Polymer Chemistry

Accepted Manuscript

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Polymer Chemistry

www.rsc.org/polymers

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

Journal Name

ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xue Lin,[a] Xiaohua He,[a*] Chaoqun Hu,[a] Yuxiang Chen,[a] Yiyong Mai [b*] and Shaoliang Lin [c*]

An unprecedented two-dimensional (2D) disk-like micelle with cylindrical pores was achieved for the first time by self-assembly of the amphiphilic block copolypeptide poly (ethylene glycol)-block-poly (γ-benzyl-L-glutamate) (PEG-*b*-PBLG) in solution. The aggregate structures were fully characterized by TEM, SEM, 1H NMR, AFM and CD. The research results showed that α-helical conformation of PBLG blocks plays a key role in the formation process of disk-like morphology. By tuning the ratio between hydrophilic block and hydrophobic block in PEG-*b*-PBLG copolymers, various aggregate structures including micelles, disk-like micelles, vesicles and large vesicles can be achieved. The research results are helpful to expand the self-assembly fields and can provide more nanostructural materials.

Introduction

Various nanostructures including spherical micelles, vesicles, cylinders and toroid, from amphiphilic block copolymers through self-assembly have attracted more and more attentions during the past decades.[1-3] These assembled nanostructures possess not only academic interest but also potential applications in many fields, such as catalysts, microelectronics, photoelectric materials, etc.[2, 4-8] Among amphiphilic block copolymer self-assemblies, polypeptide-based self-assembly is one of the most interesting research fields because polypeptide segments can adopt various conformations including a random coil, α-helix and β-sheet, which have a significant influence on the self-assembly behavior of copolypeptides in solution. For example, Deming and co-workers reported the preparation of large vesicles from copolypeptides through conformation-specific self-assembly.[9, 10] Recently, Lin et al found that a binary system consisting of amphiphilic block copolypeptide poly(ethylene glycol)-*block*-poly(γ-benzyl-L-glutamate) (PEG-*b*-PBLG) and homopolypeptide PBLG can be assembled into super-helical structures and abacus-like structures with increasing the molecular weight.[11, 12] More recently, Cheng and co-workers reported polypeptide vesicles with densely packed multilayer membrane structures from poly(ethylene glycol)-block-poly(γ-(4,5-dimethoxy-2-nitrobenzyl)-L-glutamate) (PEG-*b*-PL).[13] On the other hand, polypeptides have excellent biocompatibility and degradability in comparison with other common polymers.[6, 14, 15] Therefore, polypeptide-based self-assemblies can be applied into bio-related fields, such as tissue engineering, drug and gene delivery, membrane protein stabilization, mimicking biomineralization, etc.[15-25]

In the past decade, some novel aggregation structures including disk- or sheet-like micelles have been observed for amphiphilic block copolymer aggregates in dilute solution.[3] Disk- or sheet-like micelles can be obtained from copolymers with variously chemical structures, including ABC or AB-type amphiphilic block copolymers with a perfluoro-block component,[26-28] ABC-type amphiphilic ionic block copolymers in the presence of diamino counterions,[29-31] copolymers with a crystallizable block,[32-34] coil-rod diblock copolymers,[35] supramolecular block copolymers,[36] and bottlebrush copolymers.[37] The research systems have greatly expanded the range of accessible aggregated morphologies besides common spherical and cylindrical micelles.

Herein, we report that a novel disk-like micelle with cylindrical pores can be achieved by self-assembly of amphiphilic block copolymers poly(ethylene glycol)-*block*-poly(γ-benzyl-L-glutamate) (PEG-*b*-PBLG) in water. To our best knowledge, it is the first time that reports the disk-like micelles with cylindrical pores from amphiphilic block copolymers. We explored the formation mechanism of disk-like structures and cylindrical pores. It is proposed that the formation of disk-like structures is a thermodynamic process and the α-helical conformation of PBLG plays an important role in the formation process of the disk-like morphology. By tuning the ratio between hydrophilic block and hydrophobic chain in PEG-*b*-PBLG copolymers, various aggregate structures including micelles, disk-like micelles, vesicles and large vesicles can be achieved.

