Electronic Supplementary information (ESI)

Disk-like micelles with cylindrical pores from amphiphilic polypeptide block copolymers

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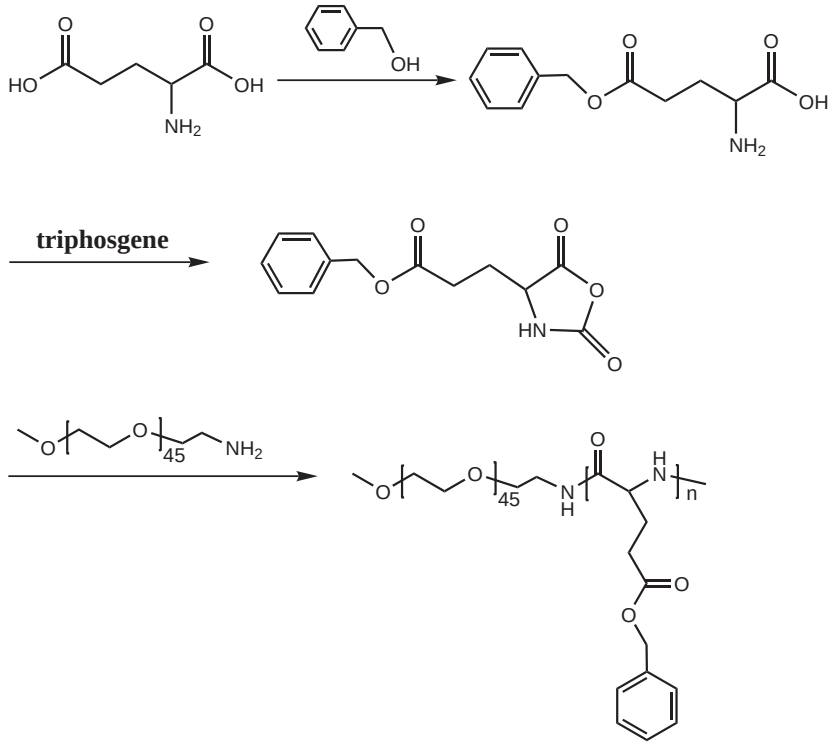
1. The synthesis routes of poly(ethylene glycol)-*block*-poly(γ-benzyl-L-glutamate) (PEG-*b*-PBLG)



Scheme 1 The synthesis of PEG-*b*-PBLG diblock copolymers.

2. Results and Analysis

2.1 Chemical structures of PEG-*b*-PBLG block copolymer

The obtained block copolymers were characterized by the combination techniques of ^{1}H NMR, FT-IR and GPC.

Fig. 1S shows ^{1}H NMR spectrum of PEG_{45}-*b*-$PBLG_{150}$ in $CDCl_3$ with 15% TFA. The resonance signals of the protons of amide group (Fig. 1S: d), phenyl group, methylene group of benzyl (Fig. 1S: g), α-methine group (Fig. 1S: c), and β- and γ-methylene groups (Fig. 1S: e and f) appeared at 7.88, 7.30, 5.04, 4.53 and 2.45-1.94 *ppm*, respectively. The signals originating from the PEG block at 3.80 and 3.52 *ppm* (Fig. 1S: b and a) were clearly observed at Fig. 1S. The DP value of 150 can be obtained by integral ratio of protons from the methoxy group at 3.52 ppm (Fig. 1S: a) to the methylene groups of benzyl at 5.04 ppm (Fig. 1S: g) or

