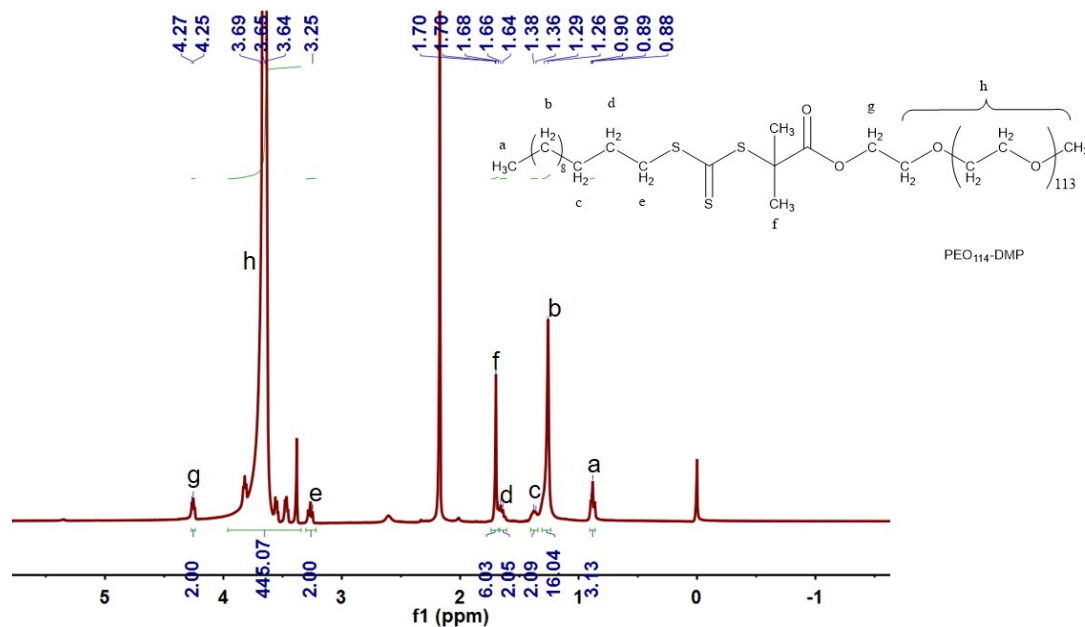
Figure S2. 400 MHz ^{1}H NMR spectra of PEG macro-CTAs recorded in CDCl$_3$.

