

Self-assembly Behavior of Copolymers with Super Segregated Structure Containing Fluorinated Segments^{*}

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Abstract Copolymers with super segregated structure of hydrophilic methoxy poly(ethylene glycol) (mPEG) and fluorophilic poly(1H,1H,2H,2H-perfluorodecyl acrylate) (PFA) were prepared. And just because of this super segregated structure which was resulted from the extremely strong incompatibility between the two blocks, several interesting self-assembly behaviors of the copolymers were displayed and studied under different conditions. Transmission electron microscope (TEM) showed that with the increase of PFA in the polymerization system, the incompatibility in this super segregated structure became stronger, and the self-assembly behavior changed from ball-like or rod-like to vesicles, and finally collapsed to sheet-like. The self-assembly behavior changed likewise when the initial concentration increased. And the interesting formation of these barrel-like and spindle-like vesicles was finally studied with different cooling speeds. It's finally found that with this super segregation structure, these new self-assembly morphology might be formed due to the extremely strong incompatibility between mPEG and PFA segments.

Keywords: Super segregated structure; Self-assembly behavior; Barrel-like and spindle-like vesicles.

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INTRODUCTION

Recently, the self-assembly of amphiphilic block copolymers in a dilute solution has attracted great interest, because of the formation of a variety of nanoscopic aggregates with predetermined sizes and well defined shapes, like typically sphere micelles, cylinder micelles, bilayer vesicles, which could be potentially applied in nanotechnology^[1]. And most of the self-assembly systems investigated up to now were based on hydrophilic-lipophilic block copolymers, such as polystyrene-*b*-poly(acrylic acid), polystyrene-*b*-poly(ethylene oxide). For these block copolymers, rigidity^[2] and crystallinity^[3] could determine the morphology of the self-assembly morphology. More importantly, the incompatibility between the two segments, which resulted in segregation, was the basic driving force for the assembly. However, as reported before, the self-assembly of block copolymers was mainly concentrated on the weak, medium or strong segregation, and little was reported on super segregation which could be caused by extremely strong incompatibility in polymers. Very recently, incorporation of fluorinated segments into block copolymers with strong segregation resulted in interesting self-assembly characteristics^[4]. Lodge and coworkers reported that ABC miktoarm star block terpolymers with a flexible coil fluorinated segment self-assembled into multicompartment micelles^[5], polygonal bilayer sheets^[6]

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and segmented wormlike micelles^[7]. This was mainly due to the fact that the fluorinated segments tend to be hydrophobic and lipophobic which would lead to super-segregation. Therefore, researches on the self-assembly behavior of fluorophilic and hydrophilic diblocks that could easily cause super segregation should draw much attention. Copolymer of super segregation^[8] which was caused by the strongest incompatibility when the Flory-Huggins χ was high enough, might self-assemble into more different novel nanostructures.

In this work, we first synthesized diblock copolymers of super segregated structure with a hydrophilic methoxy poly(ethylene glycol) (mPEG) block and a fluorophilic poly(1H,1H,2H,2H-perfluorodecyl acrylate) (PFA) block. Then their self-assembly behavior in solution was investigated. At last, with the drive of super segregation, barrel-like and spindle-like vesicles were formed by self-assembly of mPEG-*b*-PFA copolymers in low alcohols or 1-propanol through a single-solvent method.

EXPERIMENTAL

Diblock copolymers mPEG-*b*-PFA was synthesized *via* chain transfer polymerization (RAFT) using of a mPEG-based macro-chain-transfer agent. And micellar solutions of mPEG-*b*-PFA block copolymers were prepared through a single-solvent method^[9].

Both the copolymers and solvent (ethanol or 1-propanol) were first placed in a flask, and then heated to the desired temperature, which was maintained overnight. The morphology of aggregates, characterized by transmission electron microscopy (TEM), was finally formed when the whole system was cooled to 30 °C during different period of time. And more details of the preparation procedures were described in Supporting Information.

