Electronic Supplementary Information (ESI)

Regulating Morphology and Size of Homopolypeptide Self-assembles Via Selective Solvents

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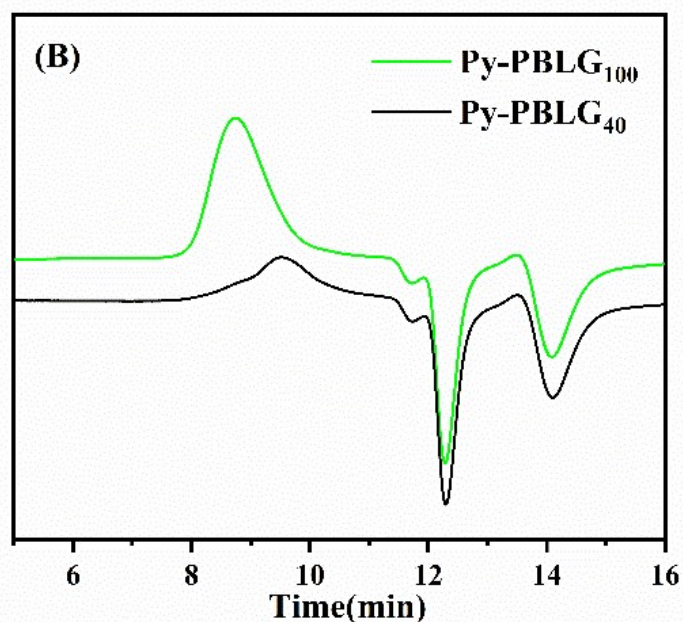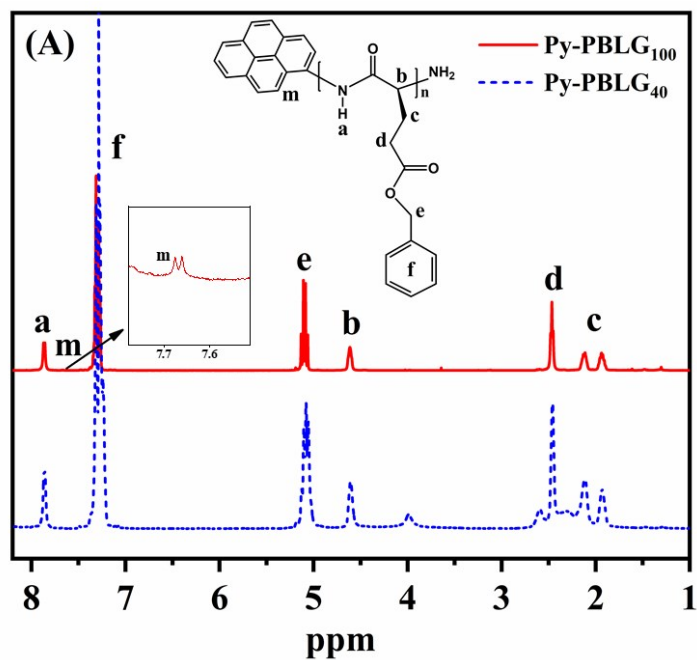
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1. The synthesis route of Py-PBLG$_n$
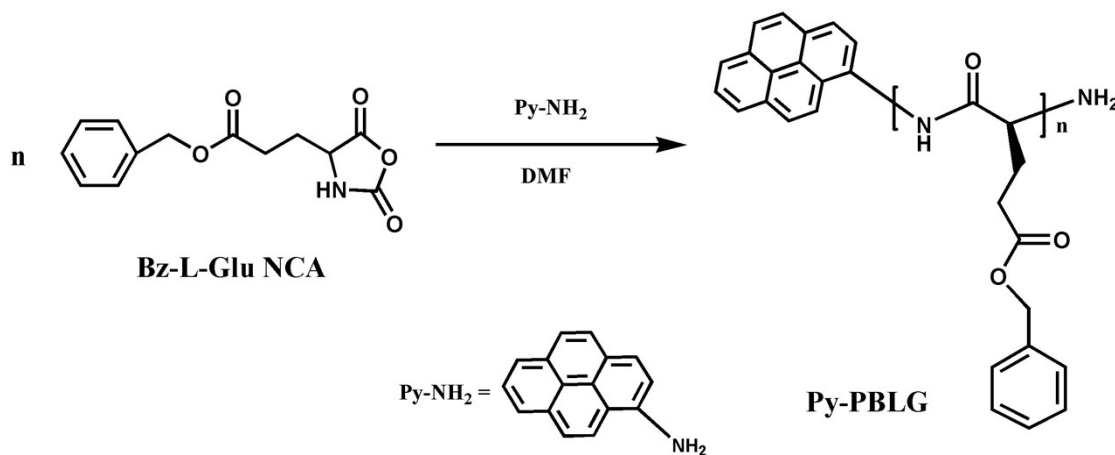
Scheme S1. Synthesis route of Py-PBLG$_n$ (n=100 and 40)

