

Supporting Information

Mechanochemical Reactions within Graft Copolymeric Assemblies :

Ultrasound-Induced Multimechanophore Activation, Arm Chain Scission, and Aggregation Morphology/Size Changes

Lijun Wang,^{a} Qiang Zhou,^b Yanfang Chen,^a Xiaoke Yang,^a Yangyang Zhang,^a Hanyi Duan,^c Haixiang Song,^a Yanfei Wang,^a and Yongjun Zheng^a*

^aSchool of Materials Science and Engineering, Henan Joint International Research Laboratory of Nanocomposite Sensing Materials, Anyang Institute of Technology, Anyang 455000, China.

^bCAS Key Laboratory of Soft Matter Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China

^cPolymer program, Institute of Materials Science, University of Connecticut, Storrs, CT 06268, USA

E-mail: 20190015@ayit.edu.cn

Experimental

I Materials

Maleic anhydride (99%, Aladdin), Furan (99%, Aladdin), Ethanolamine (99%, J&K), Triethylamine (98%, Aladdin), 2-Bromo-2-methylpropionyl bromide (98%, Aladdin), 9-anthracenemethanol (97%, Aladdin), Dimethyl amino pyridine (DMAP) (98%, Aladdin), Methacrylic acid (99%, Aladdin), Trifluoroacetic acid (99%, Energy Chemical), and N,N'-dicyclohexylcarbodiimide (DCC) (99%, Aladdin) were obtained from commercial suppliers and used without further purification. N,N-Azo-bisisobutyronitrile (AIBN) was purchased from J&K and recrystallized from methanol before use. 4-Cyano-4-[[[(dodecylthio)carbonothioyl]thio]pentanoic acid (TTC-CTA) was purchased from Energy Chemical and used as received. Tris(2-dimethylaminoethyl)amine (Me₆TREN) (99%, Alfa Aesar), CuBr (99%, Energy Chemical) was purified by stirring in glacial acetic acid for 5 h, washed with absolute

ethanol and anhydrous diethyl ether, dried under vacuum for 12 h at room temperature, and stored under nitrogen. Tert-butyl acrylate (99%, Energy Chemical) was filtered through a plug of basic alumina for removing the inhibitor. Dry Dimethyl sulfoxide (DMSO, 99.5%, extra dry), dry Acetonitrile (MeCN, 99.9%, extra dry), dry *N,N*-Dimethylformamide (DMF, 99.9%, extra dry), and dry Tetrahydrofuran (THF, 99.5%, extra dry) were all purchased from Energy Chemical and used as received. All polymerizations were performed under N₂ unless otherwise specified, and all glassware was dried in an oven before use.

II General Methods and instrumentation

¹H NMR spectra were recorded on a Bruker Advance DMX 400-MHz spectrometer. Chemical shifts were referenced to TMS as internal standard at 0.0 ppm.

The weight-averaged molecular weight (*M_w*) and polydispersity index (*D_M*) were determined by using a multimode Viscotek GPCmax system consisting of a pump, a low angle/right angle light scattering (LALS/RALS) detector, a differential refractive index (RI) detector, and a viscometer detector. For Poly(9-anthracene methyl methacrylate) (PolyAnMMA, P0) and Diels-Alder adduct functionalized polymer PolyAnMMA-DA-Br (P1), size exclusion chromatography (SEC) were conducted in THF at 1.0 mL/min at 35 °C, and the sample concentration was 3 mg/mL. For graft copolymers, SEC were conducted in *N,N*-dimethylformamide (DMF) with LiBr (0.05 M) at 45 °C and a flow rate of 0.7 mL*min⁻¹, and the sample concentration was 6 mg/mL. The GPC were calibrated with monodisperse polystyrene standards and monodisperse PMMA standards, respectively.

All ultrasonication experiments were performed on a sonifier cell disrupter with a solid probe of a diameter of 3.24 mm (XO-650, Nanjing Xianou Instruments Manufacture Co.Ltd., Nanjing, China.). The distance between the titanium tip and bottom of the Suslick cell was 1.0 cm. The sonicator was set to 30 % amplitude (the corresponding sonication power was about 5.52W, which had been calibrated in our previous work¹) and the temperature was recorded at 3-5 °C.

UV-Vis spectra were recorded on a Shimadzu UV-2401PC and a Cary 100 instrument (Varian Australia Pty Ltd).

Fluorescence spectra were recorded using a RF-5301/PC (Shimadzu) spectrofluorometer. The slit widths were set at 5 nm for both excitation and emission. The excitation wavelength was 390 nm. Scan speed: 12000 nm/min. Scanning range: 400–650 nm.

Differential scanning calorimetric (DSC) measurements were conducted on a TAQ200 instrument (New Castle, DE) with a ramping rate of 10 °C/min under a N₂ atmosphere.

The hydrodynamic diameter and size distribution of the obtained micelles were measured by dynamic light scattering (DLS) at a scattering angle θ of 90° as a function of temperatures by using a 90 Plus Particle Size Analyzer (Brookhaven Instruments Corp). The corresponding characterization was carried out after micellar solutions being sonicated and rested over 24 h, to ensure that the degraded amphiphilic graft copolymer can effectively reassemble after sonication.

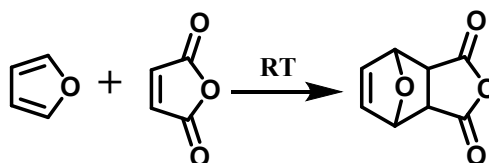
The TEM morphologies of the obtained micelles were observed by transmission electron microscopy (TEM) on a JEM 1230 electron microscope operated at an acceleration voltage of 100 kV.

The AFM imaging was performed by Bruker Dimension Icon. Samples were prepared by spin-coating of one drop of polymer solutions in ~0.001 g/L ethanol solution on mica substrates (spinning rate = 3000 rpm for 10 secs). The AFM images were obtained with tapping and non-contact mode and tips from Nanoworld.

III Synthesis

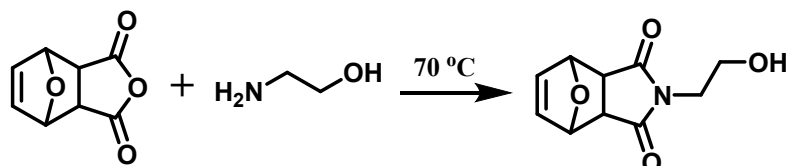
1 Synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl) ethyl ether (1)¹

The functionalized Furan-Protected N-(2-Hydroxyethyl)-maleimide initiator 1 was synthesized according to modified procedures of Duan and co-workers¹.



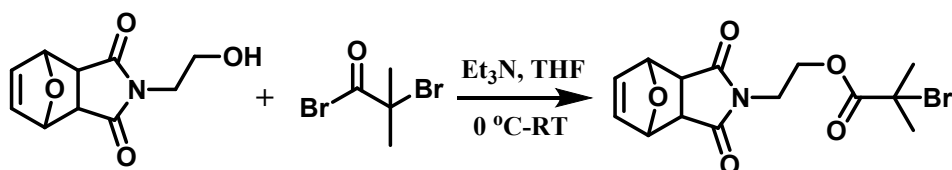
Synthesis of Furan-Protected Maleic Anhydride

30.0 g maleic anhydride (305.9 mmol, 1 equiv) and 25.0 g furan(367.6mmol, 1.2 equiv) were mixed and stirred in 300 ml toluene at room temperature .After the mixture had been stirred for 36 h, the reaction was stopped and a white solid powder was precipitated . The mixture was vacuum filtered and dried to obtain the product (yield 79%), a further purification was not necessary. ¹H NMR:(400 MHz, d₆-DMSO) δ 7.27, 6.79, 5.09, 2.85.