---

[a] *Department of Chemistry, School of Chemistry and Molecular Engineering, East China Normal University, 500 Dongchuan Road, Shanghai 200241, China. E-mail: xhhe@chem.ecnu.edu.cn*

[b] *School of Chemistry & Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China. E-mail: mai@sjtu.edu.cn*

[c] *The Key Laboratory of Advanced Polymer Materials of Shanghai, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: slin@ecust.edu.cn*

†Electronic Supplementary Information (ESI) available: block copolymer characterization details (1H NMR, FT-IR and GPC) and additional supporting materials for self-assembly. See DOI: 10.1039/x0xx00000x

Experimental section

Materials

Methoxy poly(ethylene glycol) amine (mPEG-NH_2, Mn=2 kDa) was purchased from Sigma-Aldrich Co.. Tetrahydrofuran (THF, A.R. grade), dimethylformamide (DMF, A.R. grade), petroleum ether (PE, A.R. grade) and other reagents were purchased from Shanghai Chemical Reagent Co. and purified by conventional procedures if need. Dialysis bag (Green Bird, 3500 molecular weight cut-off) and ultrapure water (18KΩ) were used in the experiments. γ-benzyl-L-glutamate-N-carboxyanhydrides (BLG-NCA) were synthesized according to a method described in the literature. [38]

Synthesis of Poly(ethylene glycol)-*block*-poly(γ-benzyl-L-glutamate) (PEG-*b*-PBLG)

PEG-*b*-PBLG block copolymers were synthesized by the ring-opening polymerization(ROP) of BLG-NCA using mPEG-NH_2 as an initiator according to a reported similar procedure.[39] Briefly, BLG-NCA (7.88 g 29.9 mmol) and mPEG-NH_2 (0.33 g 0.17 mmol) were weighed under pure nitrogen and then added into an already dried round-bottom flask equipped with a magnetic bar. 46 mL of anhydrous DMF was introduced into the flask and the solution was stirred under pure nitrogen at room temperature for 3 days. After polymerization, the block copolymer was recovered by precipitation in an excess amount of anhydrous diethyl ether, and further purified by reprecipitating from THF to diethyl ether three times and dried at room temperature in a vacuum oven for 48 h. According to a similar method, other samples with different degree of polymerization (DP) were also prepared by controlling the molar ratio of the monomer BLG-NCA to the initiator mPEG-NH_2. The DP of diblock copolymers was estimated by ^{1}HNMR measurement (500 Bruker NMR). The diblock copolymers are designated as PEG_{45}-*b*-$PBLG_n$, in which the subscripts represent the DP of the corresponding blocks.

Self-assembly procedures

The self-assembled aggregate solutions were prepared by a dialysis method. Briefly, the corresponding block copolymer was dissolved in THF with a concentration of about 0.5 mg mL^{-1}, and stirred overnight at ambient temperature to obtain homogeneous solutions. Then ultrapure water was added dropwise to the solution at a rate of 1 mL min^{-1} with continuously stirring until the water content of 50 % (by volume) was reached. The aggregate solutions were equally divided into several parts and continuously stirred for different time intervals (i.e. 5 min, 10 min, 24 h and 72 h) and quenched by adding 10-fold amount of ultrapure water. Subsequently, the solutions were dialyzed against water for 48 h to remove all organic solvents.

The samples for TEM or SEM measurements were prepared by using three different preparation methods: drying under vacuum, drying under ambient conditions and freeze-drying.[40]

Characterization

The molecular weights and polydispersity (M*w*/M*n*; M*w* = weight-average molecular weight; M*n* = number-average molecular weight) of the block copolymers were recorded on a gel permeation chromatograph (GPC) equipped with two Mixed-B columns (Polymer Laboratory Corp., pore size = 10 μm; column size = 300 × 7.5 mm) and a refractive index detector (Perkin-Elmer Series 200) using DMF (0.01 mol L^{-1} LiBr) as the eluent at 40 ºC with a flow rate of 1 mL min^{-1}. The column system was calibrated by a set of mono-dispersed standard PMMA.

^{1}H NMR spectra were measured on a 500 Bruker NMR instrument using $CDCl_3$ as the solvent and TMS as a reference standard for chemical shifts. The aggregate was freeze-dried from the aggregate aqueous solution and redispersed in D_2O for the measurement.

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS50 spectrometer at frequencies ranging from 400 to 4 000 cm^{-1}. Solid samples were thoroughly mixed with KBr and pressed into pellets. After dialysis, the aggregation solution was directly detected through the attenuated total reflectance (ATR)-FTIR.