2. Results and Analysis

Figure S1. ^{1}H NMR spectra (A) and GPC curves (B) of Py-PBLG$_n$ (n=100 and 40).

Fig. S1(A) shows ^{1}H NMR spectra of Py-PBLG$_n$ (n=100 and 40) in CDCl$_3$ with 15% TFA.

The resonance signals of the protons of amide group (Fig. S1A: a), pyrene group (Fig. S1A: m),

phenyl group (Fig. S1A: f), methylene group of benzyl (Fig. S1A: e), α-methine group (Fig. S1A: b), and β- and γ-methylene groups (Fig. S1A: c and d) appear at 7.88,7.67, 7.33, 5.08, 4.61 and 2.15-1.93 ppm, respectively. The DP value of Py-PBLG can be obtained by integral ratio of protons from the pyrene group at 7.67 ppm (Fig. S1A: m) to the methylene groups of benzyl at 5.08 ppm (Fig. S1A: e) or the α-methine groups at 4.61 ppm (Fig. S1A: b), which are consistent within the experimental error of ^{1}H NMR measurement. By controlling the molar ratio of the initiator Py-NH$_2$ to monomer BLG-NCA, two samples with different DP values (n=100 and 40) (see Table S1) can be prepared.

The GPC curves of Py-PBLG$_n$ (n=100 and 40) are unimodal and symmetrical, clearly shifting toward the higher molecular weight region with increasing the DP of Py-PBLG, as shown in Fig. S1: B. The obtained results are listed in Table S1 and the molecular weight distributions (Mw/Mn) are narrow (~1.30)

Table S1. characteristics of homopolypeptides

| Sample	[a] M_n (g/mol)	[a] DP	[b] PDI
Py-PBLG$_{100}$	21 000	100	1.10
Py-PBLG$_{40}$	9 000	40	1.30

a. Determined by GPC.

b. Determined by ^{1}H NMR.
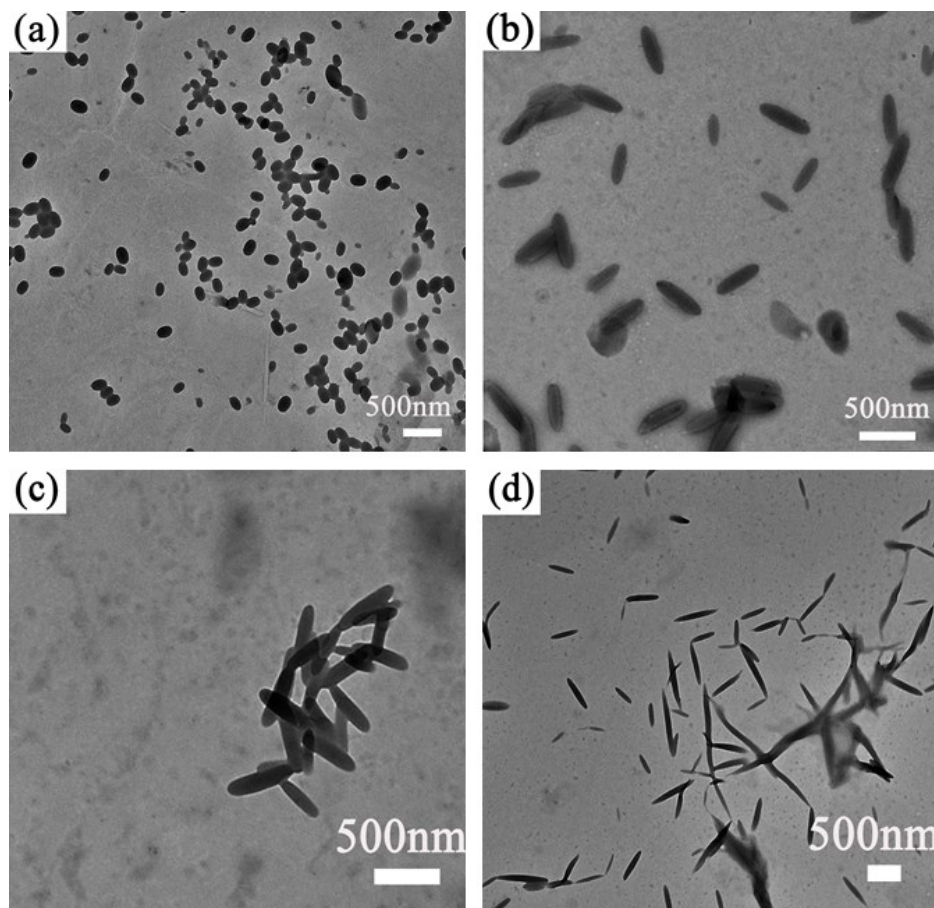
Figure S2. TEM images of the aggregate self-assembled from Py-PBLG$_{100}$ with various volume fraction of methanol: (a) 0, (b) 50%, (c)75%, (d) 87%.