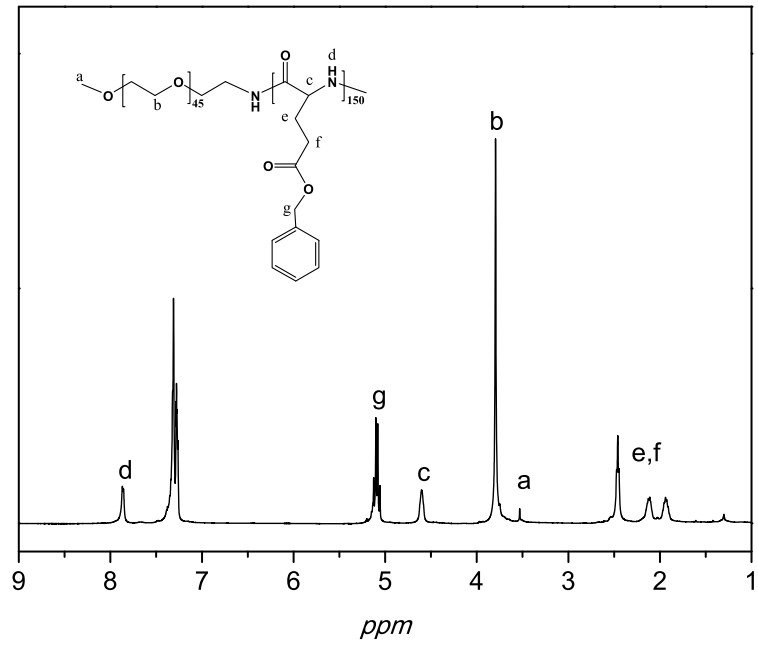


Fig. S1 ^{1}H NMR spectrum of PEG_{45}-*b*-$PBLG_{150}$ diblock copolymer in $CDCl_3$+15% TFA

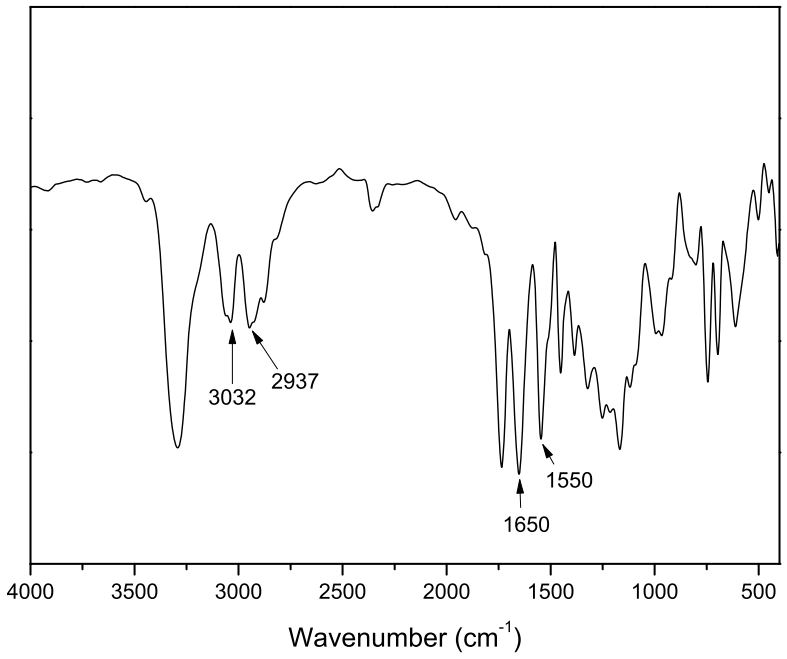


Fig. S2 FT-IR spectrum of PEG_{45}-*b*-$PBLG_{150}$ diblock copolymer

The α-methine groups at 4.53 ppm (Fig. 1S: c), which are consistent within the experimental error of ^{1}H NMR measurement. By controlling the molar ratio of the initiator mPEG-NH_2 to monomer BLG-NCA, Four samples with different DP values (n=80, 150, 200 and 250) can be prepared. At the same time, the characteristic absorption peaks of the amide bonds originated from polypeptide chain at 1650 and 1550 cm^{-1} and those originated from PEG block at 3032

and 2937 cm^{-1} can be clearly observed in the FT-IR spectrum of PEG_{45}-*b*-$PBLG_{150}$, as shown in Fig. 2S.