1.3 Synthesis of EMDA$_3$-PW$_{12}$ complex

EMDA (266 mg, 1 mmol) was dissolved in 100 mL ethanol, and PW$_{12}$ (979 mg, 0.33 mmol) was dissolved in 80 mL ethanol. And then, the EMDA solution was added dropwise into the PW$_{12}$ solution with stirring for 2 hours. The white precipitate was filtered, and washed with ethanol two times. After vacuum drying, 1.05 g EMDA$_3$-PW$_{12}$ was obtained. Yield was 91.6%. The EMDA$_3$−PW$_{12}$ complex is insoluble in water, but readily soluble in organic solvents such as DMF and DMSO. ^{1}H NMR (DMSO-d$_6$, ppm): 6.08 (s, 1H, CH=C), 5.76 (s, 1H, CH=C), 1.91 (s, 3H, C=CCH_3), 4.52 (s, 2H, COOCH_2), 3.67 (s, 2H, COOCH$_2$CH_2), 3.07 (s, 6H, N(CH_3)$_2$), 3.42 (t, 2H, NCH_2), 1.25 (t, 3H, NCH$_2$CH_3). IR (KBr, cm^{-1}): 1081 (P-O); 976 (W-O); 891, 809, 518 cm^{-1} (W-O-W). Elemental analysis calculated (%) for (C$_{10}$H$_{20}$NO$_2$)$_3$PW$_{12}$O$_{40}$: C 10.48, N 1.22, H 1.75; found: C 10.54, N 1.25, H 1.75.
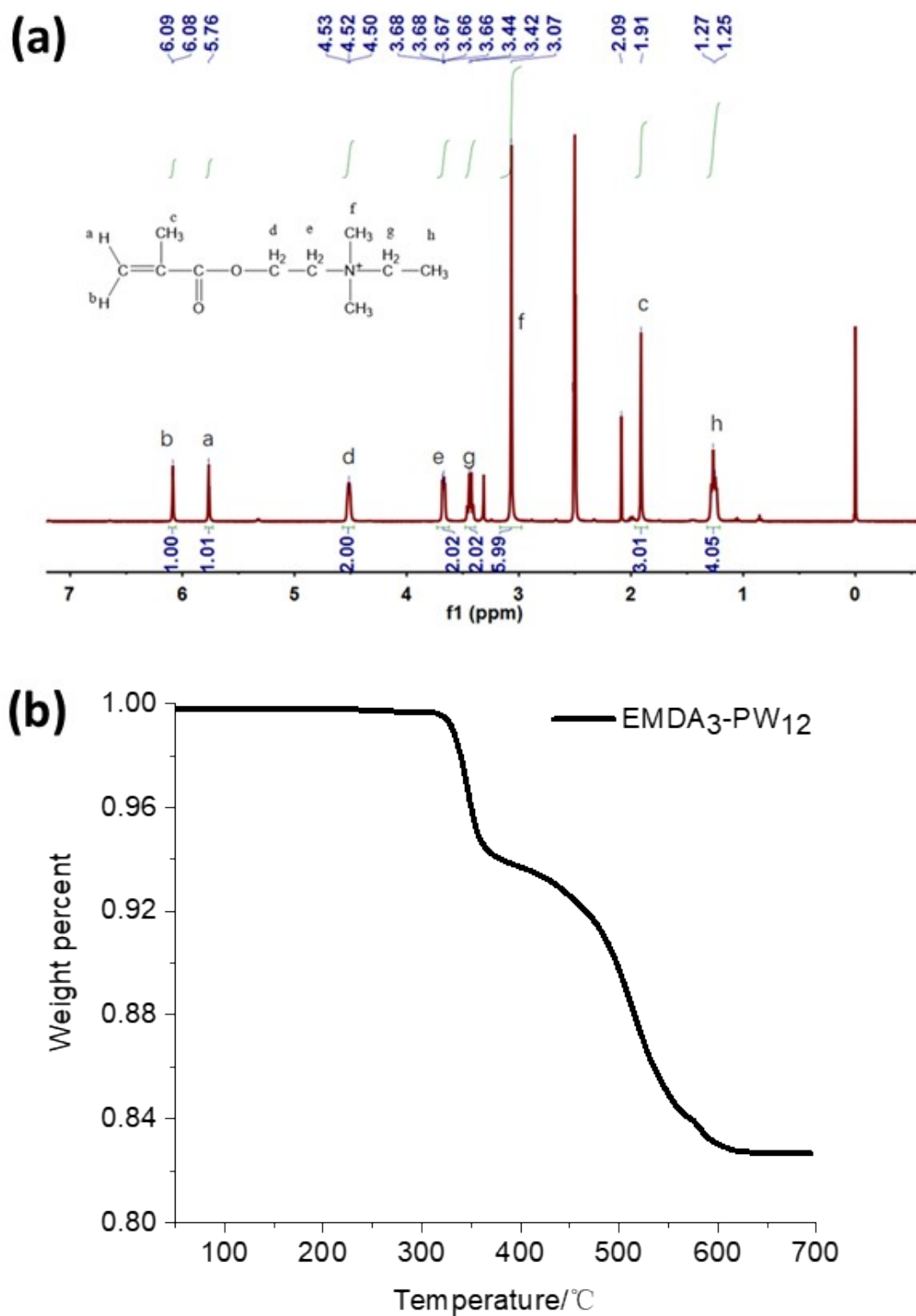
Figure S3. (a) 400 MHz ^1H NMR spectra of $EMDA_3$-PW_{12} recorded in DMSO-d_6; (b) TGA of $EMDA_3$-PW_{12} complex.