Figure S2 shows TEM images of the aggregates self-assembled from Py-PBLG$_{100}$. It is obvious that the length of the spindle-like micelles increases with the increase of the methanol content in the selective cosolvents.
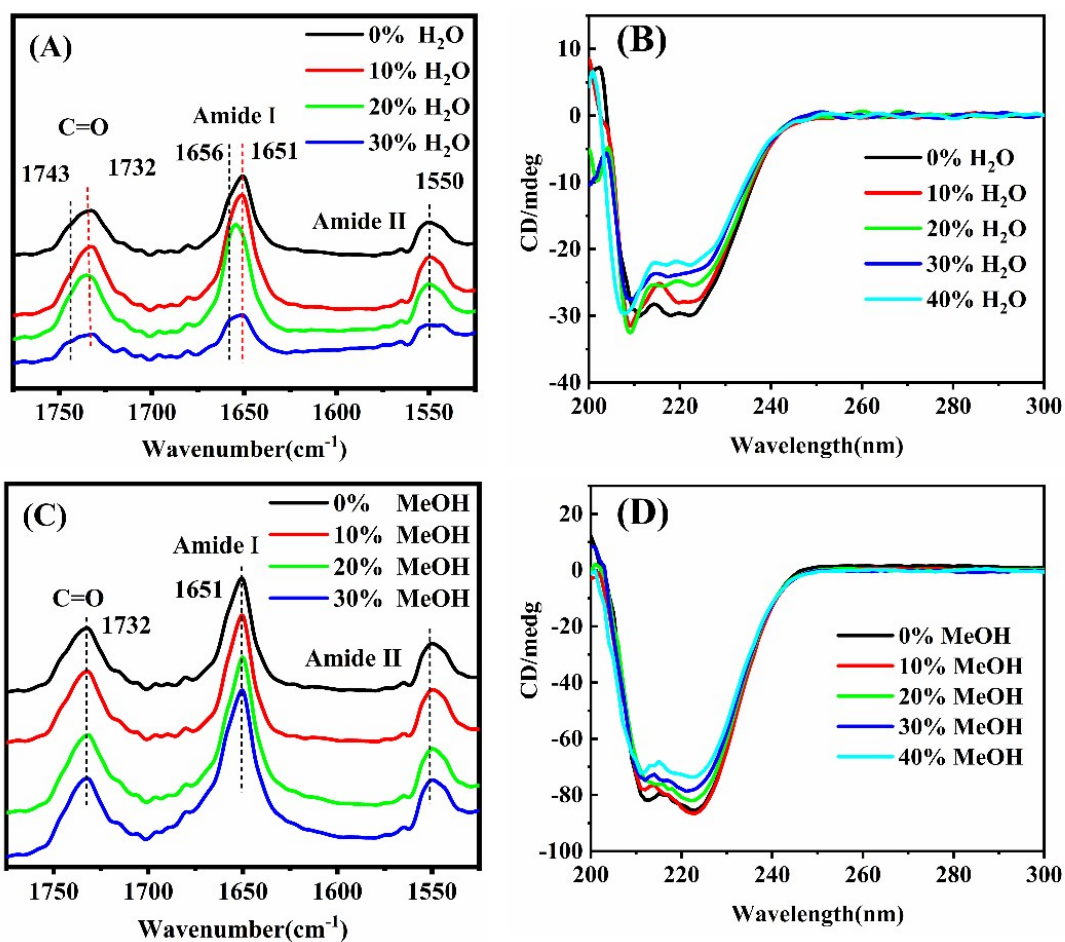
Figure S3. FT-IR spectra of Py-PBLG$_{40}$ in THF (2.0 mg/mL) with the different amount of D$_2$O (A) and methanol (C), respectively. CD spectra of the Py-PBLG$_{40}$ in THF (0.5 mg/mL) with the different amount of H$_2$O (B) and methanol (D), respectively
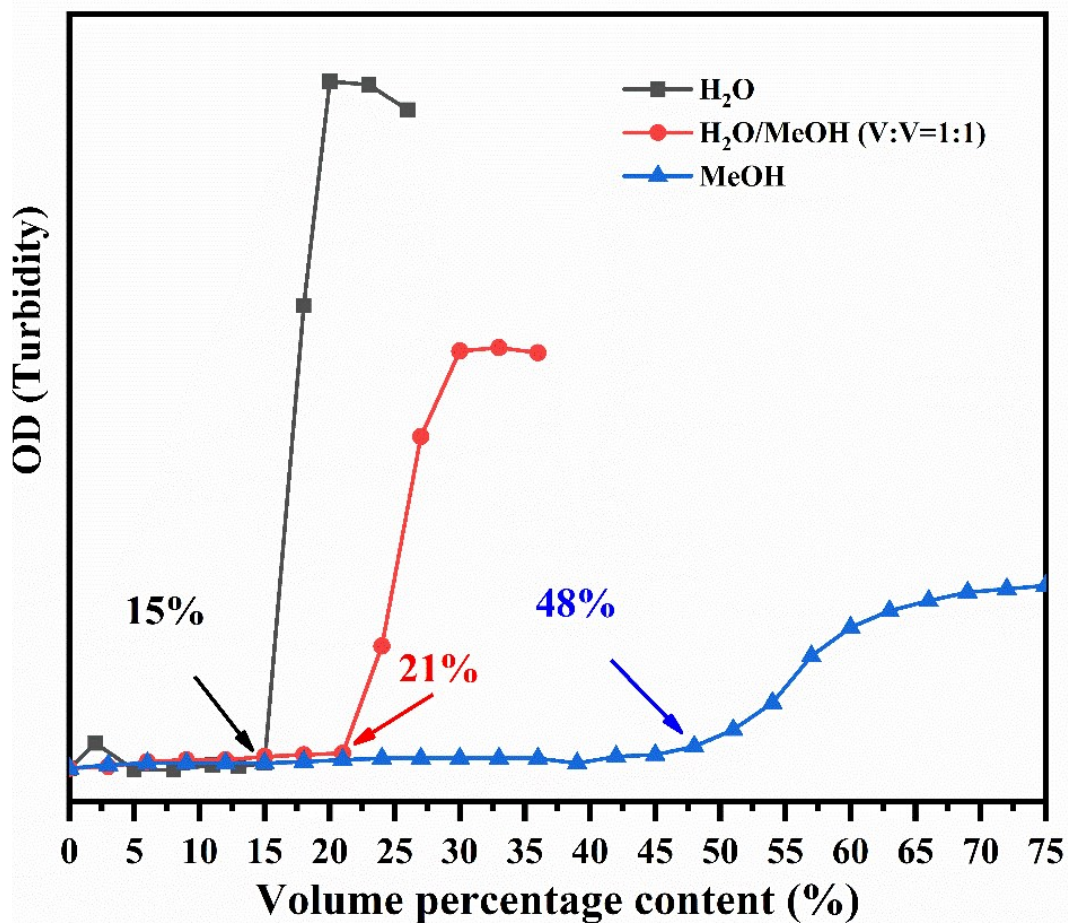
Figure S4. Turbidity (optical density) curves of Py-PBLG$_{100}$ with the amount of the addition selective solvents.

UV−Vis spectroscopy was used to monitor the variation of the turbidity of the solution during the self-assembly. The turbidity increases rapidly when the water content is ~15%, indicating the onset of self-assembly and that the critical water content (CWC) is around 15%. According to the same condition, the values of the critical H$_2$O/MeOH content and the critical methanol content were obtained as ~21% and ~48%, respectively, by changing the selective solvents.