Synthesis of Furan-Protected N-(2-Hydroxyethyl)-maleimide

10g furan-protected maleic anhydride (60.24mmol, 1 equiv) and 20 ml methanol which served as solvent were added into a three-neck flask (50 ml), the mixture was kept in a ice bath for 15 min. Then the mixture of 3.68 g ethanolamine(60.33 mmol,) and 5 ml methanol was slowly added into the flask in the ice bath under stirring. The final mixture was kept in ice bath for 30 min and then at room temperature for 25 min under stirring. The solution was refluxed for 24 h. After the reaction was stopped, the solution was cooled to room temperature and stored in freezer overnight. The product crystallized from the solution and a slightly yellowish solid powder was collected by vacuum filtered (yield 47.4%). ¹H NMR: (400 MHz, d₆-DMSO) δ 6.55, 5.12, 4.79, 3.41, 2.92.



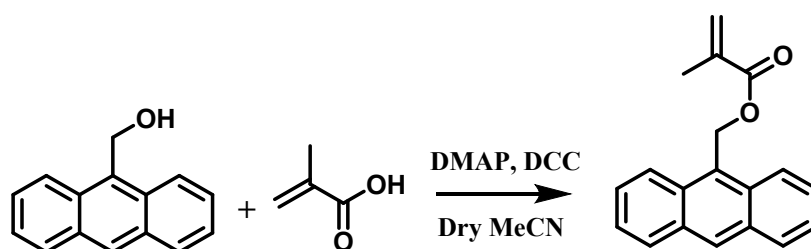
Synthesis of 2-bromo-2-methyl-propionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0.2,6] dec-8-en-4-yl) ethyl ether (1)

Furan-Protected N-(2-Hydroxyethyl)-maleimide (6.0 g, 29 mmol) was dissolved in triethylamine (4.33 mL, 31.6 mmol) and THF (325 mL). The solution was cooled to 0 °C. A solution of 2-bromo isobutyryl bromide (3.78 mL, 31 mmol) in THF (110 mL) was added dropwise during 30 min. The reaction mixture was stirred at 0 °C for 3 h and

then let to react overnight at room temperature. The ammonium salt was filtered off and a pale yellow residue was obtained after solvent removal under reduced pressure. The product was purified by column chromatography (silica, cyclohexane/ethyl acetate = 9/1 (v/v)) to yield compound 1 (3.2 g, 9 mmol) as a light brown solid with a yield of 31%. ¹H-NMR (400 MHz, CDCl₃): δ(ppm) = 6.52 (t, 3JH, H = 0.9 Hz, 2H, CH=CH), 5.27 (t, 3JH, H = 0.9 Hz, 2H, CH-O-CH), 4.34 (t, 3JH, H = 5.28 Hz, 2H, CH₂O), 3.82 (t, 3JH, H = 5.28 Hz, 2H, NCH₂), 2.88 (s, 2H, CH-CH), 1.90 (s, 6H, C(CH₃)₂Br) (Figure S1).

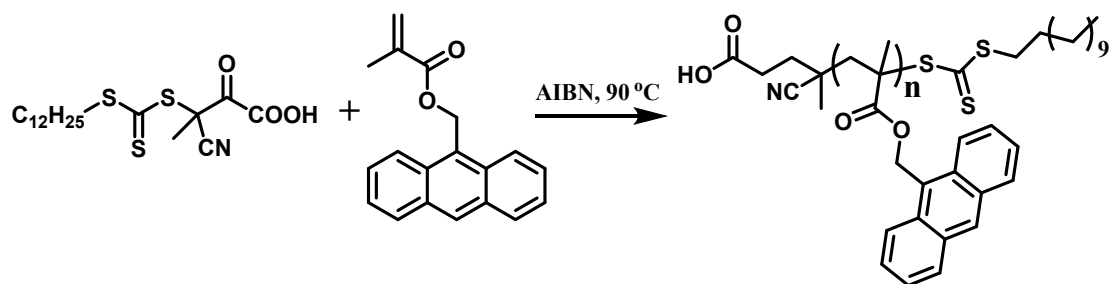
2 Synthesis of 9-anthracenylmethyl methacrylate (AMMA)

The fluorescent monomer 9-anthracenylmethyl methacrylate (AMMA) was synthesized according to modified procedures of Rodriguez and co-workers².



A 250 mL round bottom flask was equipped with a magnetic stir bar, 9-anthracenemethanol (2.5 g, 12.0 mmol), DCC (4.95 g, 24.0 mmol), DMAP (0.22 g, 1.8 mmol), and methacrylic acid (2.1 g, 24.0 mmol). 30 mL of dry acetonitrile was added to generate a slurry. The mixture was stirred for 24 h under argon. After, the mixture was vacuum filtered to remove DCU. The filtrate was concentrated under reduced pressure and the product was isolated as a yellow band via flash column chromatography using silica (5:1 toluene/ethyl acetate). The product was concentrated under reduced pressure and precipitated in methanol. Yield: 2.31 g (70%). ¹H NMR (CDCl₃, 400 MHz): δ 8.54 (s, 1H), 8.40 (d, 2H), 8.06 (d, 2H), 7.58 (m, 2H), 7.49 (m, 2H), 6.25 (s, 2H), 6.08 (m, 1H), 5.53 (m, 1H), 1.94 (m, 3H), (Figure S2).

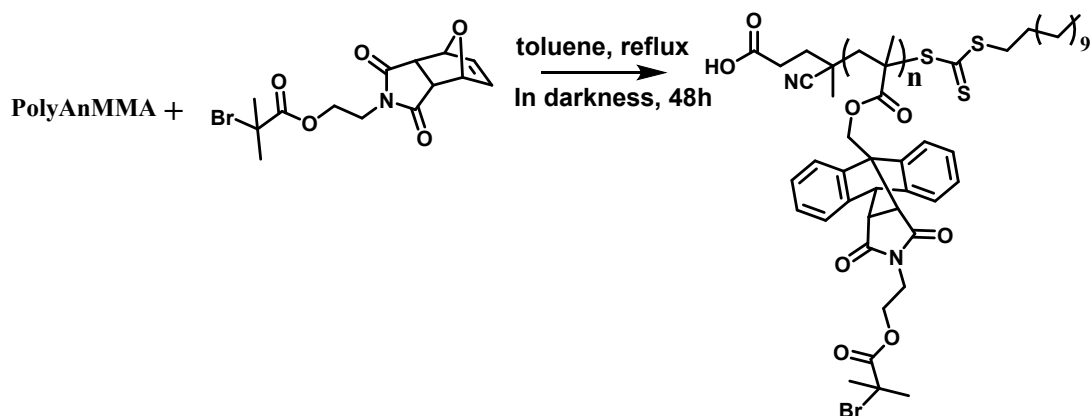
3 Synthesis of Poly(9-anthracene methyl methacrylate) (PolyAnMMA, P0)



RAFT Polymerization of AnMMA

Well-controlled poly (9-anthrylmethyl methacrylate) (**PolyAnMMA**) was synthesized as follow: AnMMA (0.9 g, 3.2 mmol) was placed into a 25 mL Schlenk flask with magnetic stirring bar, dried in vacuo and purged with nitrogen. **TTC-CTA** (13 mg, 32.1 μ mol) and AIBN (2.2 mg, 12.8 mmol) were dissolved in dry DMF (1.5 mL) and then transferred into the flask using a syringe. The mixture was degassed by three freeze–pump–thaw cycles, and then placed under nitrogen atmosphere at 80 °C for 48 h. The reaction mixture was diluted by THF and precipitated into a 50/50 mixture of CH₃OH/H₂O. The resulting precipitate was dried in vacuo and then purified through reprecipitation using THF–tert-butyl methyl ether combination. The isolated polymer was dried in vacuo at 45°C for 24 h. GPC: Mw = 15750 g/mol, PDI (Mw/Mn) = 1.27.