The GPC curves of diblock copolymers PEG-*b*-PBLG are unimodal and symmetrical, clearly shifting toward the higher molecular weight region with increasing the DP of the PBLG block, as shown in Fig. 3S. The obtained results are listed in Table S1 and the molecular weight distributions (M*w*/M*n*) are narrow (~1.30).

Table S1. Characterization of the Synthesized Diblock Copolypeptides

Samples	[a] M_n(g.mol^{-1})	[a] M_w/M_n	[b] DP
PEG_{45}-*b*-$PBLG_{80}$	15 200	1.18	80
PEG_{45}-*b*-$PBLG_{150}$	17 800	1.23	150
PEG_{45}-*b*-$PBLG_{200}$	18 600	1.28	200
PEG_{45}-*b*-$PBLG_{250}$	20 500	1.31	250

a) Determined by GPC in DMF-LiBr (0.01mol L^{-1}) with calibrated PMMA standards at 35 ^{o}C; b) Determined by ^{1}H NMR.

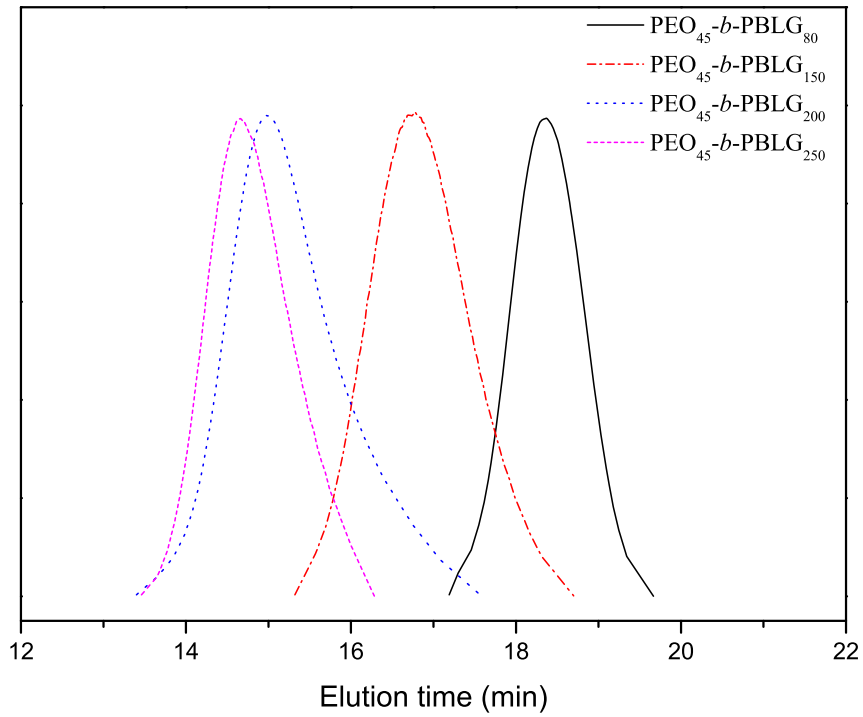


Fig. S3 GPC traces of PEG_{45}-*b*-$PBLG_{80}$, PEG_{45}-*b*-$PBLG_{150}$, PEG_{45}-*b*-$PBLG_{200}$ and PEG_{45}-b-$PBLG_{250}$ diblock copolymers.