RESULTS AND DISCUSSION

As diblock copolymers with super segregated structure of hydrophilic and fluorophilic segments were prepared, for studies on the self-assembled morphology of the aggregates the method of temperature-controlling assembly was performed in the solvent of ethanol, in which mPEG-*b*-PFA could be dissolved at high temperatures but incompatible at room temperature. So mPEG-*b*-PFA was dissolved in ethanol at 70 °C, then cooled down to room temperature. And several self-assembled morphologies were obtained for copolymers of different compositions (Fig. 1). With the increase of the content of PFA, the morphology of the aggregates changed from ball-like and rod-like to barrel-like and spindle-like vesicles, and finally collapsed to sheet-like vesicles in micro size when the content of PFA was high enough.

The explanation of these changes was that with the increase of the hydrophobic segments, the segregation of the structure tended to be greater, which led to the decrease of conformational entropy of the nucleation. So with this super segregated structure, the morphology of aggregates would change from ball-like and rod-like to vesicle in order to minimize the free energy of the system^[10, 11]. And because of the intense segregation in blocks and the straight conformation of PFA, the interface between PFA and mPEG phases was almost straight instead of curved. Consequently, the interface between PFA and mPEG phases was more difficult to be curved in mPEG₅-*b*-PFA₃₂ with more rigid segments of PFA, and the sheet-like vesicles with micro size easily formed. The formation mechanism of mPEG₅-*b*-PFA₂₃, which could be detected in Figs. 1(b, c, d), with a new morphology, barrel-like and spindle-like vesicles, would be discussed later.

As we have found, the initial concentration of copolymers in ethanol was another important factor that affected the new morphology^[10, 12]. mPEG₅-*b*-PFA₂₃ was employed to self-assembly in ethanol slowly from 70 °C to room temperature. In Fig. 2, when the initial concentration of ethanol was 0.03 wt% (a), the morphology of aggregates was rod-like with the diameter of 30 nm. And it changed to be sheet-like and micro-vesicle, when the initial concentration reached 1 wt% (c). Just as the initial concentration increased to 0.12 wt%, the unsealed spindle-like vesicle was obtained (b).

In order to study deeply on formation mechanism of the barrel-like and spindle-like vesicles of mPEG-*b*-PFA with super segregated structure, temperature regulation was one of the important means. And these

experiments would be taken at several high temperatures, in which ethanol would volatilize easily. So 1-propanol was used instead of ethanol.

