

SUPPORTING INFORMATION

Aggregation-Induced Emission Block Copolymers Based on Ring-Opening Metathesis Polymerization

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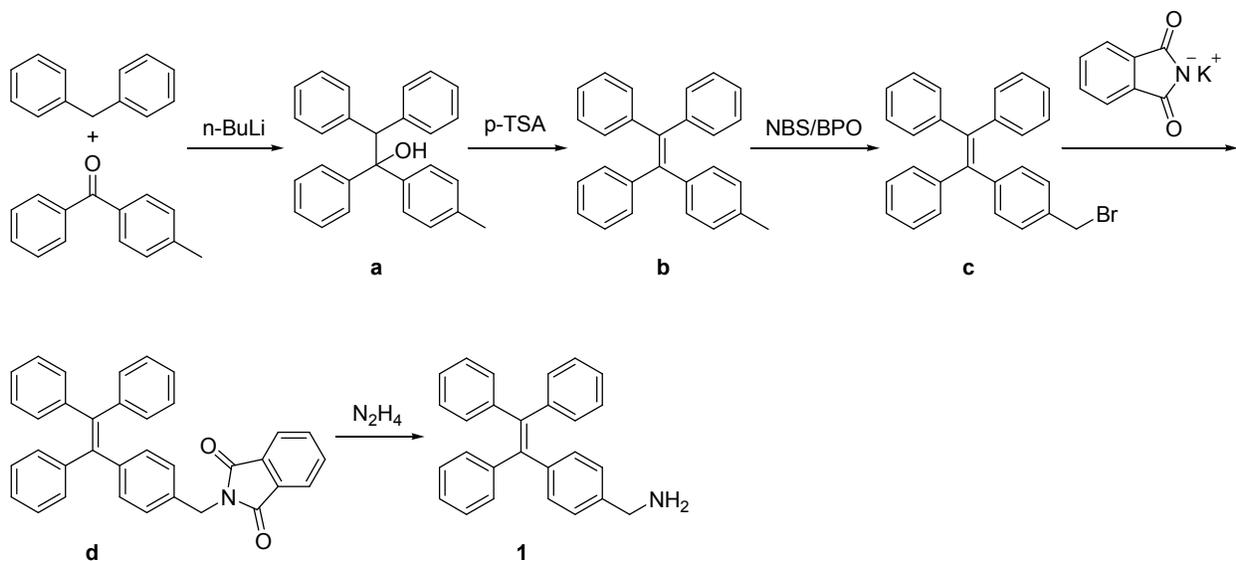
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Experimental

Preparation of Compound 1

Compound 1 was synthesized according to the literature^{1,2} and detailed as follows.



Compound a and b:

Diphenylmethane (10.00 g, 59.52 mmol) was dissolved in dry THF (60 mL) under N_2 . After cooling to $0\text{ }^\circ\text{C}$, $n\text{-BuLi}$ (2.4 M in hexane) (23.60 mL, 56.64 mmol) was slowly added by a syringe. After stirring the reaction for 1 h at $0\text{ }^\circ\text{C}$, 4-methylbenzophenone (11.11g, 56.68 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for 6 h. After that, the reaction was quenched with saturated NH_4Cl solution and extracted with DCM. The organic layers were collected and concentrated to produce the crude product **a**, which was used without further purification and characterization in the next reaction step. The resultant crude product **a** and 1.00 g $p\text{-TSA}$ were dissolved into 150 mL toluene. The mixture was heated to reflux for overnight. After cooled down to room temperature, the reaction mixture was extracted

with DCM. The organic layer was collected and concentrated. The crude product was purified by a silica gel column with petroleum ether/ethyl acetate (50/1, v/v) as eluent to provide the white solid product **b** (10.56 g, 53.82 % yield). ¹H-NMR (CDCl₃), δ (ppm): 7.15 - 7.06 (m, 9H), 7.06-6.98 (m, 6H), 6.90 (s, 4H), 2.25 (s, 3H).

Compound c:

Compound **b** (10.56 g, 30.52 mmol), NBS (5.97 g, 33.54 mmol), and BPO (0.15 g, 0.61 mmol) were dissolved in 120 mL CCl₄. After refluxing the mixture for 12 h, the crude reaction mixture was evaporated under reduced pressure and purified by a silica gel column with petroleum ether/ethyl acetate (50/1, v/v) as eluent to provide the white solid product **c** (12.16 g, 93.75 % yield). ¹H-NMR (CDCl₃), δ (ppm): 7.15-7.06 (m, 11H), 7.05-6.96 (m, 8H), 4.41(s, 2H).