2.2 Self-assembly of PEG-*b*-PBLG block copolymer

2.2.1 CD and Attenuated total reflectance (ATR)-FTIR

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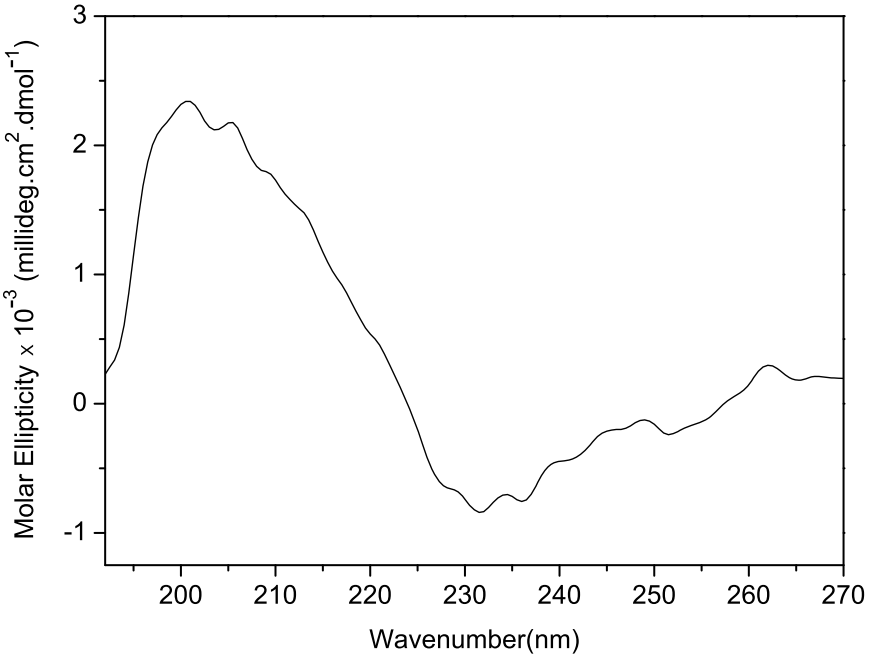


Fig. S4 Circular Dichroism (CD) spectrum of PEG_{45}-*b*-$PBLG_{150}$ after self-assembly in water

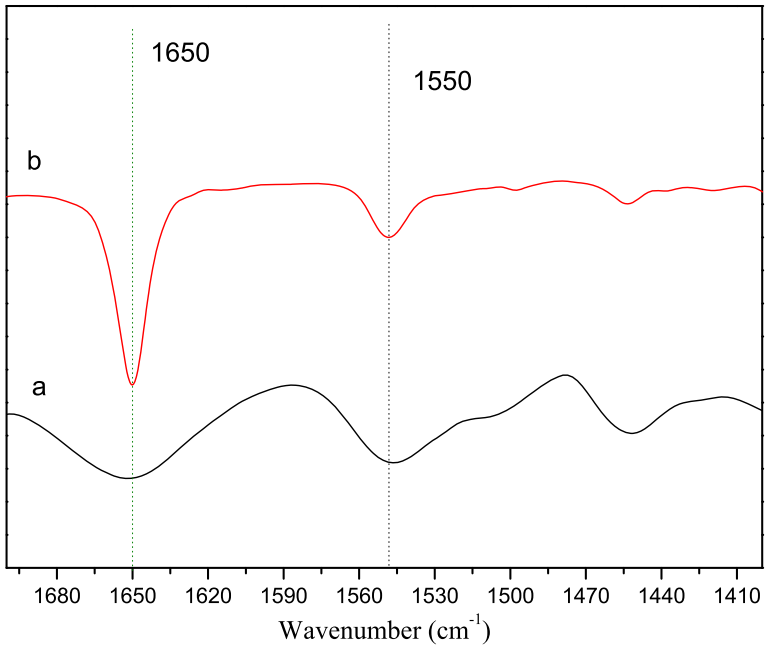


Fig. S5 ATR-FTIR spectra of PEG_{45}-*b*-$PBLG_{150}$ in solid and assembled states: (a) disk-like micelle aqueous suspension; (b) solid powders. Amide I band (1650 cm^{-1}) and amide Π band (1550 cm^{-1}) in all samples indicate α-helical conformation.