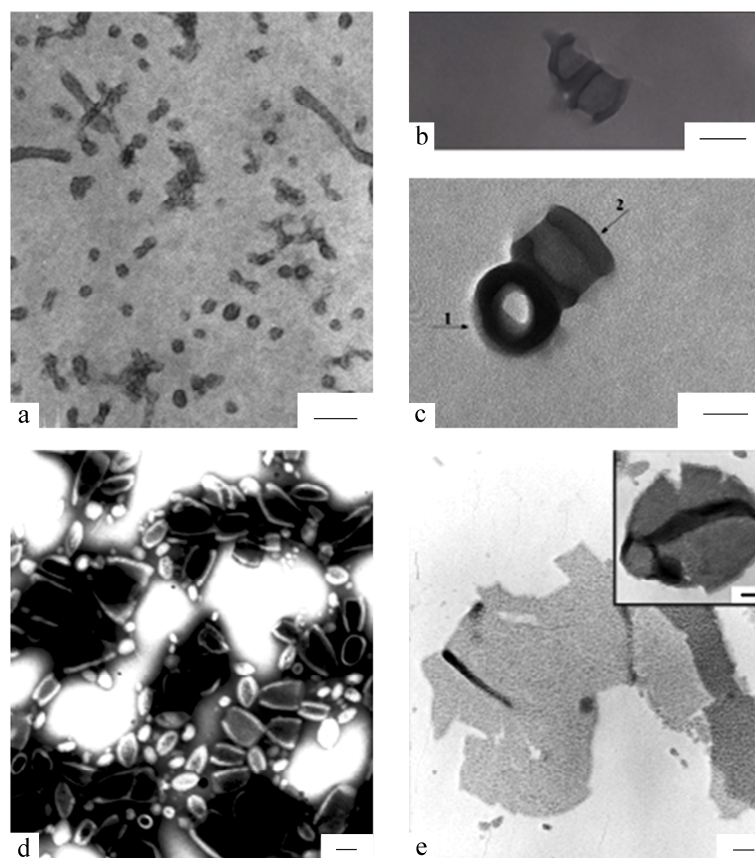


Fig. 1 Morphologies of the aggregates from self-assembly of block copolymers in ethanol: (a) mPEG₅-b-PFA₉, (b, c, d) mPEG₅-b-PFA₂₃ and (e) mPEG₅-b-PFA₃₂. The inset in (e) shows a ~800 nm vesicle. (b), (c) are not negatively stained, others are negatively stained with tungstophosphoric acid. All scale bars indicate 100 nm. (In mPEG_a-b-PFA_n, *a* and *n* represent the polymerization degrees of PEG and PFA respectively.)

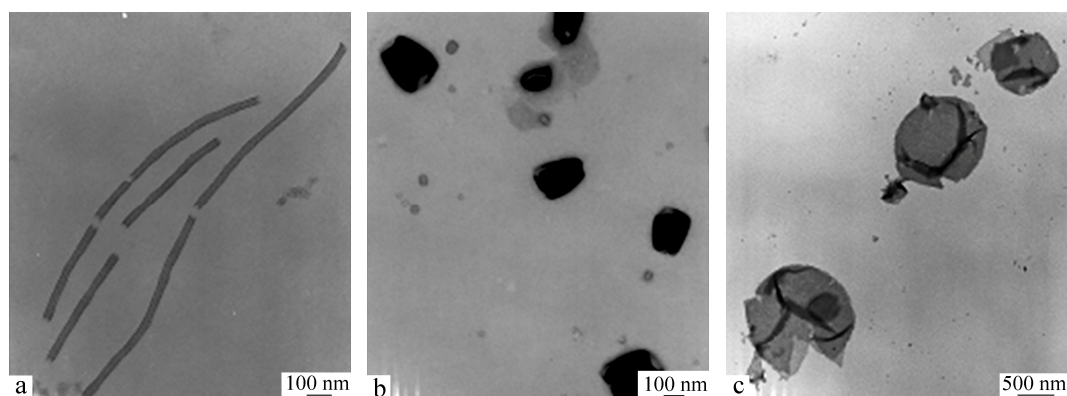


Fig. 2 Morphologies of the aggregates from self-assembly of mPEG₅-b-PFA₂₃ in ethanol with different copolymer concentration: (a) 0.03 wt%, (b) 0.12 wt% and (c) 1 wt% (Scale bars in (a, b) and (c) indicate 100 nm and 500 nm, respectively.)

Aggregates from cooling the 1 mg/mL mPEG₅-*b*-PFA₂₃1-propanol solution (90 °C) to 30 °C with different time lengths were observed by TEM. When the polymer solutions were cooled to 30 °C with the time of 2 h, elliptical aggregates (with minority of spherical aggregates) were obtained (Fig. 3a). And with the increase of cooling time, the size and quantity of elliptical aggregates increased (20 h, 60 h in Figs. 3b, 3c, respectively). Finally, spindle-like vesicles (Fig. 3d) were formed by cooling with 100 h. Therefore, these observation indicated that the spindle-like vesicles were formed by a nucleation pathway (*i.e.* the spherical aggregates grew to semi-vesicle, then to full vesicles), rather than a closing pathway of bilayer membrane (*i.e.* the spherical aggregates changed from rod-like and bilayer membrane, and then closed to form vesicles), which was also reported by Schmid^[13] and Jiang^[14]. Thus the barrel-like vesicles (Fig. 1) could not be considered as the intermediate states during the formation of spindle-like vesicles, but more likely be formed by melting of spindle-like vesicles. It was also confirmed by the facts that some large-size elliptical aggregates with solid centers were observed in Fig. 1(d) (indicated by arrow). Additionally, the initial elliptical aggregates and the intermediate large-size elliptical aggregates also confirmed that the vesicles had a spindle-like shape.