The transmission electron microscopy (TEM) observation was carried out on a JEM-2100F JEOL TEM microscope with an accelerating voltage of 200 kV. The scanning electron microscopy (SEM) measurement was performed on a field emission microscope (S-4800, HITACHI) with the accelerating voltage of 15.0 kV. Before the observation, the samples were sputtered by Au.

AFM images were obtained with a multimode atomic force microscopy (Dimension3100, Veeco), employing the tapping using mode. Sample was prepared by placing one drop of solution on a freshly cleaved mica surface and dried at room temperature for 3 day in air.

Circular dichroism (CD) measurements were carried out on a JASCO J-815 CD spectrometer (JASCO, Japan). The aggregate solution was prepared at a concentration of 4.2×10^{-3} mg mL^{-1} after dialysis and placed in a quartz cell with a path length of 0.10 cm. The mean residue molar ellipticity of each polypeptide was calculated on the basis of the measured apparent ellipticity by following the literature-reported formulas: ellipticity ([θ] in deg cm^2 $dmol^{-1}$) = (millidegrees × mean residue weight)/(path length in millimetres × concentration of polypeptide in mg mL^{-1}). [13]

Results and Discussion

PEG-*b*-PBLG diblock copolymers were synthesized by ring-opening polymerization (ROP) of γ-benzyl-L-glutamate-N-carboxyanhydrides (BLG-NCA) using methoxy poly(ethylene glycol) amine (mPEG-NH_2, Mn=2 kDa) as an initiator in DMF (see ESI). The synthesized diblock copolymer is denoted as PEG_{45}-*b*-$PBLG_n$, in which the subscripts (45 and n) represent the degree of polymerization (DP) for the respective blocks. 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 and the DP values can be obtained on the basis of the corresponding ^{1}H NMR in $CDCl_3$ with 15% TFA by integral ratio of protons from the methoxy group at 3.52 ppm to the methylene groups of benzyl at 5.04 ppm or the α-methine groups at 4.53 ppm (See ESI, Fig. S1), which are consistent within the experimental error of ^{1}H NMR measurement. The chemical structures were

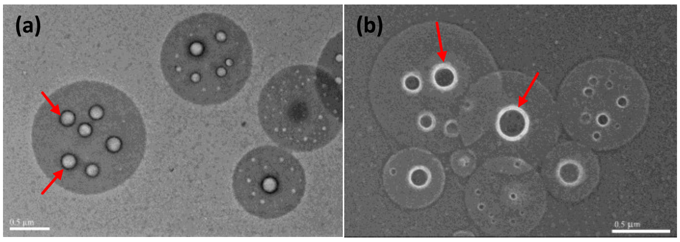


Fig. 1 Typical images of the aggregates obtained from PEG$_{45}$-*b*-PBLG$_{150}$ block copolymer: (a) TEM and (b) SEM. Scale bars, 0.5 μm.

characterized by the combination techniques of ^{1}H NMR, FT-IR and GPC (See ESI, Fig. S2 and S3), and the data were listed in Table S1 (See ESI.).

To explore the aggregation behavior of PEG-*b*-PBLG block copolymers, the corresponding copolymer was first dissolved in tetrahydrofuran (THF) at initial concentration of about 0.5 mg mL^{-1}, and then ultrapure water was added dropwise into the solution at a rate of 1 mL min^{-1} with continuously stirring until the water content reached vol.50 %. After stirring for 5 min, the aggregates were quenched by adding 10-fold amount of ultrapure water to prevent any morphological changes. Finally, residual THF solvent was removed by dialysis (See ESI.).[12] The combination techniques of TEM, SEM, AFM and NMR were used to examine the morphologies and structures of the aggregates.

Fig. 1 shows typical TEM and SEM images of the aggregates obtained from PEG$_{45}$-*b*-PBLG$_{150}$ block copolymer by directly drying method under vacuum.[40] We found that PEG$_{45}$-*b*-PBLG$_{150}$ can form disk-like micelles with a diameter around 0.5-1μm. As can be clearly seen from these images, there are some bright regions surrounded by deep-dark rings (red arrows in Fig. 1a) or deep-dark regions surrounded by bright rings (red arrows in Fig. 1b). To further confirm the novel disk-like micelles, AFM was employed to detect them. From AFM images shown in Fig. 2, we can find that the disk-like micelles are 2-dimensional and contain some cylindrical pores. The thickness of the disk-like micelles was 23.3 nm (the selected in Fig. 2a) and the diameter of the hole in the hollow cylinders was 6.4 nm (the selected in Fig. 2b). As the disk-like micelles were perpendicular to the electron beam axis, these cylindrical pores showed bright regions surrounded by deep-dark rings in TEM images (red arrows in Fig. 1a) or deep-dark regions surrounded by bright rings in SEM images (red arrows in Fig. 1b) due to their different electron densities.[40]