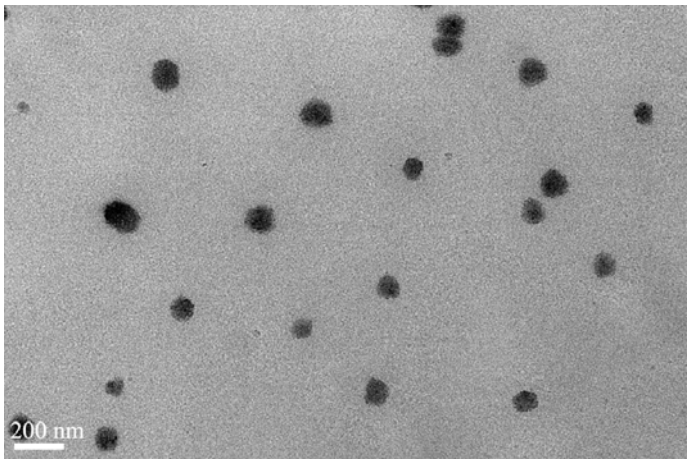
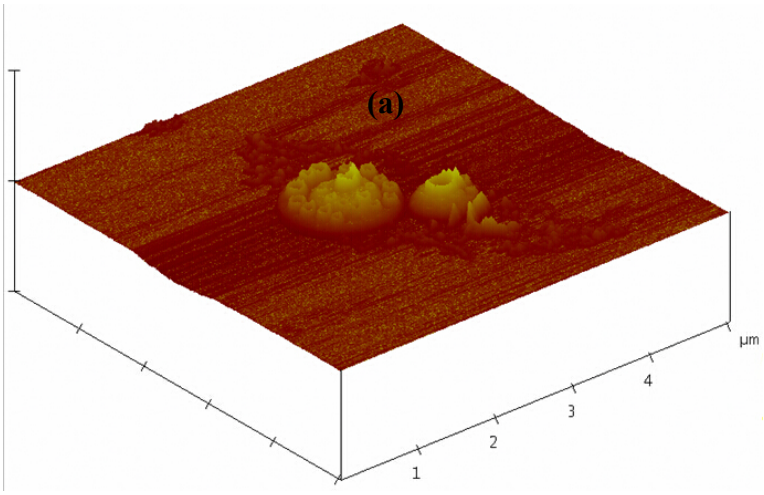


Fig. 6S TEM image of PEG_{45}-*b*-$PBLG_{150}$ from TFA/THF mixture solvent



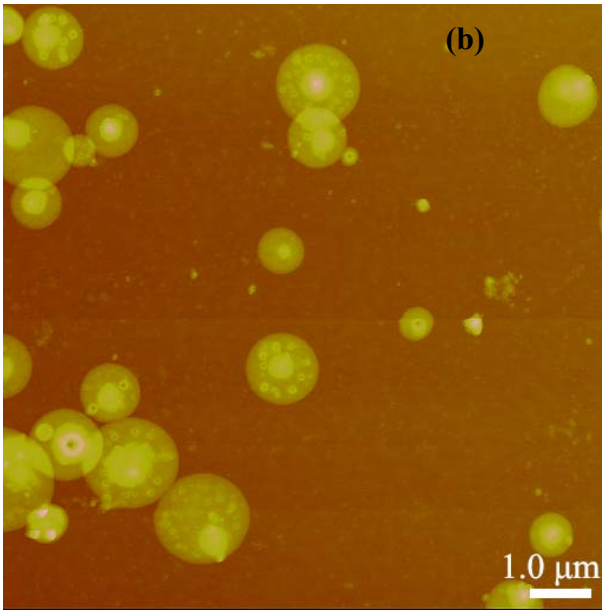


Fig. 7S AFM image of disk-like micelles self-assembled from PEG_{45}-*b*-$PBLG_{150}$: (a), 3D image and (b) tapping mode height image.