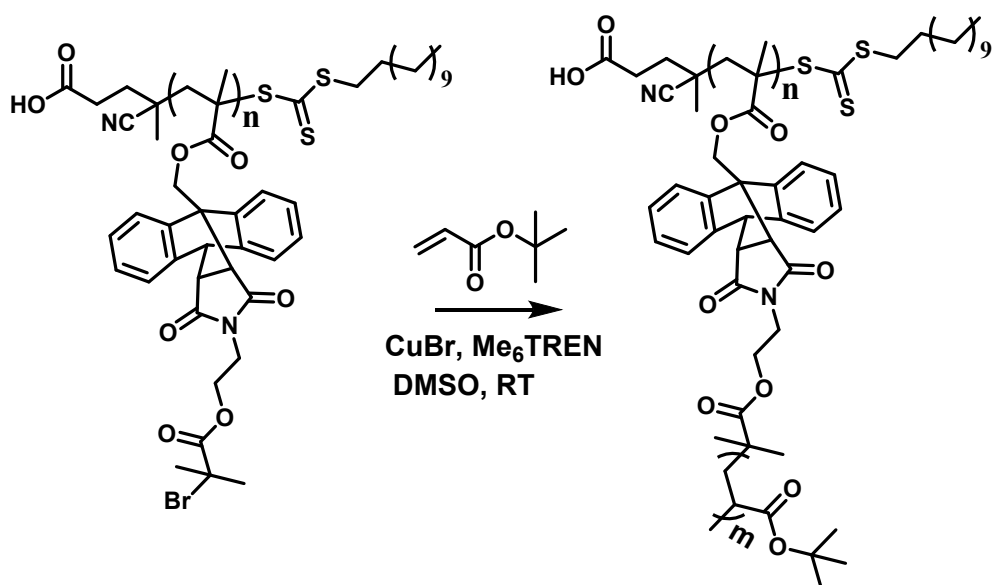
4 Synthesis of Diels-Alder adduct functionalized polymer: Poly(AnMMA-DA-Br) (P1)



PolyAnMMA (250 mg, 0.925mmol of An) and compound 1 (357 mg, 357.02g/mol, 1.0 mmol) were dissolved in 20 mL toluene and heated in the darkness at 120 °C for 48 h. Then, the reaction mixture was precipitated into a large excess of cold methanol (β 3) and thoroughly dried under vacuum at room temperature to yield the

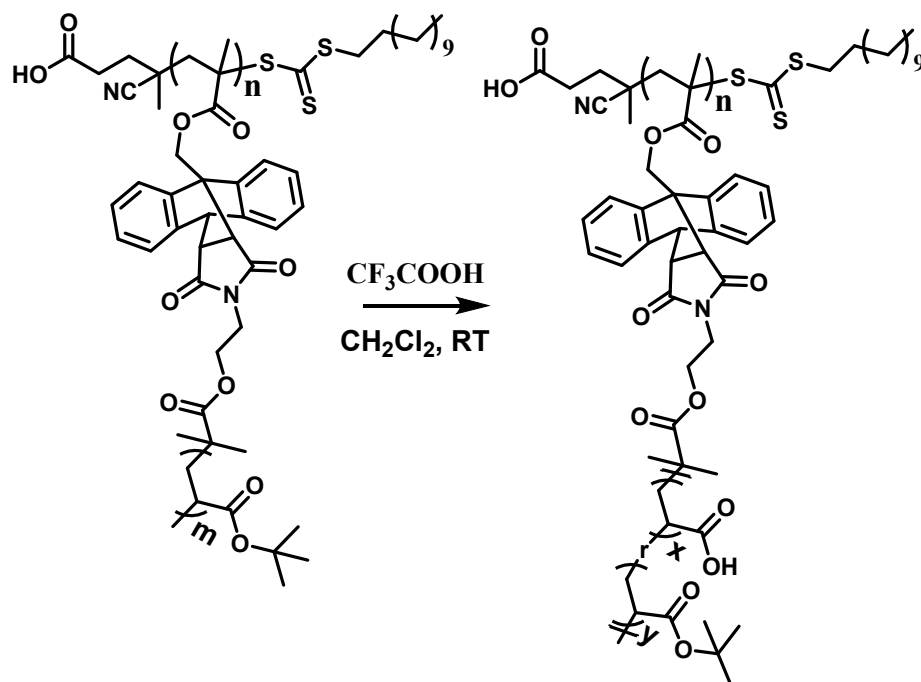
target polymer **P1**. GPC: $M_w = 33660$ g/mol, PDI (M_w/M_n) = 1.25, 56 Br per chain.

5 Synthesis of Poly(AnMMA-DA)-g-PtBA (P2-P6)



Typically, tert-butyl acrylate (6.0 mL, 41.34 mmol), Me_6TREN (18.41 μL , 68.9 μmol), CuBr (9.88 mg, 68.9 μmol), the polymer initiator **P1** (41 mg, 68.9 μmol Br), and dry DMSO (1 mL) were added into a Schlenk flask. Three freeze-pump-thaw cycles were carried out to remove oxygen. Then, the Schlenk flask was allowed to stir at room temperature. After the desired time, the isolated solution was diluted with THF and then filtered through a plug of basic Al_2O_3 to remove the copper catalyst. The polymer solution was added dropwise to a stirred ice-cold ethanol/water (1:1, v/v) mixture. The ethanol/water mixture was decanted and the polymer solid redissolved in DMF. After repeating the precipitation process 2 times, the obtained polymer solid was dried under vacuum. To synthesize graft copolymers with different arm length, several polymerization processes were carried out by changing the equivalent of tert-butyl acrylate added. The volumes of tert-butyl acrylate were 0.8 ml, 1.5 ml, 3.0 ml, 4.5 and 6.0 mL respectively. Notably: the equivalent of other components kept constant. Four kinds of graft copolymer with different M_w were synthesized. GPC: **P2**, $M_w = 3.054 \times 10^6$ g/mol, PDI (M_w/M_n) = 1.56, DP=420; **P3**, $M_w = 2.622 \times 10^6$ g/mol, PDI (M_w/M_n) = 2.36, DP=360; **P4**, $M_w = 2.076 \times 10^6$ g/mol, PDI (M_w/M_n) = 1.54, DP=280; **P5**, $M_w = 1.792 \times 10^6$ g/mol, PDI (M_w/M_n) = 1.33, DP=236; **P6**, $M_w = 1.131 \times 10^6$ g/mol, PDI (M_w/M_n) = 1.41, DP=148.