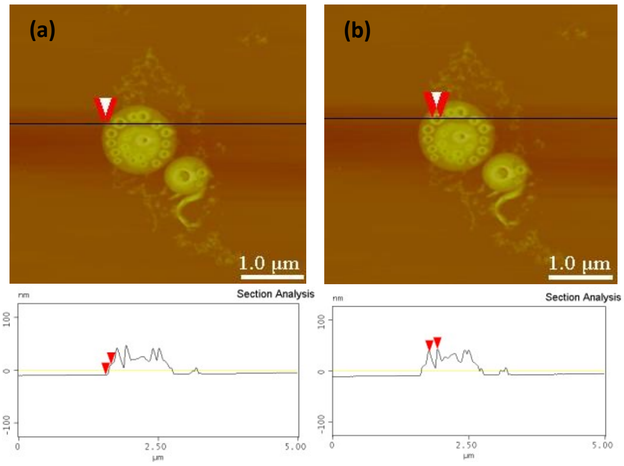


Fig. 2 AFM images of disk-like micelles self-assembled from PEG$_{45}$-*b*-PBLG$_{150}$: (a) thickness and (b) diameter.

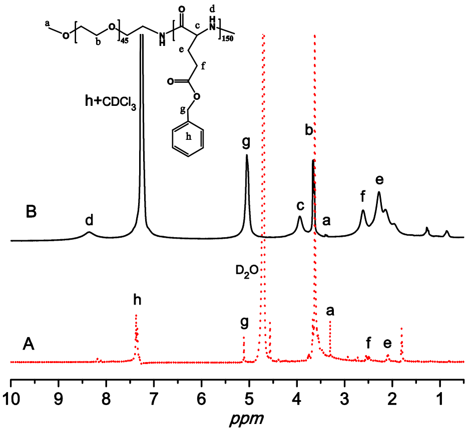


Fig. 3 ^{1}H NMR spectra of (A) PEG$_{45}$-*b*-PBLG$_{150}$ aggregates in D_2O and (B) PEG$_{45}$-*b*-PBLG$_{150}$ in $CDCl_3$

The aggregation formation is also evidenced by their ^{1}H NMR spectra in D_2O (Fig. 3).[11, 41] Compared with PEG$_{45}$-*b*-PBLG$_{150}$ in $CDCl_3$ (Fig. 3B), the characteristic signal peaks originating from PBLG block (Fig. 3A: g, f and e) relative to those assigned to PEG blocks (Fig. 3A: a and b) are reduced markedly when PEG$_{45}$-*b*-PBLG$_{150}$ assemble into their aggregates in water (see ESI). It implies that the PBLG segments form the middle layer of the disk-like micelles and the PEG segments form shell layer due to their hydrophilicity, which are benefit to maintaining the stability of the aggregates.[13, 27, 35, 42, 43] It is well-known that PBLG chains in α-helical conformation can be modeled by cylindrical rods with a diameter of 1.25 nm and a length of 0.15 nm for per monomer unit (here γ-benzyl-L-glutamate).[6, 7, 44, 45] Given the DP of 150 for PBLG block in PEG$_{45}$-*b*-PBLG$_{150}$ and 0.15 nm per γ-benzyl-L-glutamate for α-helix, the length of the rod-like hydrophobic PBLG block will be calculated to about 22.5 nm, which is consistent with the measured value from AFM (Fig. 2A) except for considering the contribution from the PEG shell. The secondary structure of PBLG blocks in the aggregates was further confirmed by circular dichroism (CD) spectroscopy and attenuated total reflectance (ATR)-FTIR spectroscopy (see Fig. 4S and Fig. 5S). CD spectrum (see Fig. 4S) revealed that the PBLG adopted a α-helical conformation with a negative band at about 230 nm, which is characteristics of α-helix.[45, 46] ATR-FTIR spectra of PEG$_{45}$-*b*-PBLG$_{150}$ in solid powder and disk-like micelle aqueous suspension displayed typical amide bands of α-helical conformation (1650 and 1550 cm^{-1}) (see Fig. 5S).[13, 46] If PEG$_{45}$-*b*-PBLG$_{150}$ block copolymer was first dissolved in 1% (V/V) trifluoroacetic acid in THF, followed by addition of water until the water content of 50 % (by volume), quenched and then dialysis against water, only spherical vesicles of 50-100 nm diameter were observed (see Fig. 6S).[9] On the basis of these results, it is proposed that the α-helical conformation in

PBLG chains was one of the key factors to form the disk-like micelles. On the same time, this implies that the PBLG helices are interdigitated in the middle layer wall for the aggregates, as shown in Fig. 4.