1.4 Preparation of E_x-H_y (E = PEG, H = PHPMA, Subscripts represent the DPs)

E_x-H_y diblock copolymeric assemblies were prepared by RAFT aqueous dispersion polymerization of HPMA with PEG_{113}-DMP or PEG_{45}-DMP as the macro-chain-transfer agent (macro-CTA). The feed ratio of HPMA and PEG-DMP was varied to target DP at 10 wt% solid concentration (listed in Table S1). In a typical formulation targeting E_{113}-H_{100}, V-50 (0.006 mmol, 1.7 mg), PEG_{113}-DMP (0.025 mmol, 135.6 mg), HPMA (2.5 mmol, 364.4 mg) and deionised water (5 mL) was added into a 10 mL Schlenk tube, which was equipped with a magnetic stir bar and sealed with rubber stopper. These solutions were stirred magnetically until all reagents had dissolved. After sparging with N_2 for approximately 30 min, each polymerization was placed into an oil bath of 70 °C for 5 h and then quenched in an ice bath and subsequent exposure to air.
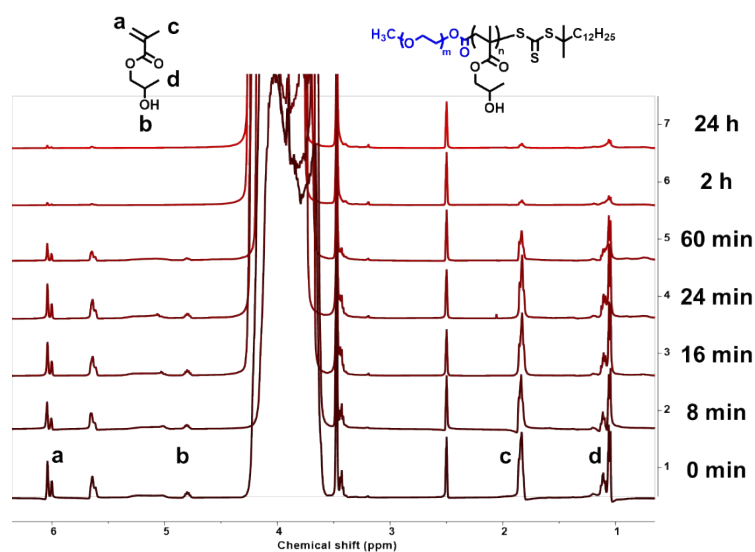
Figure S4. ^{1}H NMR spectra of the E_{113}-H_{100} polymerization solution (200 µl of polymer solution and 500µl of DMSO-d_6 were added to the NMR tube).

1.5 Preparation of E_x-H_y-W_z (E = PEG, H = PHPMA, W = PW_{12}, subscripts represent the DPs)

E_x-H_y-W_z assemblies were prepared by RAFT aqueous emulsion polymerization of HPMA with PEG_{113}-DMP or PEG_{45}-DMP as macro-CTA and EMDA-POM complex as crosslink agent. The feed ratio of HPMA, PEG-DMP and EMDA-POM was

varied to target DP at 10 wt% solid concentration. In a typical formulation targeting E_{113}-H_{100}-W_1 (PW$_{12}$), V-50 (0.005 mmol, 1.5 mg), PEG$_{113}$-DMP (0.021 mmol, 115.5 mg), HPMA (2.1 mmol, 310.5 mg), EMDA$_3$-PW$_{12}$ (0.021 mmol, 74 mg) and deionised water (5 mL) was added into a 10 mL Schlenk tube, which was equipped with a magnetic stir bar and sealed with rubber stopper. These solutions were stirred magnetically to form a steady emulsion. After sparging with N$_2$ for approximately 30 min, each polymerization was placed into an oil bath of 70 °C for 24 h and then quenched in an ice bath and subsequent exposure to air.

1.6 Polymer characterization

DLS studies were performed using a NanoBrook 90Plus PALS (Brookhaven Instruments Corporation, USA) at 25 °C at a scattering angle of 90°. Copolymer solutions/dispersions were prepared at the desired concentration and ultrafiltered prior to dynamic light scattering studies. The mean diameter and polydispersity (PDI) were automatically analyzed. Transmission electron microscopy (TEM) studies were conducted using a JEM-2100 instrument operating at 200 kV. Carbon-coated copper grids were used for TEM measurement and then glow-discharged for 20–30 s to create a hydrophilic surface. For the sample preparation of E_x-H_y, grids were immersed in aqueous copolymer dispersions for 1 min and then negatively stained by immersion in a 0.75 w/v% uranyl formate solution for 20 s. And then, the grid was blotted with filter paper and dried using a vacuum hose. For the sample preparation of E_x-H_y-W_z, grids were immersed in aqueous copolymer dispersions for 1 min and then blotted with filter paper.
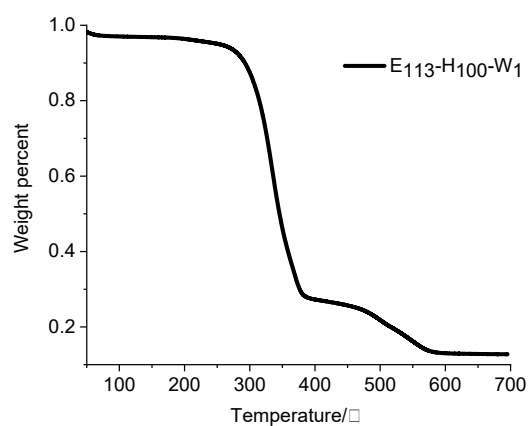
1.7 Photocatalysis synthesis of Au nanoparticles

