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Communications to the Editor

Self-Assembly of PEG-*b*-Liquid Crystal Polymer: The Role of Smectic Order in the Formation of Nanofibers

Rafael Piñol,[†] Lin Jia,[‡] Francesca Gubellini,[†] Daniel Lévy,[†] Pierre-Antoine Albouy,[§] Patrick Keller,[†] Amin Cao,*[,‡] and Min-Hui Li*[,†]

Institut Curie, CNRS UMR168, Laboratoire Physico-Chimie Curie, 26 rue d'Ulm, 75248 Paris Cedex 05, France; Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, China; and Laboratoire de Physique des Solides, CNRS UMR8502, Université Paris-Sud, 91405 Orsay Cedex, France

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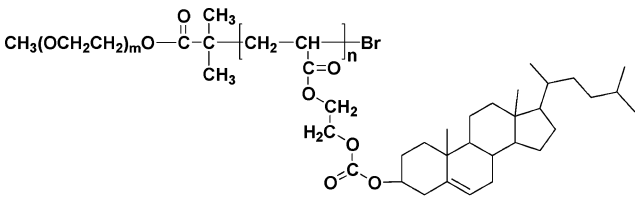
Self-assembly of macromolecules is a very useful molecular tool for the engineering of functional nanomaterials,[1,2] which are interesting objects in material science and biomimicry research. In nature, a variety of highly smart nanomaterials systems are constructed by association of various kinds of biomacromolecules and biomolecules, including proteins, DNA, and phospholipids, through well-controlled intermolecular and/or intramolecular interactions. Complex cytoskeletal nanofibrils made of biopolymers and cell membrane made of transmembrane proteins, phospholipids, and other biomolecules are good examples. Their nanofiber and vesicle architectures are very important for the realization of diverse properties like anisotropic strength, structural stability, motility, material transport, and compartimentation. An amphiphilic block copolymer is a typical synthetic system that reveals a controlled balance of amphiphilicity and can assume various well-organized architectures, including spherical, rod, and lamellar structures.[3] In recent years, the studies on self-assembly of block copolymers in solution have been extensively pursued.[4] Nanofibers or rodlike micelles have been reported in different block copolymer systems.[5−9] A well-known example is nanofibers made of peptide-based amphiphilic block copolymers.[7−9] The β-sheet arrangement within the peptide region plays a crucial role in directing the self-assembly into nanofibers as opposed to spherical micelles or vesicles.[8,9]

Scheme 1. Amphiphilic LC Block Copolymers Containing a Cholesteryl-Based Mesogen: PEG5000-*b*-PAChol(14/86) and PEG2000-*b*-PAChol(28/72)



PEG5000-*b*-PAChol (14/86): m=114, n=60, M_n=36000, M_w/M_n=1.50

PEG2000-*b*-PAChol (28/72): m=45, n=10, M_n=7100, M_w/M_n=1.13

Recently, we have reported well-structured unilamellar polymer vesicles (polymersomes) as well as nanotubes formed by amphiphilic liquid crystal (LC) block copolymers, in which the LC block is a side-on nematic polymers containing an aromatic mesogen composed of three phenyl rings and the hydrophilic block is a poly(ethylene glycol).[10] We describe in this Communication nanofibers and vesicles formed in water by two new amphiphilic LC block copolymers, in which the LC block is a polymer containing a cholesteryl-based mesogen and the hydrophilic block is again a poly(ethylene glycol). A smectic structure in the LC block is associated with the nanofiber formation in the first LC block copolymer, while the second copolymer which does not present smectic phase in bulk self-assembles into vesicles instead of nanofibers. The role of the smectic order here is reminiscent of that of the β-sheet structure in the nanofiber formation in peptide-based amphiphilic copolymers.

* Corresponding author: Tel 33 1 42346763; Fax 33 1 40510636; e-mail min-hui.li@curie.fr.
[†] Institut Curie.
[‡] Chinese Academy of Sciences.
[§] Université Paris-Sud.