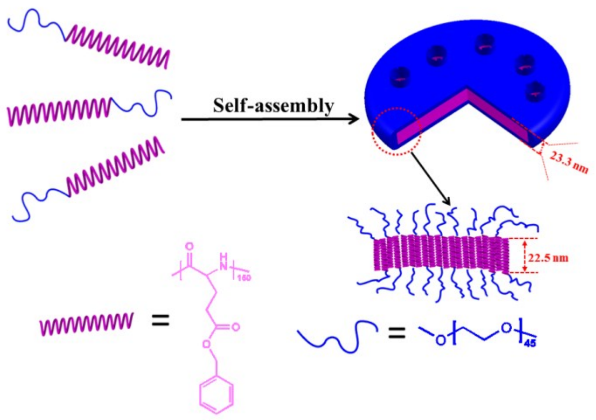


Fig. 4 Schematic showing the aggregation formation of PEG_{45}-*b*-$PBLG_{150}$: the blue lines represent the PEG blocks, and the red lines represent PBLG blocks

To further understand the formation process of the cylindrical pores in the disk-like micelles, when the ultrapure water dropping was finished, the aggregates in solution were stirred continually for 10 min, 24 h or 72 h and then quenched in a large amount of ultrapure water (see ESI). The TEM images in different periods are shown in Fig. 5. The cylindrical pores in the disk-like micelles are observed clearly after stirring for 10 min and then quenching (Fig. 5a), become small after stirring for 24 h (Fig. 5b) and vanish after stirring 72 h (Fig. 5c). One possible mechanism for the formation of disk-like micelles with cylindrical pores is proposed on the basis of the α-helical conformation in PBLG blocks and initial water content, as shown in Fig. 4. THF is good solvent for PEG_{45}-*b*-$PBLG_{150}$ and PBLG blocks adopt a α-helical conformation. When water, a non-solvent for PBLG but a good solvent for PEG, is added to the solution to induce the aggregation of the PBLG blocks, the rod-like PBLG helices packed together side by side into the middle layer to reduce interfacial energy. On the same time, the amphiphilic copolymers containing rod-like PBLG helices would rather laterally associated into a flat structure to lower the interfacial curvature between the hydrophobic and hydrophilic domains.[9, 10] Therefore, the disk-like micelles rather than spherical micelles are formed. This aggregation process is very fast and controlled by thermodynamics. This parallel packing of the PBLG chain blocks are further stabilized by the strong dipolar π-π interactions between the adjacent phenyl groups in PBLG blocks and the good hydrophilicity of PEG chains in shell is also benefit to improve the stability of the aggregates.[11, 47] The combined effects synergistically increase the stability of the disk-like micelles and make the size of the formed disk-like micelles up to micrometer-scale level due to more polymer chains joining in the aggregation process.[35] On the other hand, the aggregation of PEG_{45}-*b*-$PBLG_{150}$ in the solution starts when the water content reaches a critical point. At this point, the viscosity of the system is low. Nevertheless, the extraction of THF solvent from the surface region of the precursor aggregates may increase more the surface viscosity surrounding the structures than their internal viscosity with further adding water, to yield a “skin” of high viscosity surrounding the structure, which is helpful to stabilize the precursor aggregates. At the same time, the extraction of THF from the precursor aggregates will induce the occurrence of phase separation within the aggregates, to yield polymer-rich and polymer-poor regions. The polymer-poor regions contain THF/water mixtures and some dissolved polymers, which can coalesce into some larger THF/water-filled bubbles (inclusions) to reduce interfacial energy. Once the bubbles are close to the edge of the aggregates, the high surface-to-volume ratio in the thin regions will drive the bubbles to break through the surface.[48] Simultaneously, some dissolved polymers in the bubbles with other polymers from the solution rapidly assemble into the hollow cylinder structure in the periphery of the breakthrough and the following quench will stabilize the structure. The irregular edge at the top of the hollow cylinder structure observed from the AFM image of the aggregates may testify the occurrence of the breakthrough (see Fig. 7S: a).