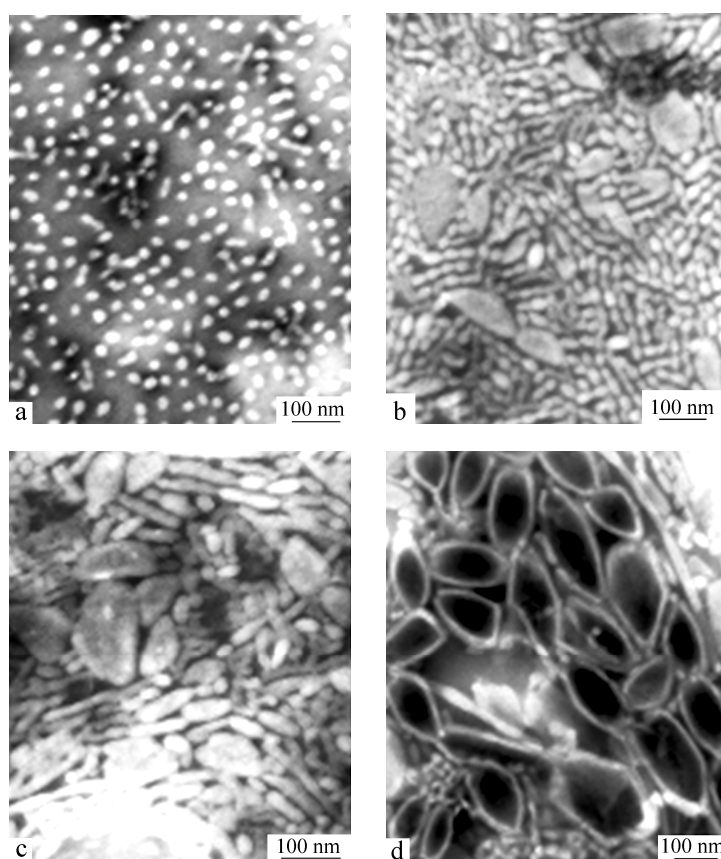


Fig. 3 Morphology of aggregates from cooling the 1 mg/mL mPEG₅-*b*-PFA₂₃1-propanol solution (90 °C) to 30 °C with different time lengths: (a) 2 h, (b) 20 h, (c) 60 h and (d) 100 h (All scale bars indicate 100 nm.)

As we know, with the decreasing in temperature, the Flory-Huggins χ parameter between the PFA blocks and the solvent would increase instead, which would drive phase separation of the PFA blocks and could finally result in super segregation. And various aggregates could be formed based on the different χ (The increase of χ usually results in the change of morphology from spheres to rods, or from rods to vesicles^[10]). However, It has been known that the self-assembly of copolymers in solution was also controlled by kinetics. In this system,

when the polymer solution was cooled to some temperature (*e.g.* below the crystallization temperature of PFA) with a rapid cooling speed, the super segregated structure of the aggregates would be kinetically frozen with the initial elliptical morphology. On the contrary, as the cooling speed decreases, the elliptical micells would grow. And when the cooling speed was so slow that the morphological transition could occur and then vesicles were formed. Thus with the decrease of cooling speed, elliptical micelles and spindle-like vesicles were formed sequentially.

We proposed that the formation of this super segregated structure which resulted in non-spherical spindle-like vesicles could be assigned to the asymmetry and anisotropy of PFA chains. Because of the parallel alignment of per-fluorinated side chains, the character of rigid-rod and the extended conformation of PFA, the expected conformation of mPEG-*b*-PFA block copolymers was illustrated in Fig. 4(a). For a polymer chain, the length was ~ 4 nm^[15] along the *X* axis, while along the *Z* axis it was ~ 0.5 nm^[16]. Moreover, for the steric hindrance of the rigid perfluorinated side chains, it was harder for PFA chain to curve in *xy* plane than in *yz* plane. Therefore, low interfacial curvature and big radius were preferred along the axis of fluorinated side chains ($R_{xy} > R_{yz}$ as depicted in Figs. 4b, 4c), and non-spherical aggregates were formed. And Fig. 2(e) illustrated the proposed chain packing of the spindle-like vesicle.