Compound d:

Compound **c** (12.00 g, 28.23 mmol) and N-potassium phthalimide (6.27 g, 33.85 mmol) were dissolved in 80 mL DMF and stirred at room temperature for 12 h. After adding 150 mL CHCl₃, the mixture was washed with 0.2 M NaOH solution and then by saturated NaCl aqueous solution. The organic phase was collected and dried over anhydrous MgSO₄ and then concentrated. The crude product was purified by a silica gel column with DCM as eluent to provide the white solid product **d** (12.78 g, 92.21 % yield). ¹H-NMR (CDCl₃), δ (ppm): 7.87-7.82 (m, 2H), 7.73-7.68 (m, 2H), 7.12-7.03 (m, 11H), 7.03-6.92 (m, 8H), 4.75(s, 2H).

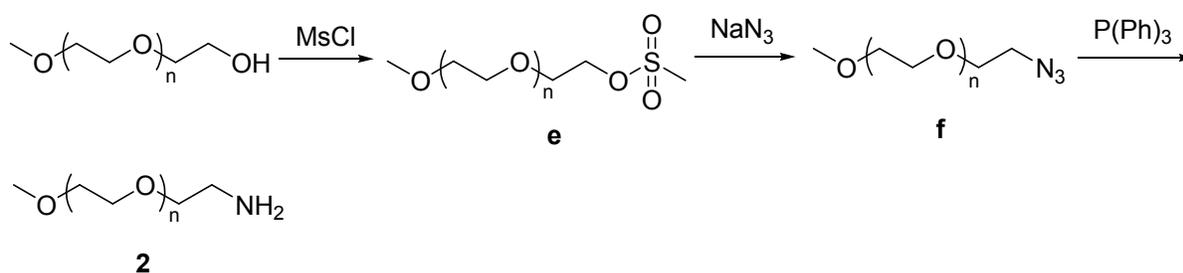
Compound 1:

Compound **d** (12.75 g, 25.97 mmol) and N₂H₄ (80 wt.% solution in H₂O, 4.73 mL) were dissolved in the mixture of THF (150 mL) and C₂H₅OH (20 mL). After refluxing the mixture for

12 h, the crude mixture was evaporated under reduced pressure to remove THF and C₂H₅OH. The crude solid was then dissolved in 200 mL DCM and filtered. The filtrate was concentrated and then purified by a silica gel column with DCM/CH₃OH (10/1, v/v) as eluent to provide the white solid product **e** (7.24 g, 77.27 % yield). ¹H-NMR (CDCl₃), δ (ppm): 7.12–7.05 (m, 11H), 7.03–6.95 (m, 8H), 3.85 (s, 2H).

Preparation of PEG₇₅₀-NH₂ (**2**)

PEG₇₅₀-NH₂ (**2**) was synthesized according to the literature³ and detailed as follows.



PEG₇₅₀-Ms (**e**)

PEG₇₅₀-OH (15.00 g, 20.00 mmol) and TEA (6.07 g, 60.00 mmol) were dissolved in 40 mL DCM at 0 °C, to which MsCl (6.87 g, 60.00 mmol) in 20 mL DCM was dropwise. Subsequently, the reaction was stirred at room temperature for 24 h. The mixture was washed with saturated salt water (3×20 mL). The DCM phase was concentrated and precipitated in diethyl ether at -10 °C three times to obtain the PEG₇₅₀-Ms (**f**) (14.86 g, 89.63 % yield). ¹H-NMR (CDCl₃), δ (ppm): 4.38 (m, 2H), 3.77-3.52 (m, 62H), 3.37 (s, 3H), 3.07 (s, 3H).

PEG₇₅₀-N₃ (**f**)

NaN₃ (11.65 g, 179.30 mmol) was added to the solution of PEG₇₅₀-Ms (14.86 g, 17.93 mmol) in 35 mL DMF. The reaction was performed at 45 °C for 48 h. After passing through an alumina column to remove the residual NaN₃, 100 mL DCM and 50 mL water were added to the mixture and the two phases were separated. The DCM phase was concentrated and precipitated in diethyl ether at -10 °C three times to obtain the PEG₇₅₀-N₃ (7.07 g, 52.60 % yield). ¹H-NMR (CDCl₃), δ (ppm): 3.70-3.59 (m, 62H), 3.56-3.52 (m, 2H), 3.38 (s, 3H).

PEG₇₅₀-NH₂ (2)

PEG₇₅₀-N₃ (6.31 g, 8.41 mmol) was dissolved in 30 mL THF at 0 °C and P(Ph)₃ (11.03 g, 42.06 mmol) in 20 mL THF was dropwised. After reacting at room temperature for 12 h, 5 mL H₂O was added and stirred for 12 h. The mixture was concentrated under reduced pressure and then purified through a short silica gel column to remove most of the residual P(Ph)₃. After that, the collected product was precipitated in diethyl ether at -10 °C three times to obtain the PEG₇₅₀-NH₂ (3.00 g, 47.54 % yield). ¹H-NMR (CDCl₃), δ(ppm): 3.70-3.59 (m, 62H), 3.56-3.52 (m, 2H), 3.38 (s, 3H).