6 Acidolysis of Poly(AnMMA-DA)-g-PtBA to synthesize Poly(AnMMA-DA)-g-PAAc (P2'-P6')



The acidolysis procedures and formulas of the above-synthesized 5 kinds of **Poly(AnMMA-DA)-g-PtBA** were same: 400 mg graft copolymer was first added into 100 mL single neck flask, and dissolved in 8 ml dichloromethane. Then, 1.8 mL trifluoroacetic acid was added, and the mixture was stirred at room temperature for 24 h. Thereafter, 0.4 mL trifluoroacetic acid was added additionally, and the mixture was stirred for another 24h. After removing the solvent and trifluoroacetic acid in vacuo, further elimination of the residual acid and solvent traces was carried out by washing with large amount of petroleum ether. Finally, the collected precipitation was thoroughly dried under vacuum at 45 °C to obtain the target polymer Poly(AnMMA-DA)-g-PAAc. Since the obtained graft copolymers in the acidic form cannot be dissolved in water or THF, and the solubility of the copolymers in DMF was also relatively low, the Mw and PDI information can't be measured effectively. **DP information: P2'**, DP=420; **P3'**, DP=360; **P4'**, DP=280; **P5'**, DP=236; **P6'**, DP=148.

IV Procedure of the micelle formation

The obtained graft copolymers in the acidic form cannot be dissolved directly in water. The micelle dispersed in pure water was prepared as follows: 40 mg of copolymer was dissolved in 20 mL of DMF, and then added dropwise into 20 mL of

water. The mixture was stirred at room temperature for 1.5 h. DMF was removed by dialysis against deionized (DI) water for 48 h using a dialysis membrane (MWCO 3500 Da). Finally, the equilibrium micellar concentration was 0.8 mg/mL. The micelle dispersed in water/DMF mixture was prepared as follows: 16 mg of copolymer was first dispersed in a certain amount of DMF by ultrasonication, and then the mixture was added with water dropwise. By changing the volume ratio of water with DMF, different micellar systems dispersed in water/DMF mixture were obtained. The final concentrations of the micellar systems dispersed in water/DMF were also adjusted to 0.8 mg/mL.

V Sonication experiments

Sonication experiments were carried out using a XO-650 sonifier cell disrupter with a solid probe of a diameter of 3.24 mm, a frequency of 20 kHz and 30% of the maximum amplitude. Pulsed sonication (1s on, 1s off) was used. Graft copolymer micellar solution was injected into a cooled Suslick cell (3-5 °C) with a constant flow of N₂. During the sonication, samples were withdrawn at different intervals with a syringe for analyzing by fluorescence spectroscopy, DLS and TEM.

VI DLS test

The viscosity and refractive index of mixture of H₂O/DMF are based on literature data^[3, 4] using linear interpolation method and they are summarized in Table S1.

Table S1. Data of the refractive indexes and viscosities of DMF/water mixed solvents with different DMF contents at 5.0 °C.

Volume Percent of DMF in Water	Viscosity (mPa·s)	Refractive Index
0	0.922	1.331
5	1.30	1.339
10	1.644	1.344
20	2.185	1.355
30	2.467	1.364
40	2.104	1.373
100	0.815	1.428

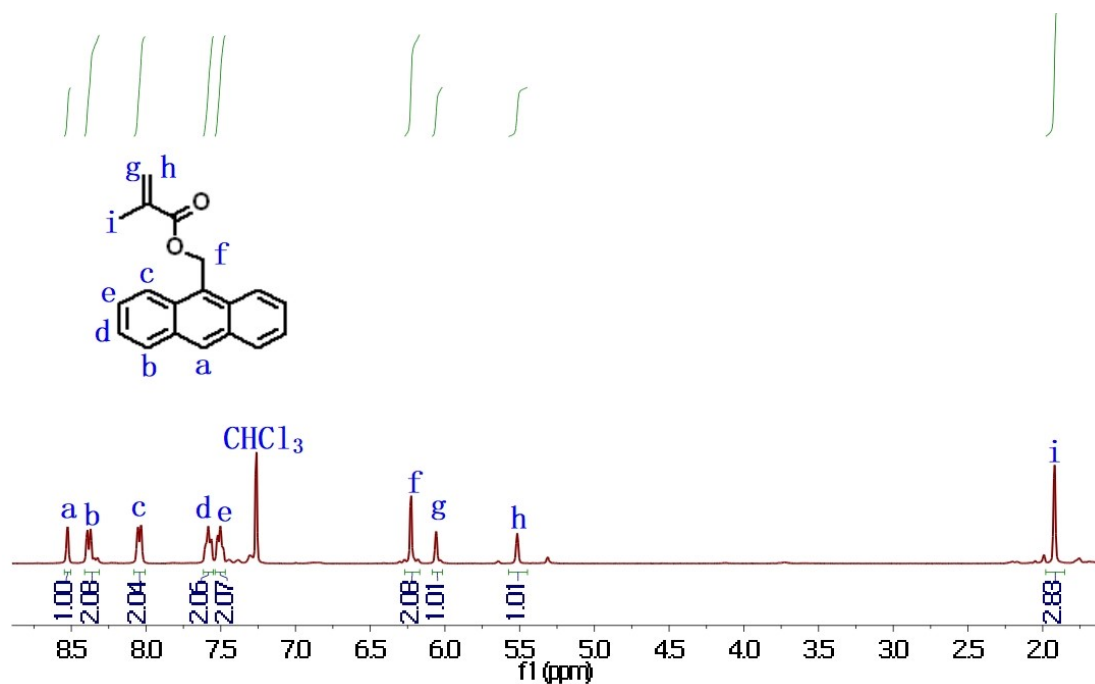


Figure S1. ^1H NMR spectrum of 9-anthracenylmethyl methacrylate (AnMMA) (400 MHz, CDCl_3).

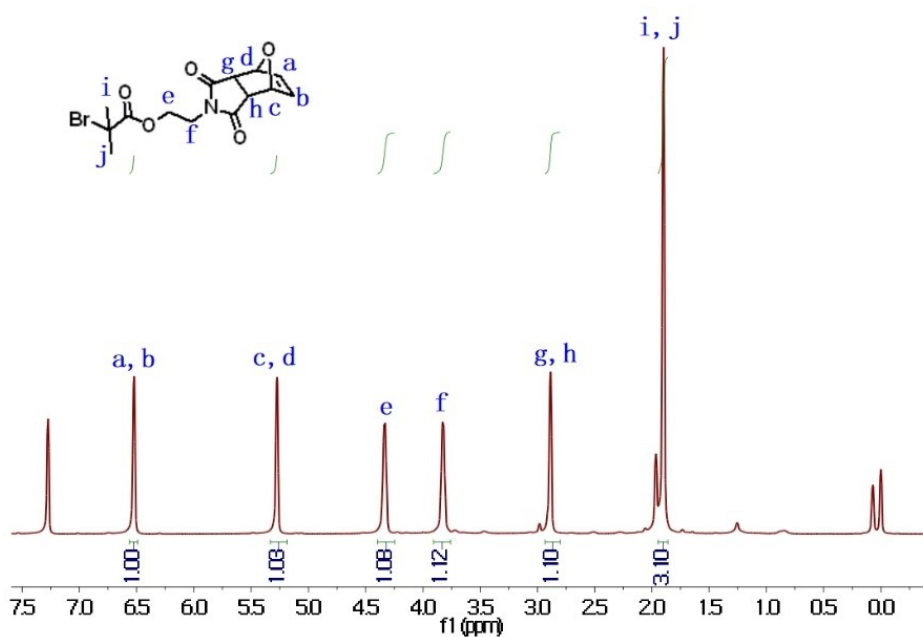


Figure S2. ^1H NMR spectrum of furan-protected N-(2-hydroxyethyl)-maleimide (FPM) initiator (400 MHz, CDCl_3).