40 μL 10 wt% E_{113}-H_{100}-$W_{0.5}$ emulsion was diluted in 5 mL deionized water, and then mixed with 100 μL 0.67 wt% HAuCl$_4$ aqueous solution. The mixed solution was then illuminated with 500 W Hg-Xe light for 50 min under stirring. The solution of E_{113}-H_{100}-$W_{0.5}$-Au are centrifuged (9000 rpm, 3 min) and the resulting products were washed to remove the unreacted HAuCl$_4$. We determine the gold content in composites
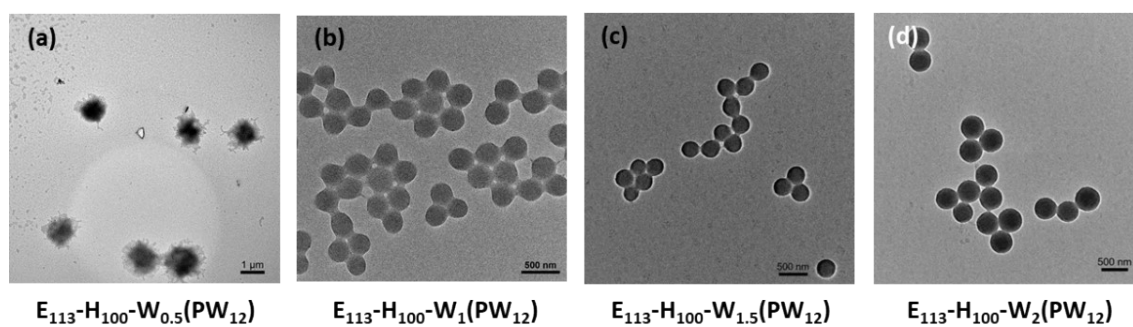
materials according to difference in mass between the remaining solids of E_{113}-H_{100}-$W_{0.5}$-Au and E_{113}-H_{100}-$W_{0.5}$ in the TGA measurement (Fig. S11). The reduction efficiency of Au was about 85%.
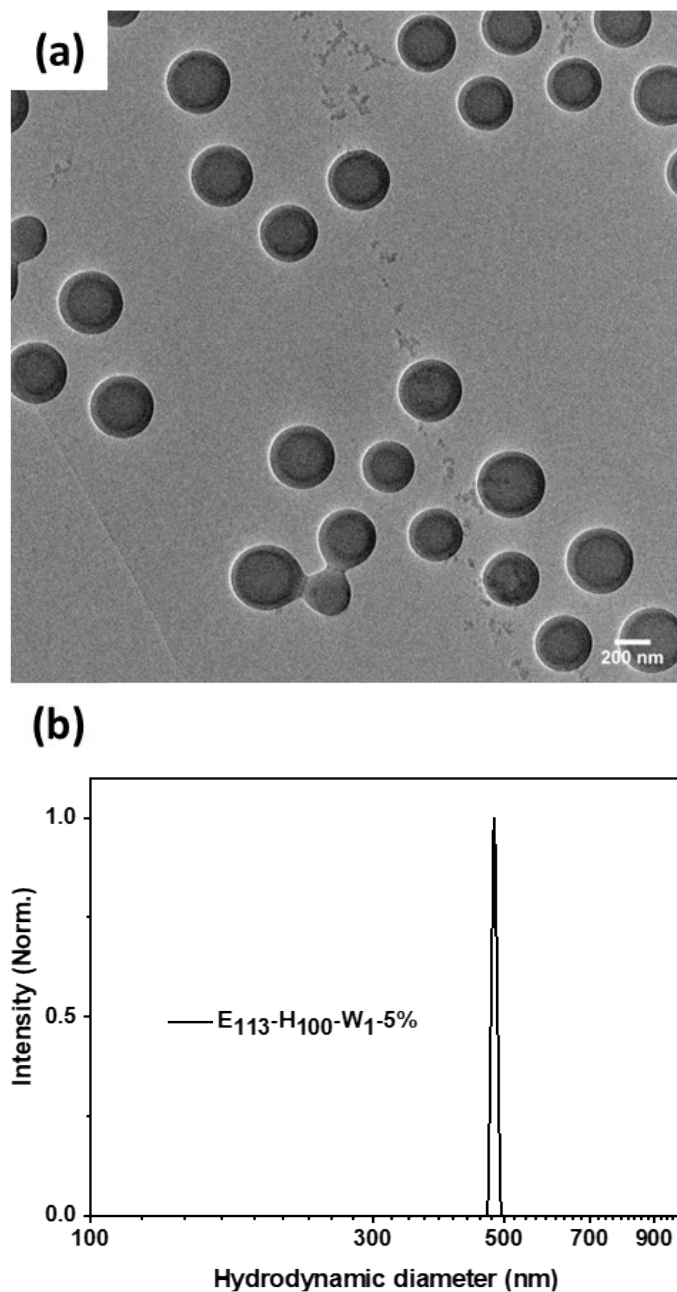
Figure S5. (a) TEM image of E_{113}-H_{100} -W_1 at the solid content 5 wt%; (b) hydrodynamic diameter of E_{113}-H_{100} -W_1 at the solid content 5 wt%.