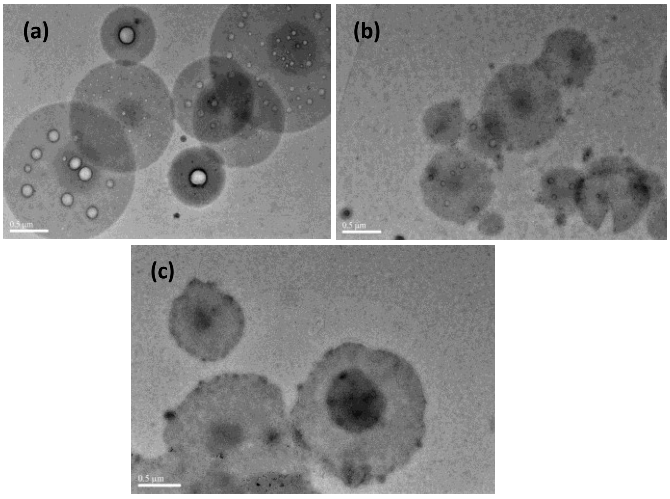


Fig. 5 TEM images in different periods: (a) 10 min, (b) 24 h and (c) 72 h. Scale bars, 0.5 μm.

When the water amount reached 50 vol. %, the aggregation solution was stirred continuously for a longer time (i.e. 24 h and 72 h) before the quenching occurred. The cylindrical pores within the disk-like micelles became small (Fig. 5b) and even vanished (Fig. 5c). We speculated that the solvent THF in the aggregation solution promoted the molecular motion due to the plasticization of THF and the local polymer chain adjustment within the aggregates resulted in the fusion of the cylinder structures into the main body of the aggregate to form a whole disk-like micelle.[27, 29] To be further convinced of the formation of the disk-like micelles with cylindrical pores during the self-assembly process, the aggregate specimens for TEM were prepared using three different methods: drying under vacuum, drying under ambient conditions and freeze-drying (see ESI),[40] in which the disk morphologies with cylindrical pores were distinctly observed from the TEM images (see Fig. 8S). Thus, before dialysis, the aggregation morphology has been already formed.

It is well known that the ratio of the hydrophilic to hydrophobic chain segments has rather a large influence on the assembled morphologies.[2] To investigate the effect of the hydrophilic/hydrophobic ratio in PEG-*b*-PBLG on the assembled morphologies, other three samples with different DP of PBLG (i.e. 80, 200 and 250) as the hydrophobic block were prepared, while the DP of PEG as the hydrophilic block was kept fixed (here, 45). The resulting morphologies were characterized using TEM and shown in Fig. 9S (see ESI). Various aggregate morphologies including micelles (Fig. 9S: a), disk-like micelles with cylindrical pores (Fig. 9S: b), vesicles (Fig. 9S: c) and large vesicles (Fig. 9S: d) can be achieved with increasing the DP of hydrophobic PBLG blocks, that is, the assembled structures depend on the relative lengths of PBLG blocks and can be tuned from micelles, disk-like micelles with cylindrical pores, vesicles to large vesicles.

Conclusions

Amphiphilic block PEG-*b*-PBLG copolymers prepared by ROP of BLG-NCA can assembled into an interesting disk-like micelle with cylindrical pores in water. The α-helical conformation of PBLG plays an important role in the formation of the disk-like morphology. The ratio between hydrophilic block and hydrophobic block in PEG-*b*-PBLG copolymers has a remarkable effect on the self-assembled morphology, in which the assembled structures with increasing the DP of PBLG blocks from 80 to 250 can be tuned from micelles, disk-like micelles with cylindrical pores, vesicles to large vesicles. The research results enriched our knowledge in self-assembly of amphiphilic block copolymers and expanded the application of polypeptide-based copolymers in the biomedical field.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21174038 and 21304057), the Natural Science Foundation of Shanghai (13ZR1421200) and the Projects of Shanghai Municipality (12JC1403102). The Graduate Innovation Foundation of East China Normal University and the Large Instruments Open Foundation of East China Normal University is also appreciated.