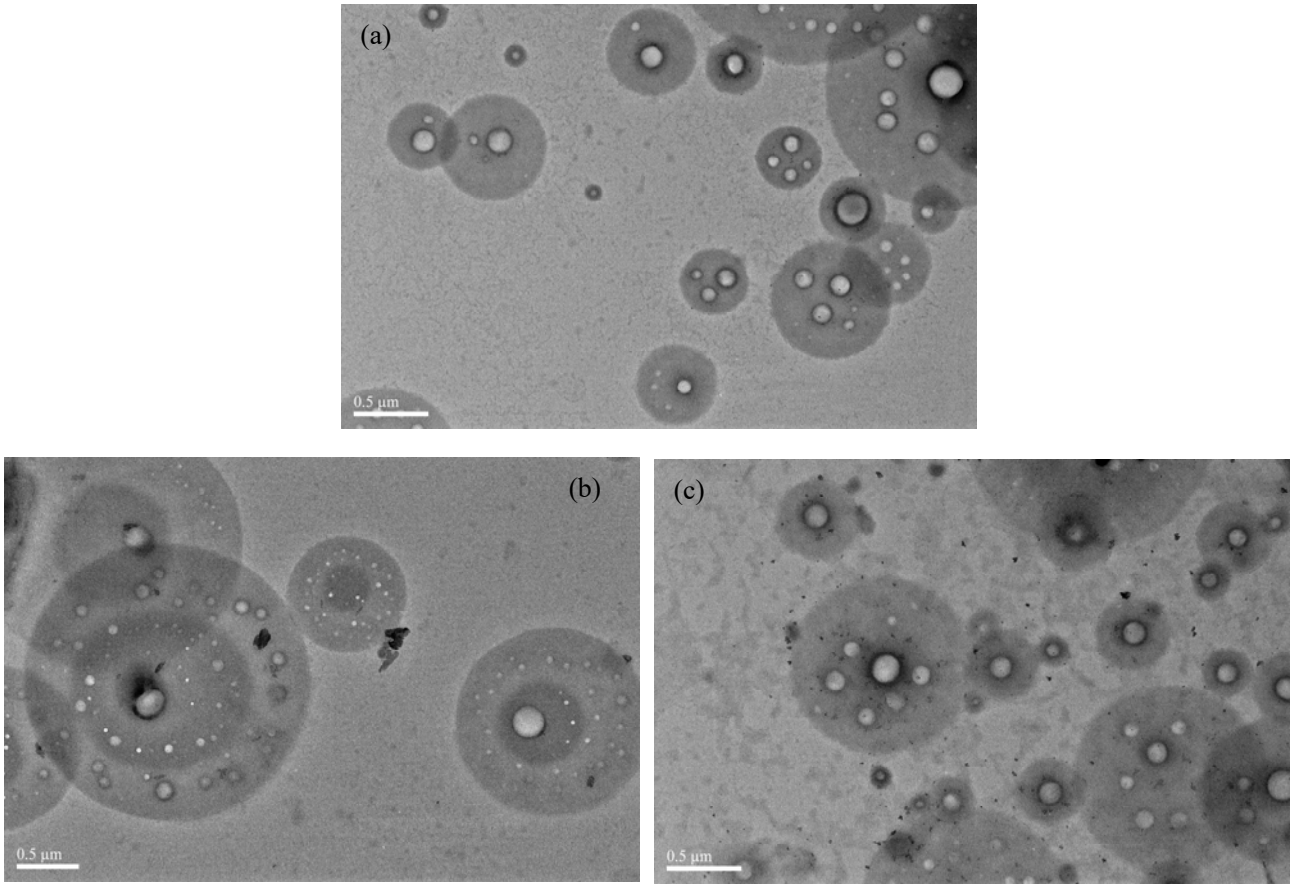


Fig. 8S TEM images of the aggregate specimen of PEG_{45}-*b*-$PBLG_{150}$ from three different preparation methods: (a) drying under vacuum, (b) drying under ambient conditions and (c) freeze-drying