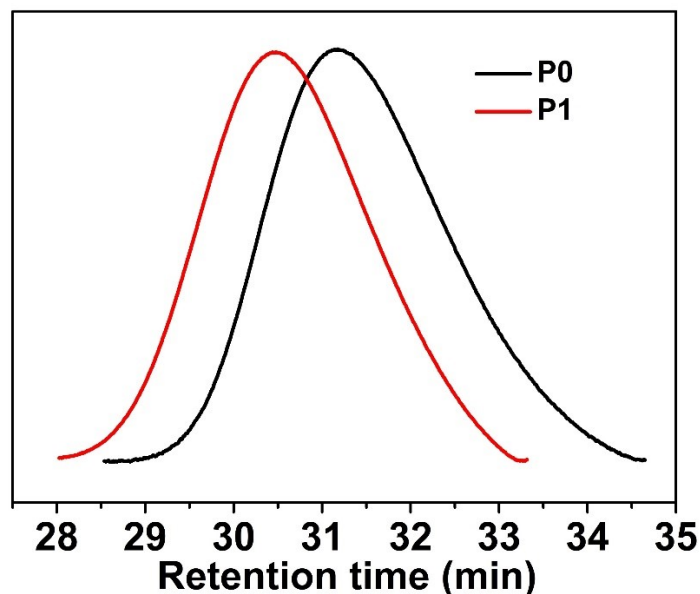


Figure S3. SEC traces of Poly AnMMA (P0) and Poly (AnMMA-DA-Br) (P1) shown in Table 1; P0: Mw = 15750 g/mol, PDI (Mw/Mn) = 1.27, dark line; P1: Mw = 33660 g/mol, PDI (Mw/Mn) = 1.25, red line.

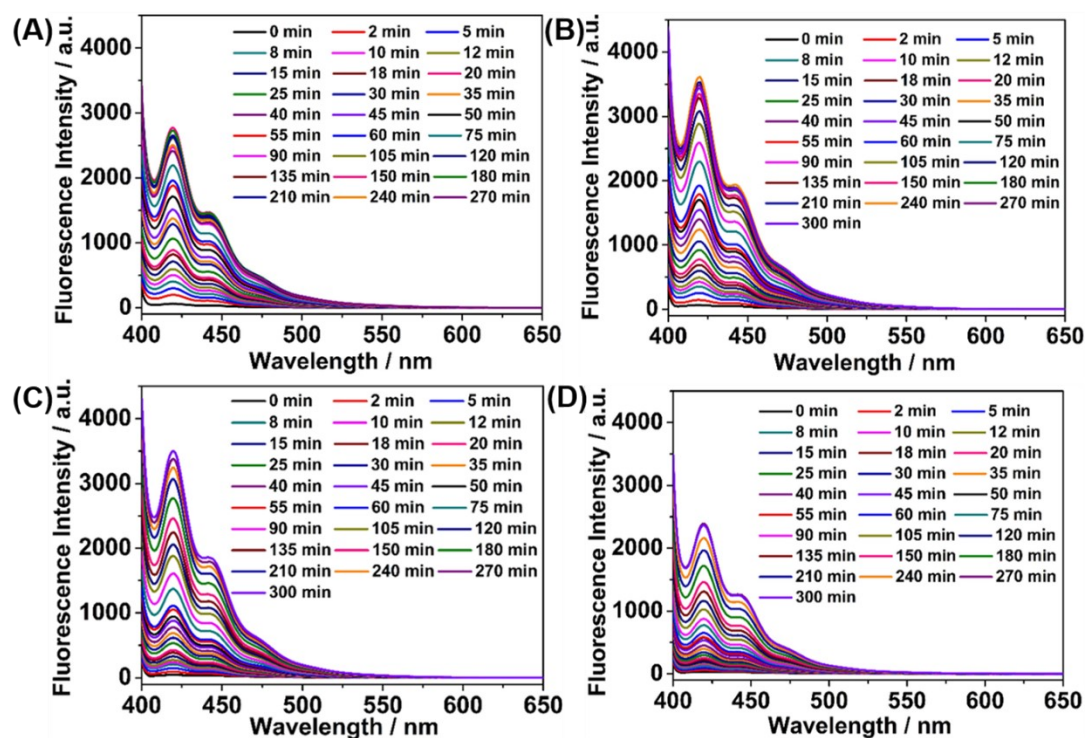


Figure S4. Fluorescence spectra as a function of sonication time for (A) P2, (B) P3, (C) P5, and (D) P6 dissolved in DMF subjected to ultrasound (3-5 °C, ultrasonic mode: 1s on and 1s off).

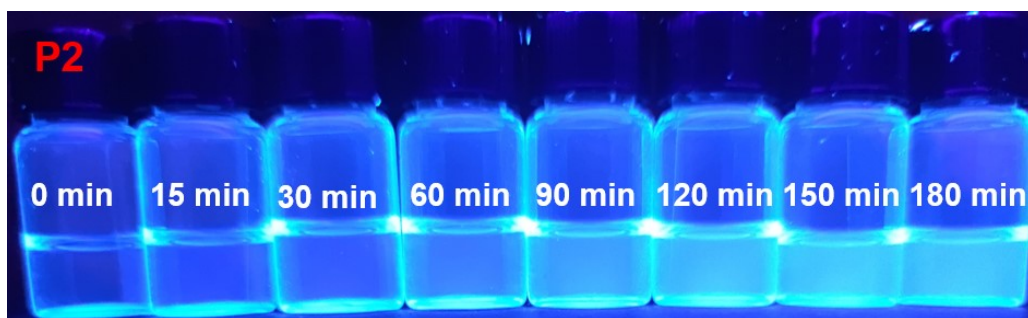


Figure S5. The dynamic photoluminescent photographs of the polymer (**P2**) solutions taken after sonicating for different time (with the irradiation of 365 nm UV light).