Notes and references

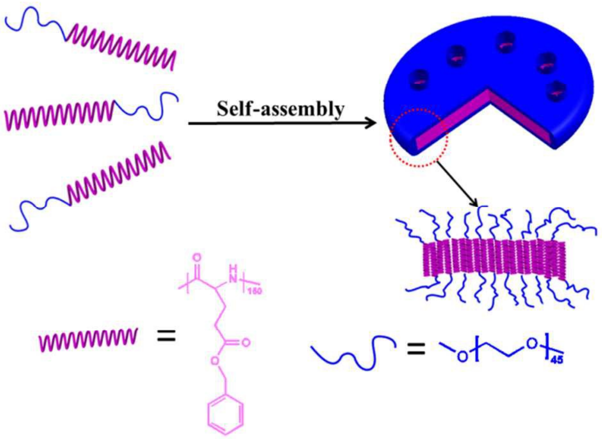
1 C. Fong, T. Le and C. J. Drummond, *Chem. Soc. Rev.*, 2012, **41**, 1297-1322.
2 Y. Mai and A. Eisenberg, *Chem. Soc. Rev.*, 2012, **41**, 5969-5985.
3 S. J. Holder and N. A. J. M. Sommerdijk, *Polym. Chem.*, 2011, **2**, 1018-1028.
4 M. Osada and T. Sasaki, *Adv. Mater.*, 2012, **24**, 210-228.
5 S. H. Wibowo, A. Sulistio, E. H. H. Wong, A. Blencowe and G. G. Qiao, *Chem. Commun.*, 2014, **50**, 4971-4988.
6 A. Carlsen and S. Lecommandoux, *Curr. Opin. Colloid Interface Sci.*, 2009, **14**, 329-339.
7 J. Zhang, X.-F. Chen, H.-B. Wei and X.-H. Wan, *Chem. Soc. Rev.*, 2013, **42**, 9127-9154.
8 W. Yuan and W. Guo, *Polym. Chem.*, 2014, **5**, 4259-4267.
9 E. G. Bellomo, M. D. Wyrsta, L. Pakstis, D. J. Pochan and T. J. Deming, *Nat. Mater.*, 2004, **3**, 244-248.
10 E. P. Holowka, D. J. Pochan and T. J. Deming, *J. Am. Chem. Soc.*, 2005, **127**, 12423-12428.
11 C. Cai, J. Lin, T. Chen, X. S. Wang and S. Lin, *Chem. Commun.*, 2009, 2709-2711.
12 C. Cai, Y. Li, J. Lin, L. Wang, S. Lin, X. Wang and T. Jiang, *Angew. Chem. Int. Edit.*, 2013, **52**, 7732-7736.
13 Z. Song, H. Kim, X. Ba, R. Baumgartner, J. S. Lee, H. Tang, C. Leal and J. Cheng, *Soft Matter*, 2015, **11**, 4091-4098.
14 G. Yan, D. DennisE, J. Justyna and S. Helmut, *Angew. Chem. Int. Edit.*, 2013, 2006, **45**, 7578-7581.
15 C. Cai, L. Wang and J. Lin, *Chem. Commun.*, 2011, **47**, 11189-11203.
16 X. Zhao, F. Pan, H. Xu, M. Yaseen, H. Shan, C. A. Hauser, S. Zhang and J. R. Lu, *Chem. Soc. Rev.*, 2010, **39**, 3480-3498.
17 H. Chen, L. Xia, W. Fu, Z. Yang and Z. Li, *Chem. Commun.*, 2013, **49**, 1300-1302.
18 Y. Yao, D. Wang, L. Han and S. Che, *Chem. Eur. J.*, 2013, **19**, 15489-15492.
19 B. Liu, Y. Yao and S. Che, *Angew. Chem. Int. Edit.*, 2013, 2013, **52**, 14186-14190.
20 B. Ahn, W. Kwon, H. Kim and M. Ree, *Polym. Chem.*, 2014, **5**, 1912-1922.
21 J. Fan, R. Li, X. He, K. Seetho, F. Zhang, J. Zou and K. L. Wooley, *Polym. Chem.*, 2014, **5**, 3977-3981.
22 G. Liu, N. Liu, L. Zhou, Y. Su and C.-M. Dong, *Polym. Chem.*, 2015, **6**, 4030-4039.
23 A. Peyret, J. F. Trant, C. V. Bonduelle, K. Ferji, N. Jain, S. Lecommandoux and E. R. Gillies, *Polym. Chem.*, 2015, **6**, 7902-7912.
24 J. Lin, J. Zhu, T. Chen, S. Lin, C. Cai, L. Zhang, Y. Zhuang and X.-S. Wang, *Biomaterials*, 2009, **30**, 108-117.
25 L. Wei, C. Cai, J. Lin and T. Chen, *Biomaterials*, 2009, **30**, 2606-2613.
26 Z. Zhou, Z. Li, Y. Ren, M. A. Hillmyer and T. P. Lodge, *J. Am. Chem. Soc.*, 2003, **125**, 10182-10183.
27 T. P. Lodge, M. A. Hillmyer, Z. Zhou and Y. Talmon, *Macromolecules*, 2004, **37**, 6680-6682.
28 W. F. Edmonds, Z. B. Li, M. A. Hillmyer and T. P. Lodge, *Macromolecules*, 2006, **39**, 4526-4530.
29 Z. Li, Z. Chen, H. Cui, K. Hales, K. Qi, K. L. Wooley and D. J. Pochan, *Langmuir*, 2005, **21**, 7533-7539.
30 H. Cui, Z. Chen, K. L. Wooley and D. J. Pochan, *Macromolecules*, 2006, **39**, 6599-6607.
31 H. Cui, Z. Chen, S. Zhong, K. L. Wooley and D. J. Pochan, *Science*, 2007, **317**, 647-650.
32 A. Ramzi, M. Prager, D. Richter, V. Efstratiadis, N. Hadjichristidis, R. N. Young and J. B. Allgaier, *Macromolecules*, 1997, **30**, 7171-7182.
33 W. Wang, R. Liu, Z. Li, C. Meng, Q. Wu and F. Zhu, *Macromol. Chem. Phys.*, 2010, **211**, 1452-1459.
34 L. Yin and M. A. Hillmyer, *Macromolecules*, 2011, **44**, 3021-3028.
35 J. Zhang, W. Lin, A. Liu, Z. Yu, X. Wan, D. Liang and Q. Zhou, *Langmuir*, 2008, **24**, 3780-3786.
36 L. Ren, F. Ke, Y. Chen, D. Liang and J. Huang, *Macromolecules*, 2008, **41**, 5295-5300.
37 Y. Shi, W. Zhu, D. D. Yao, M. L. Long, B. Peng, K. Zhang and Y. M. Chen, *Acs. Macro. Lett.*, 2014, **3**, 70-73.
38 M. I. Gibson and N. R. Cameron, *J. Polym. Sci. Part A: Polym. Chem.*, 2009, **47**, 2882-2891.