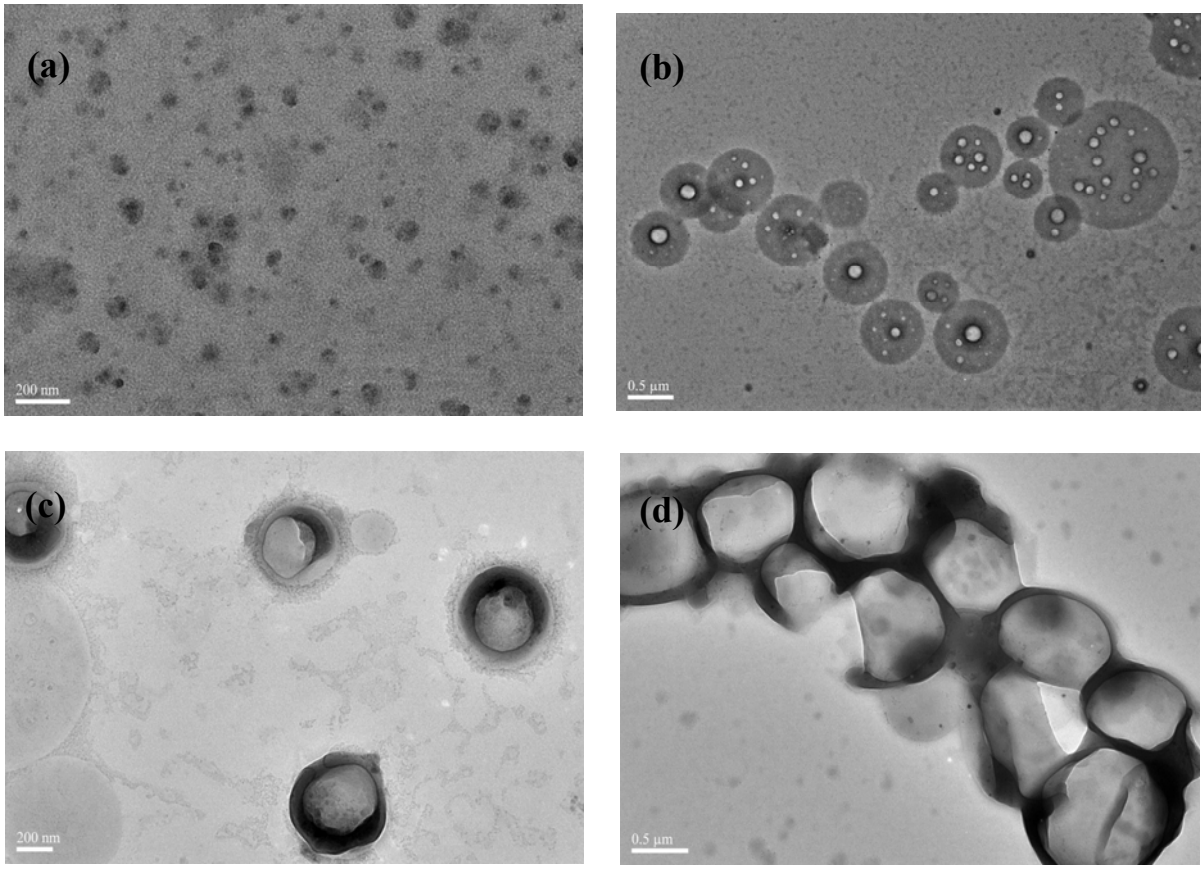


Fig. 9S TEM images of the aggregates obtained from PEG-*b*-PBLG block copolymers with different DP of PBLG blocks: (a) spherical micelles self-assembled from PEG_{45}-*b*-$PBLG_{80}$, (b) porous disk self-assembled from PEG_{45}-*b*-$PBLG_{150}$, (c) vesicles self-assembled from PEG_{45}-*b*-$PBLG_{200}$ and (d) Large vesicles self-assembled from PEG_{45}-*b*-$PBLG_{250}$.