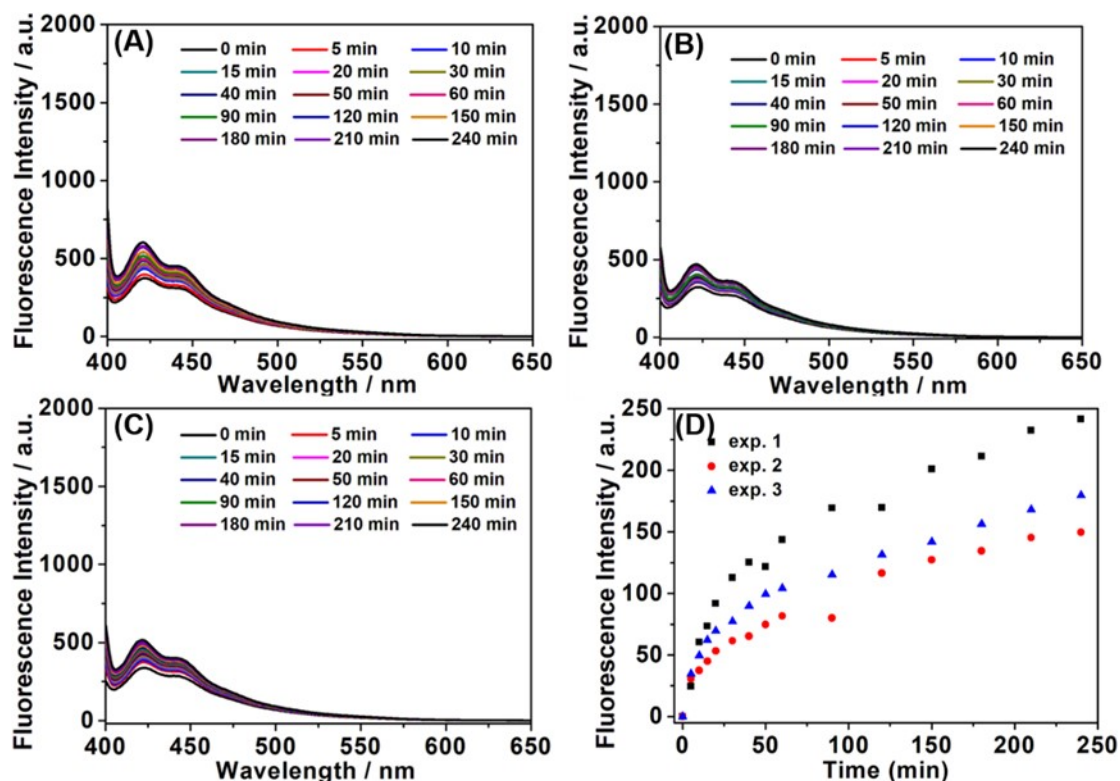


Figure S6. Fluorescence spectra as a function of sonication time for **P1** dissolved in DMF subjected to ultrasound (3-5 °C, ultrasonic mode: 1s on and 1s off); the related experiments were carried out three times: (A) data collected in the first experiment (exp. 1), (B) data collected in the second experiment (exp. 2), (C) data collected in the third experiment (exp. 3), (D) The maximum emission peak intensity (I_{\max}) increment (compared with the initial fluorescence intensity before sonication) against sonication time (time:0-240 min).

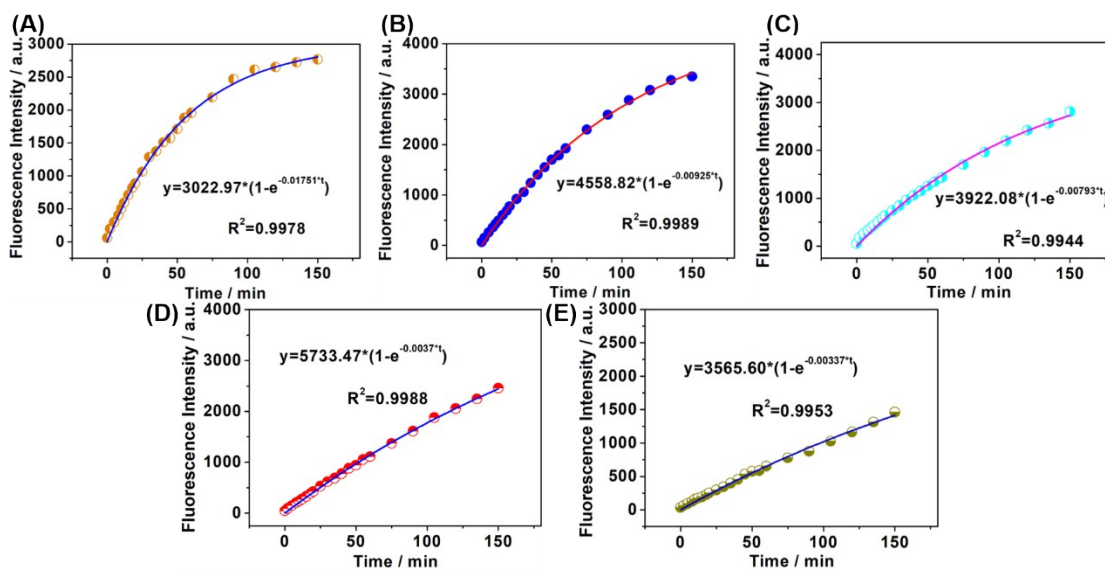


Figure S7. The corresponding maximum emission peak intensities (I_{\max}) against sonication time fitted to single-exponential equation $A_t = B(1 - e^{-kt})$ with different time constants for (A) P2, (B) P3, (C) P4, (D) P5 and (E) P6 solutions (time:0-150 min).

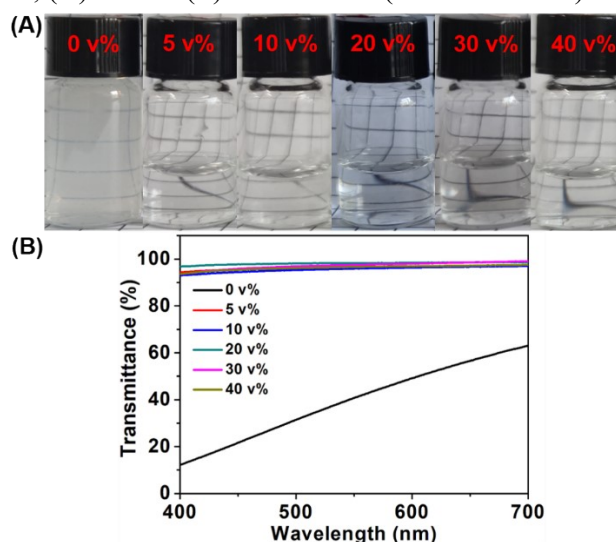


Figure S8. (A) The digital images of the P4' assembly solutions with various contents of DMF; (B) Transmittance profiles of the P4' assembly solutions with various contents of DMF before sonication.

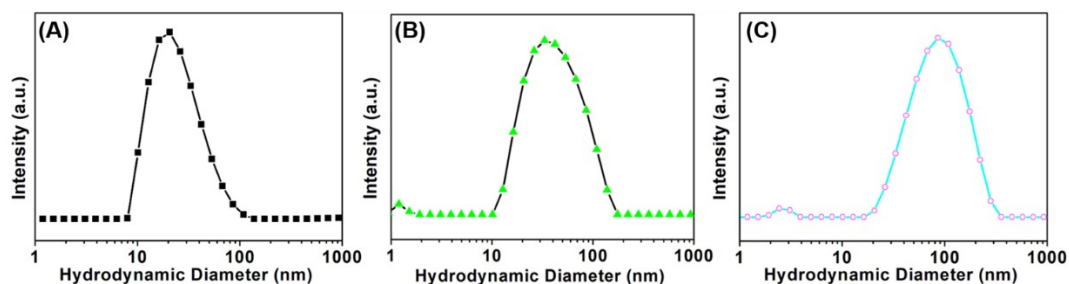


Figure S9. (A) The size distribution by DLS of P4' assemblies in (5 vol %) DMF/water mixed solvent; (B) the size distribution by DLS of P4' assemblies in (20 vol %) DMF/water mixed solvent; (C) the size distribution by DLS of P4' assemblies in (40 vol %) DMF/water mixed

solvent.