Figure S6. TGA of E_{113}-H_{100}-W_1 polymer.

E_{113}-H_{100}-$W_{0.5}(PW_{12})$ $\qquad$ E_{113}-H_{100}-$W_1(PW_{12})$ $\qquad$ E_{113}-H_{100}-$W_{1.5}(PW_{12})$ $\qquad$ E_{113}-H_{100}-$W_2(PW_{12})$

Fig. S7 TEM image of (a) E_{113}-H_{100}-$W_{0.5}$; (b) E_{113}-H_{100}-W_1; (c) E_{113}-H_{100}-$W_{1.5}$; (d) E_{113}-H_{100}-W_2.

Table S1 The hydrodynamic diameter of E_{113}-H_{100}-W_z

	Diameter (nm)	Polydispersity
E_{113}-H_{100}-$W_{0.5}$	578	0.053
E_{113}-H_{100}-W_1	562	0.005
E_{113}-H_{100}-$W_{1.5}$	538	0.003
E_{113}-H_{100}-W_2	514	0.005

By dispersing the hybrid materials in organic solvents, the stability of the materials can be demonstrated by DLS.
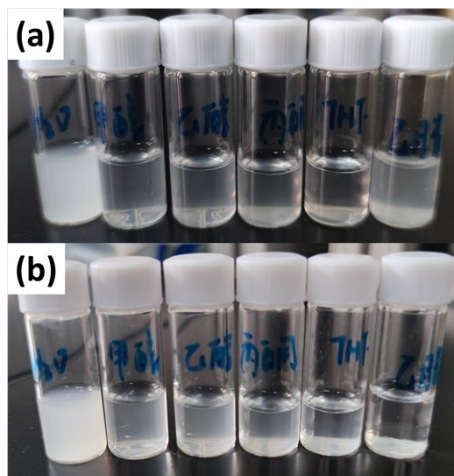
Fig. S8 Photographs of E_{113}-H_{100}-$W_{0.5}$ dissolved in H_2O, methanol, ethanol, acetone, THF and acetonitrile (0.1 wt%) for (a) 1h and (b) 7 days.

Table S2 The hydrodynamic diameter of E_{113}-H_{100}-W_1 in H_2O and organic solvents.

	Diameter-1h (nm)	Polydispersity	Diameter-7days (nm)	Polydispersity
H_2O	281	0.053	265	0.005
Methanol	299	0.005	330	0.251
Ethanol	221	0.153	292	0.169
Acetone	432	0.121	165	0.315
THF	441	0.728	Precipitation	/
Acetonitrile	124	0.124	Precipitation	/

1.8 Preparation of E_x-H_y-POM_z (E = PEG, H = PHPMA, POM = W(PW$_{12}$), W(W$_6$O$_{19}$) or Si(SiW$_{12}$), subscripts represent the DPs)