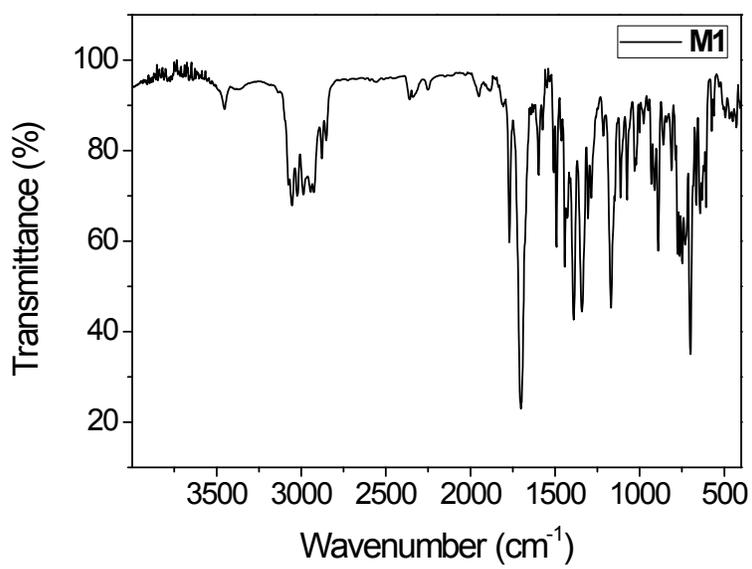


Figure S1. FT-IR spectrum of **M1**.

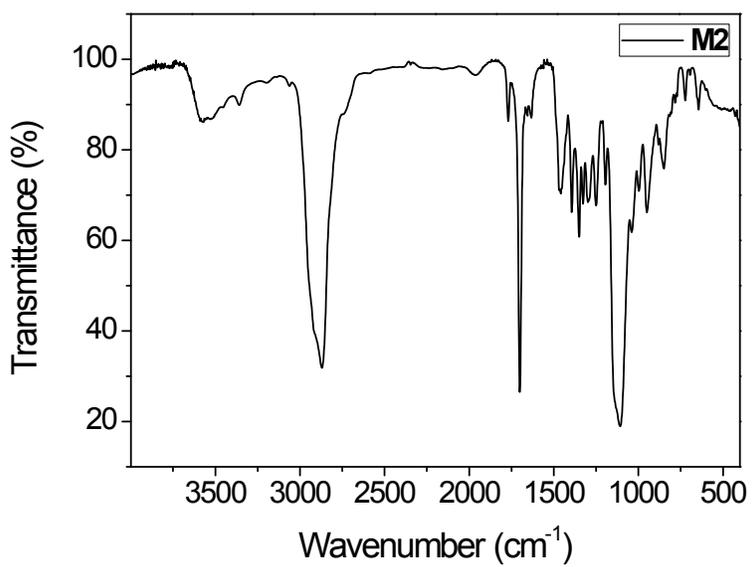


Figure S2. FT-IR spectrum of **M2**.