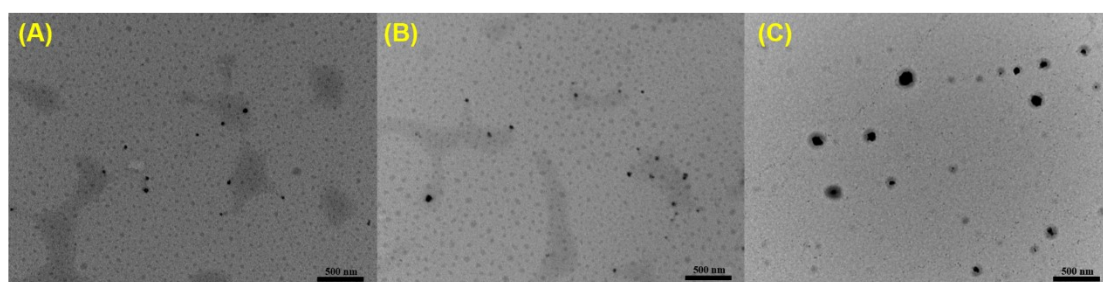


Figure S10 The size distribution by TEM images of **P4'** assemblies (A) in (5 vol %) DMF/water mixed solvent; (B) in (20 vol %) DMF/water mixed solvent; and (C) in (40 vol %) DMF/water mixed solvent.

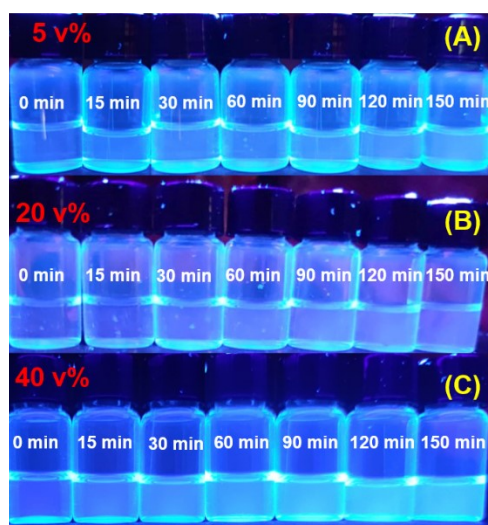


Figure S11. The dynamic photoluminescent photographs of **P4'** assemblies in (A) (5 vol %) DMF/water mixed solvent, (B) (20 vol %) DMF/water mixed solvent, and (C) (40 vol %) DMF/water mixed solvent taken after sonicating for different time (with the irradiation of 365 nm UV light).

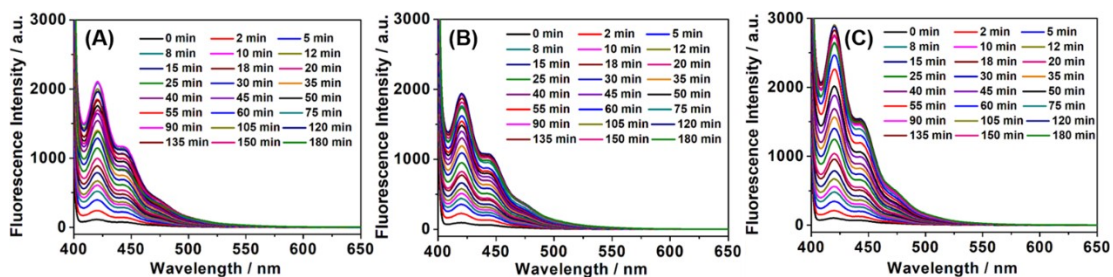


Figure S12. Fluorescence spectra as a function of sonication time for **P4'** assemblies in (A) (5 vol %) DMF/water mixed solvent, (B) (20 vol %) DMF/water mixed solvent, and (C) (40 vol %) DMF/water mixed solvent subjected to ultrasound (3-5 °C, ultrasonic mode: 1s on and 1s off).

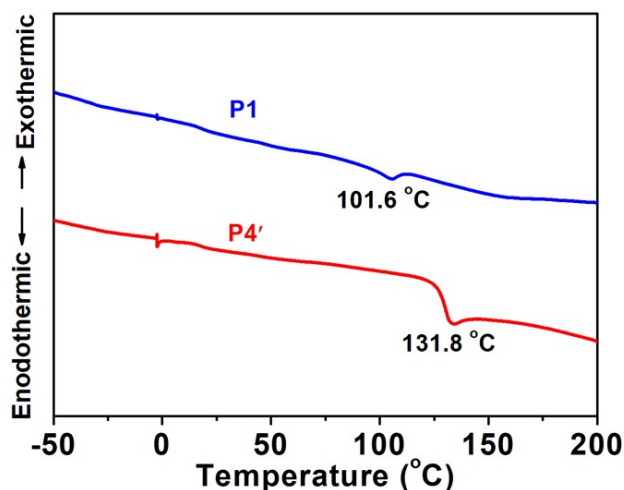


Figure S13. DSC curves of **P1** and **P4'** from -50 to 200 °C with a heating rate of 10 °C/min under N₂ atmosphere. T_g of 101.6 °C was attributed to the **Poly(AnMMA-DA-Br) (P1)**, whereas T_g of 131.8 °C was attributed to the **Poly (AnMMA-DA)-g-PAAc (P4')**.

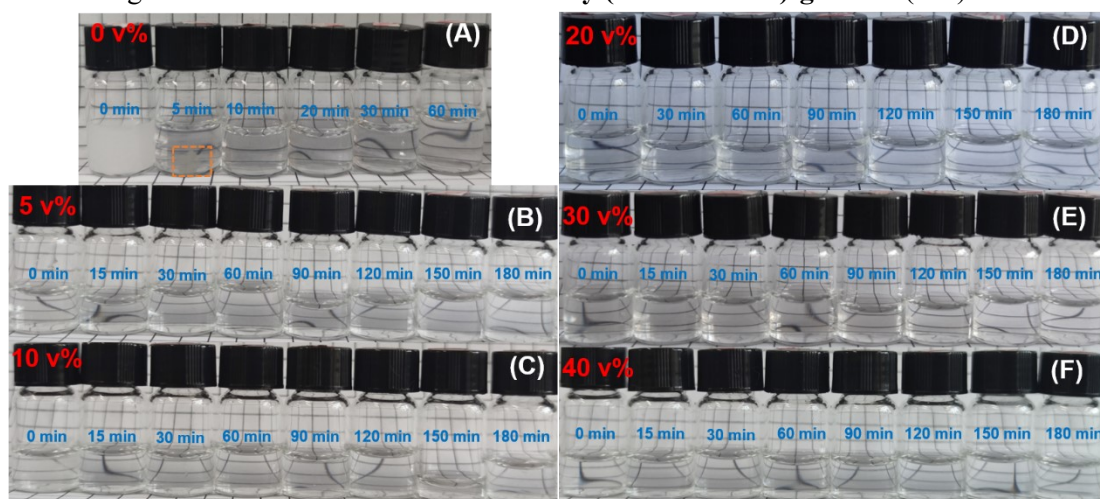


Figure S14. Digital images of **P4'** assemblies in (A) pure water, (B) (5 vol %) DMF/water mixed solvent, (C) (10 vol %) DMF/water mixed solvent, (D) (20 vol %) DMF/water mixed solvent, (E) (30 vol %) DMF/water mixed solvent, and (F) (40 vol %) DMF/water mixed solvent taken after sonicating for different time.