E_x-H_y-POM_z were prepared by RAFT aqueous emulsion polymerization as mentioned above.
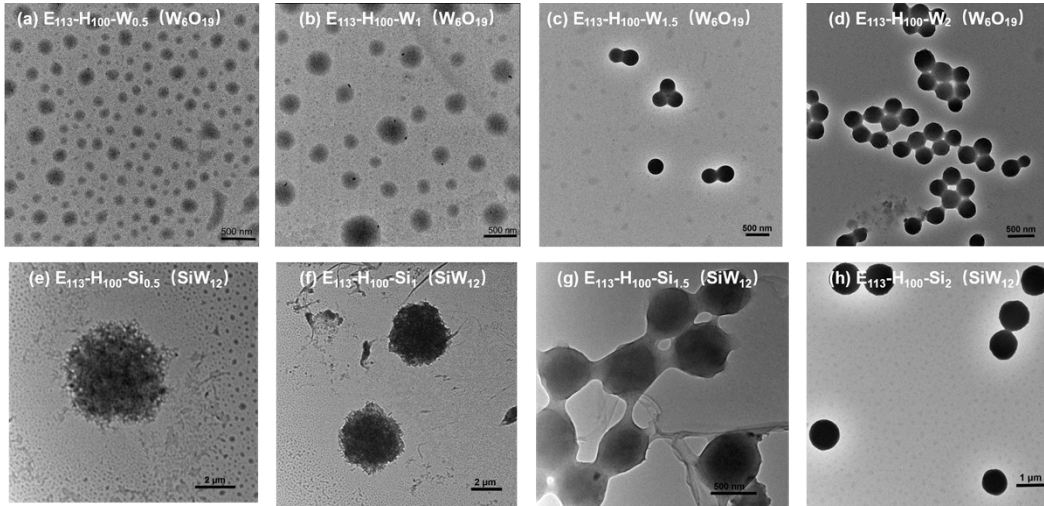
Fig. S9. TEM image of (a) E_{113}-H_{100}-$W_{0.5}$ (W_6O_{19}); (b) E_{113}-H_{100}-W_1 (W_6O_{19}); (c) E_{113}-H_{100}-$W_{1.5}$ (W_6O_{19}); (d) E_{113}-H_{100}-W_2 (W_6O_{19}); (e) E_{113}-H_{100}-$Si_{0.5}$ (SiW_{12}); (b) E_{113}-H_{100}- Si_1 (SiW_{12}); (c) E_{113}-H_{100}- $Si_{1.5}$ (SiW_{12}); (d) E_{113}-H_{100}- Si_2 (SiW_{12}).

Table S3 The hydrodynamic diameter of E_{113}-H_{100}-POM_z

	Diameter (nm)	Polydispersity
E_{113}-H_{100}-$W_{0.5}$ (W_6O_{19})	133.5	0.228
E_{113}-H_{100}-W_1 (W_6O_{19})	146.3	0.233
E_{113}-H_{100}-$W_{1.5}$ (W_6O_{19})	446.6	0.054
E_{113}-H_{100}-W_2 (W_6O_{19})	408.2	0.043
E_{113}-H_{100}-$Si_{0.5}$ (SiW_{12})	1929.1	0.249
E_{113}-H_{100}-Si_1 (SiW_{12})	2079.9	0.119
E_{113}-H_{100}-$Si_{1.5}$ (SiW_{12})	908.3	0.237
E_{113}-H_{100}-Si_2 (SiW_{12})	834.4	0.149
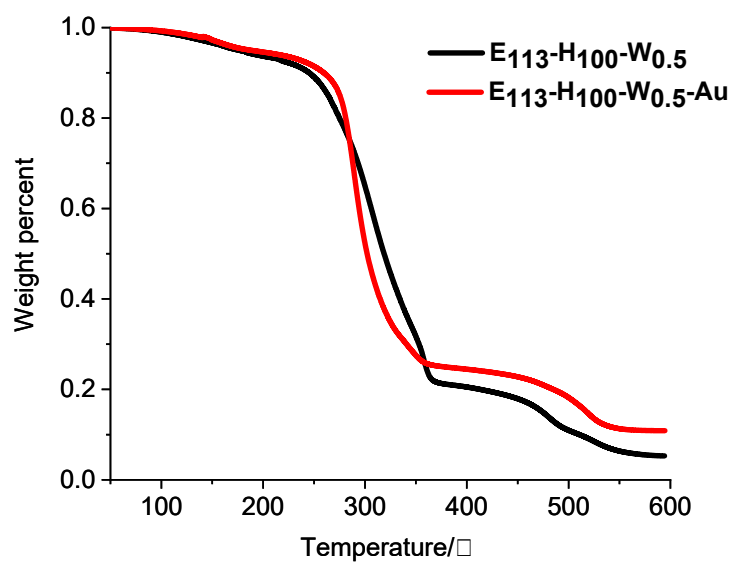
Figure S10. TGA of E_{113}-H_{100}-$W_{0.5}$ polymer and E_{113}-H_{100}-$W_{0.5}$-Au.

Reference:

[1] Skey, J.; O'Reilly, R. K. Facile One Pot Synthesis of a Range of Reversible Addition–Fragmentation Chain Transfer (RAFT) Agents. *Chem. Commun.* **2008**, *35*, 4183–4185.