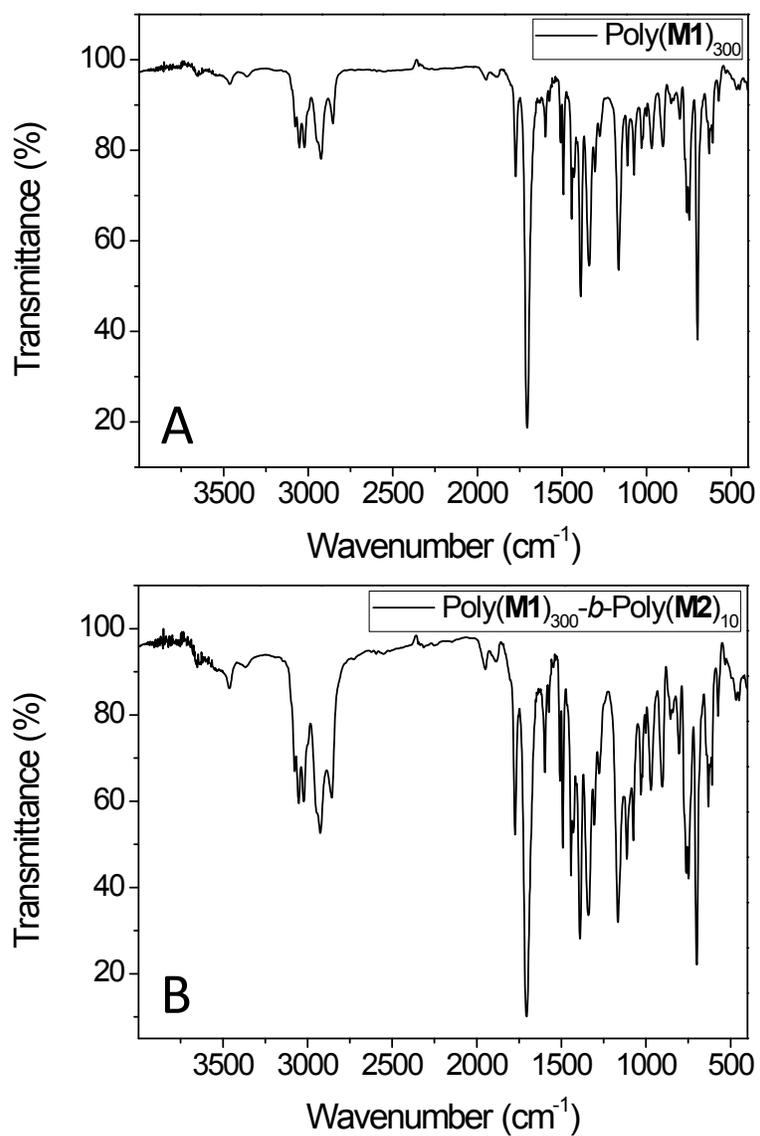


Figure S4. FT-IR spectrum of poly(M1)₃₀₀ (A) and poly(M1)₃₀₀-*b*-poly(M2)₁₀ (B).

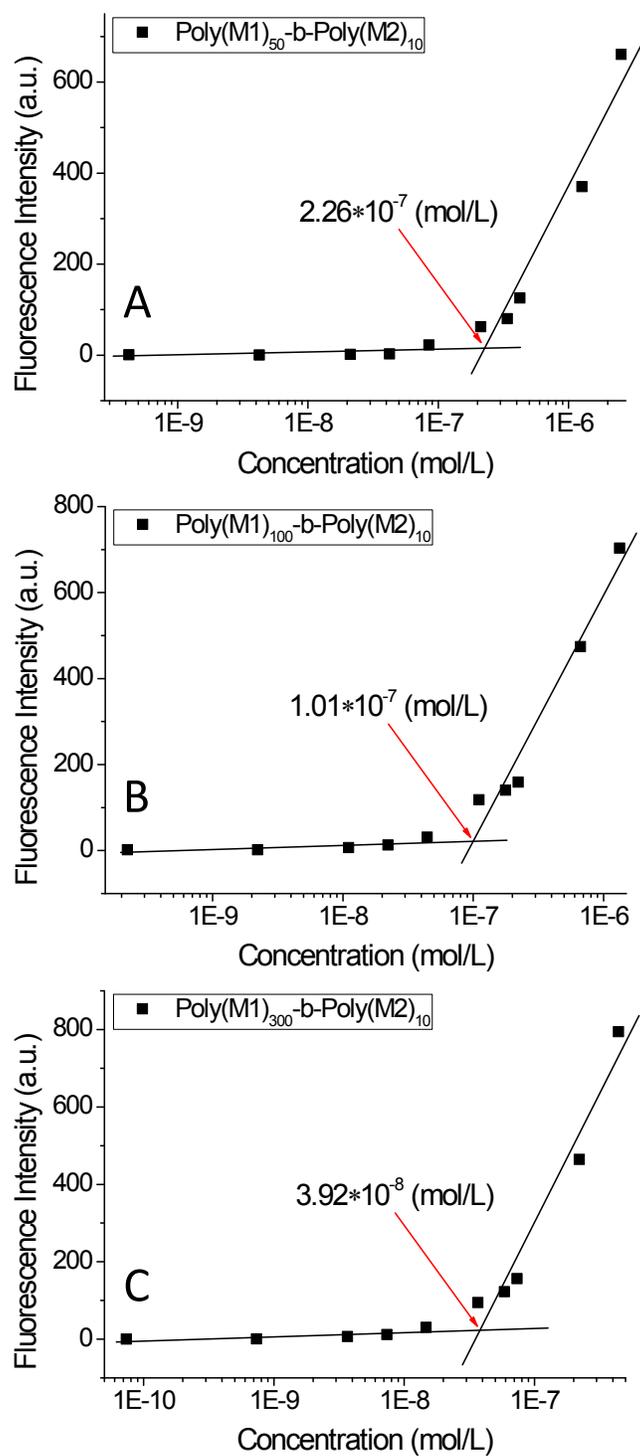


Figure S5. Determination of the critical micellar concentration using fluorescence spectroscopy for poly(M1)₅₀-b-poly(M2)₁₀ (A), poly(M1)₁₀₀-b-poly(M2)₁₀ (B), and poly(M1)₃₀₀-b-poly(M2)₁₀ (C).

References

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- (2) K. Rajagopalan, A. J. Chavan, B. E. Haley and D. S. Watt, *J. Biol. Chem.*, 1993, 268, 14230-14238.
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