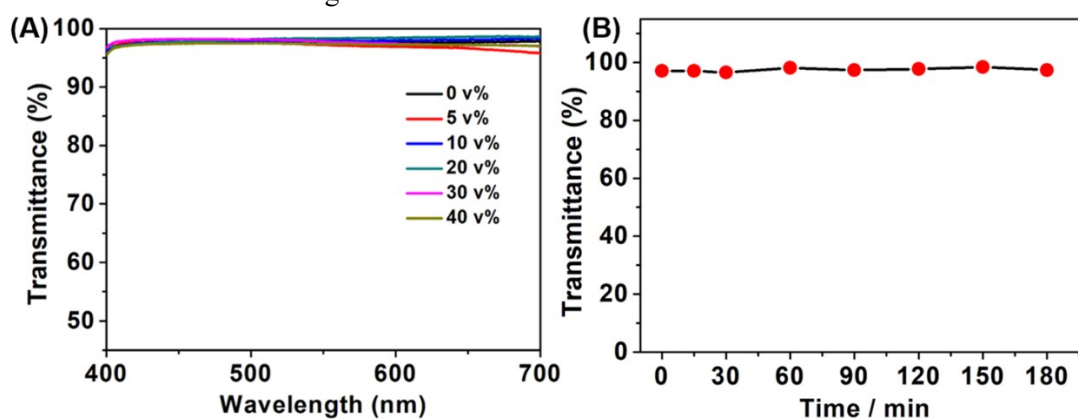


Figure S15. (A) Transmittance profiles of the **P4'** assembly solutions with various contents of DMF after sonicating for 180 min; (B) the stable high transmittance of **P4'** assembly solutions with (30 vol %) DMF/water over the sonication course.

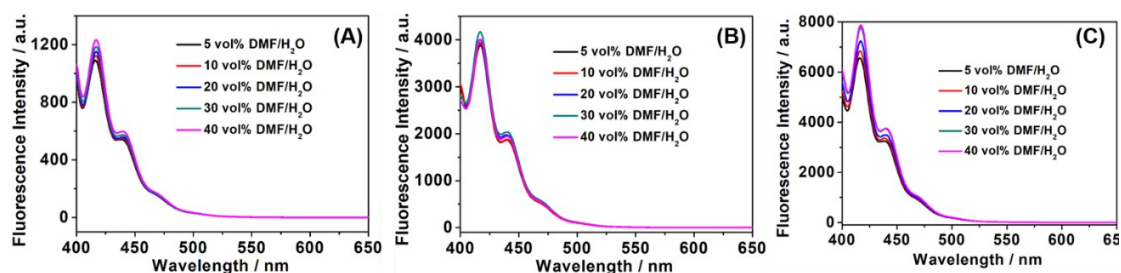


Figure S16. Fluorescence spectra as a function of DMF contents for free anthracene moieties (namely 9-anthracenemethanol) dissolved in DMF/water mixed solvent with a concentration of (A) 1.0 $\mu\text{g}/\text{mL}$, (B) 5.0 $\mu\text{g}/\text{mL}$, and (C) 10 $\mu\text{g}/\text{mL}$. Notation: the concentration of anthracene moieties embedded in the graft copolymer dissolved in the DMF/water mixture (0.8 mg/mL) was calculated to be about 3 $\mu\text{g}/\text{mL}$.

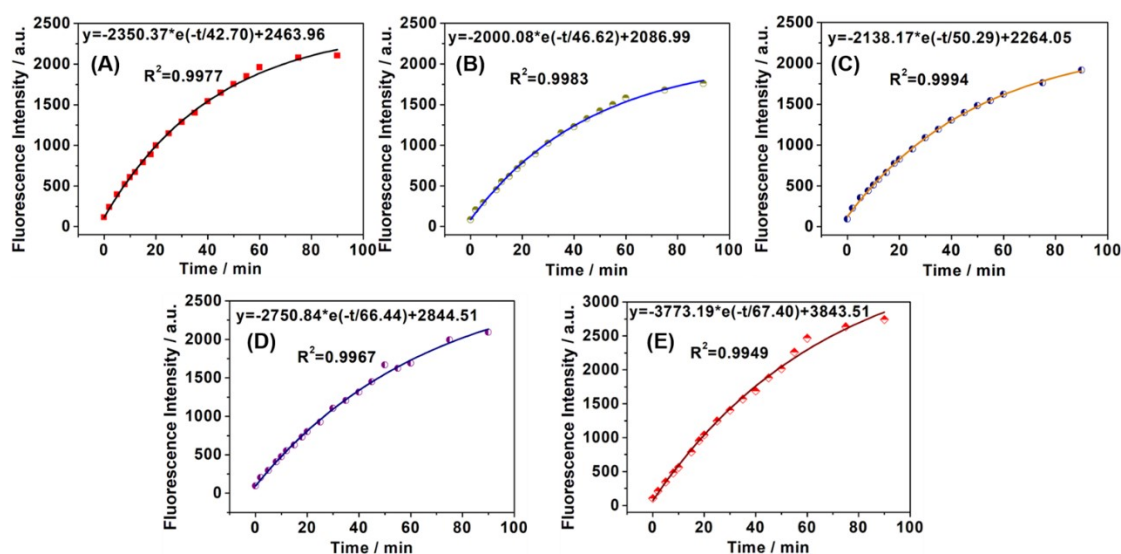


Figure S17. The corresponding maximum emission peak intensities (I_{max}) against sonication time fitted to single-exponential equation $A_t = B(1 - e^{-kt})$ with different time constants for **P4'** assemblies in (A) (5 vol %) DMF/water mixed solvent, (B) (10 vol %) DMF/water mixed solvent, (C) (20 vol %) DMF/water mixed solvent, (D) (30 vol %) DMF/water mixed solvent, and (E) (40 vol %) DMF/water mixed solvent taken after sonicating for different time.

References:

- S1: H. Y. Duan, Y. X. Wang, L. J. Wang, Y. Q. Min, X. H. Zhang, B. Y. Du, An Investigation of the Selective Chain Scission at Centered Diels–Alder Mechanophore under Ultrasonication, *Macromolecules* **2017**, *50*, 1353-1361.
- S2: K. J. Rodriguez, A. M. Hanlon, C. K. Lyon, J. P. Cole, B. T. Tuten, C. A. Tooley, E. B. Berda, S. Pazicni, Porphyrin-cored polymer nanoparticles: Macromolecular models for heme iron coordination, *Inorg. Chem.* **2016**, *55*, 9493-9496.
- S3: J. M. Bernal-García, A. Guzmán-López, A. Cabrales-Torres, A. Estrada-Baltazar,

G. A. Iglesias-Silva, Densities and Viscosities of (*N, N*-Dimethylformamide+ Water) at Atmospheric Pressure from (283.15 to 353.15) K. *J. Chem. & Eng. Data* **2008**, *53* (4), 1024-1027.

S4: C. Wohlfarth, Refractive Index of the Mixture (1) Water; (2) *N, N*-Dimethylformamide. In *Refractive indices of pure liquids and binary liquid mixtures* (supplement to III/38), Springer: 2008, pp 580-581.