39 X. He, C. Gao, W. Sun, W. Huang, S. Lin and D. Yan, *J. Polym. Sci. Part A: Polym. Chem.*, 2013, **51**, 1040-1050.
40 T. Azzam and A. Eisenberg, *Langmuir*, 2010, **26**, 10513-10523.
41 J. Sun, X. Chen, C. Deng, H. Yu, Z. Xie and X. Jing, *Langmuir*, 2007, **23**, 8308-8315.
42 Kui Yu and A. Eisenberg, *Macromolecules*, 1998, **31**, 3509-3518.
43 S. Venkataraman, A. L. Lee, H. T. Maune, J. L. Hedrick, V. M. Prabhu and Y. Y. Yang, *Macromolecules*, 2013, **46**, 4839-4846.
44 S. M. Yu, V. P. Conticello, G. Zhang, C. Kayser, M. J. Fournier, T. L. Mason and D. A. Tirrell, *Nature*, 1997, **389**, 167-170.
45 J. Shen, C. Chen, W. Fu, L. Shi and Z. Li, *Langmuir*, 2013, **29**, 6271-6278.
46 J. Huang, C. Bonduelle, J. Thévenot, S. Lecommandoux and A. Heise, *J. Am. Chem. Soc.*, 2012, **134**, 119-122.
47 B. Song, Z. Wang, S. Chen, X. Zhang, Y. Fu, M. Smet and W. Dehaen, *Angew. Chem. Int. Edit.*, 2005, **44**, 4731-4735.
48 I. C. Riegel and A. Eisenberg, *Langmuir*, 2002, **18**, 3358-3363..

Graphical abstract

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

Xue Lin, Xiaohua He, Chaoqun Hu, Yuxiang Chen, Yiyong Mai, and Shaoliang Lin



An unprecedented 2-dimensional disk-like micelle with cylindrical pores was achieved by self-assembly of amphiphilic block copolypeptides PEG-*b*-PBLG with a α-helical conformation of PBLG block.