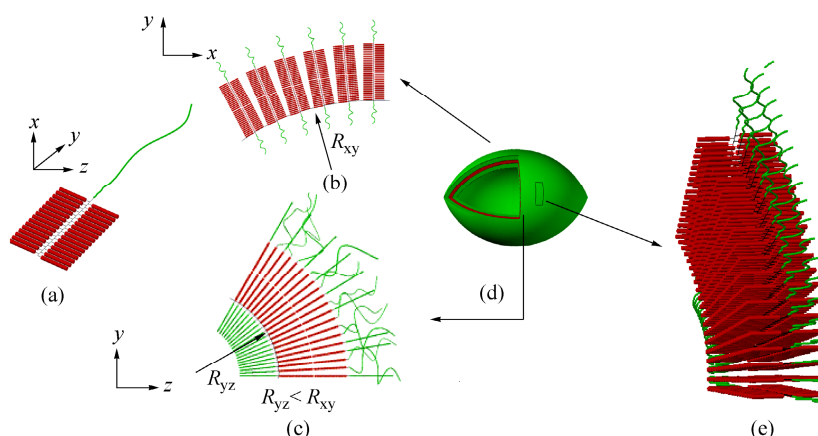


Fig. 4 Schematic drawing of (a) conformation of mPEG-*b*-PFA copolymers, (b) front views, (c) side views, (d) three dimensional non-spherical spindle-like vesicles and (e) three dimensional views of proposed chain packing of spindle-like vesicles (The red, green colors represent PFA and mPEG, respectively.)

CONCLUSIONS

In conclusion, block copolymers mPEG-*b*-PFA with super segregated structure, consisting of a hydrophilic block and a fluorophilic block, which leads to the extremely strong incompatibility, were synthesized. And for this super segregated structure, barrel-like and spindle-like vesicles were formed by self-assembly of these aggregates, which might be assigned to the asymmetry and anisotropy of PFA segments.

REFERENCES

- 1 Rodriguez-Hernandez, J., Checot, F., Gnanou, Y. and Lecommandoux, S., *Prog. Polym. Sci.*, 2005, 30(7): 691
- 2 Kuang, M., Duan, H., Wang, J. and Jiang, M., *J. Phys. Chem. B*, 2004, 108 (41): 16023
- 3 Massey, J.A., Temple, K., Cao, L., Rharbi, Y., Raez, J. and Winnik, M.A., *J. Am. Chem. Soc.*, 2000, 122(47): 11577
- 4 Lodge, T.P., Hillmyer, M.A., Zhou, Z. and Talmon, Y., *Macromolecules*, 2004, 37(18): 6680
- 5 Li, Z.B., Kesselman, E., Talmon, Y., Hillmyer, M.A. and Lodge, T.P., *Science*, 2004, 306(5693): 98
- 6 Li, Z.B., Hillmyer, M.A. and Lodge, T.P., *Nano Lett.*, 2006, 6(6): 1245

- 7 Li, Z.B., Hillmyer, M.A. and Lodge, T.P., *Langmuir*, 2006, 22(22): 9409
- 8 Gasilova, E.R., Zakharova, O.G. and Zaitsev, S.D., *E-polymers*, 2009, 029: 1
- 9 Desbaumes, L. and Eisenberg, A., *Langmuir*, 1999, 15(1): 36
- 10 Zhang, L.F. and Eisenberg, A., *Polym. Adv. Technol.*, 1998, 9(10–11): 677
- 11 Zhulina, E., Adam, M. and Larue, I., *Macromolecules*, 2005, 38(12): 5330
- 12 Zhang, L., Barlow, R. and Eisenberg, A., *Macromolecules*, 1995, 28(18): 6055
- 13 He, X.H. and Schmid, F., *Macromolecules*, 2006, 39(7): 2654
- 14 Han, Y.Y., Yu, H.Z., Du, H.B. and Jiang, W., *J. Am. Chem. Soc.*, 2010, 132(3): 1144
- 15 Corpart, J.M., Girault, S. and Juhué, D., *Langmuir*, 2001, 17(23): 7237
- 16 Honda, K., Morita, M., Otsuka, H. and Takahara, A., *Macromolecules*, 2005, 38(13): 5699