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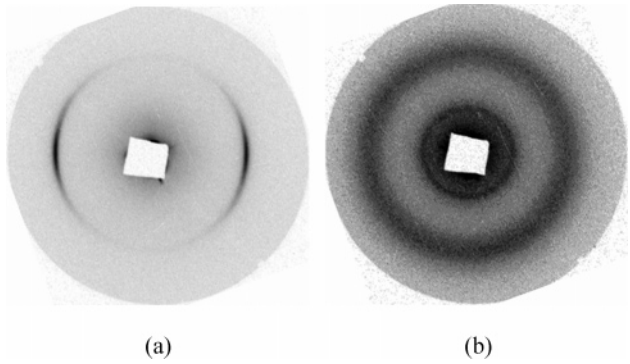

Figure 1. SAXS patterns of pure block copolymers. (a) PEG5000-*b*-PAChol(14/86) in fiber sample drawn from molten polymer. The long axis of fiber is along vertical direction. The diffraction peak corresponds to a distance of 4.29 nm. (b) PEG2000-*b*-PAChol(28/72) in powder sample in capillary. Wave vector domain measured is 0.27−2.2 nm^{-1} and distance measured 3−23 nm.

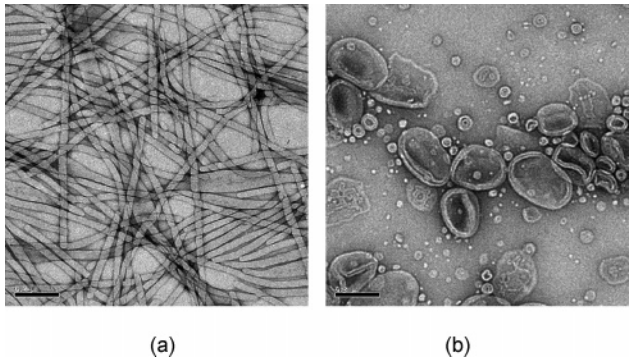

Figure 2. TEM images of self-assemblies of block copolymers in water (samples stained by uranyl acetate): (a) PEG5000-*b*-PAChol(14/86); (b) PEG2000-*b*-PAChol(28/72). The scale bars at lower left are 200 nm.

Scheme 1 shows the chemical structure of the amphiphilic LC diblock copolymers discussed in this paper, PEG5000-*b*-PAChol(14/86) and PEG2000-*b*-PAChol(28/72), which were prepared by a typical atom transfer radical polymerization (14/86 and 28/72 are the hydrophilic/hydrophobic weight ratios). PEG5000-*b*-PAChol(14/86) presents a LC mesophase between room temperature and 197 °C, as evidenced by the birefringent textures under a polarizing microscope (heating rate: 1 °C/min). The transition temperature at 197 °C was confirmed by DSC analysis, where additionally a melting point of PEG block at 63 °C was observed on heating and a T_g of LC block at 70 °C was observed on cooling (± 10 °C/min). Similar phenomena were observed for PEG2000-*b*-PAChol(28/72): the LC−isotropic transition temperature was 114 °C upon heating (1 °C/min) by microscope; additionally, a melting point of PEG block at 57 °C on heating (10 °C/min) and a T_g of LC block at 40 °C on cooling were observed by DSC.

X-ray scattering experiments on a bulk sample of PEG5000-*b*-PAChol(14/86) revealed a SmA (smectic A) phase with lamellar period $d = 4.29$ nm (see Figure 1a). This period corresponds to a value between l and $2l$, $l = 2.65$ nm being the wholly extended length of the cholesteryl mesogen estimated by Dreiding models. So it is an interdigital smectic A phase (SmA_d).[11] No signals were observed at smaller angles (up limit of observable length is 40 nm in our study) to evidence any microphase separation in PEG5000-*b*-PAChol(14/86). For PEG2000-*b*-PAChol(28/72) in the same position of reflection ($d = 4.3$ nm), only a diffuse layer reflection (outer ring in Figure 1b) was observed, which corresponds to a fluctuation of smectic structure in the LC block. The mesophase in the LC part is a chiral nematic (N*, chiral because of the chirality of the cholesterol) from the polarizing microscope observation (see Supporting Information for POM pictures). A second reflection at 9.1 nm (inner ring in Figure 1b) was observed for PEG2000-*b*-PAChol(28/72). This reflection arises from the electronic density differences between the two blocks of the copolymer. For the morphology of the microphase separation, further SAXS and/or TEM studies are necessary.[11]

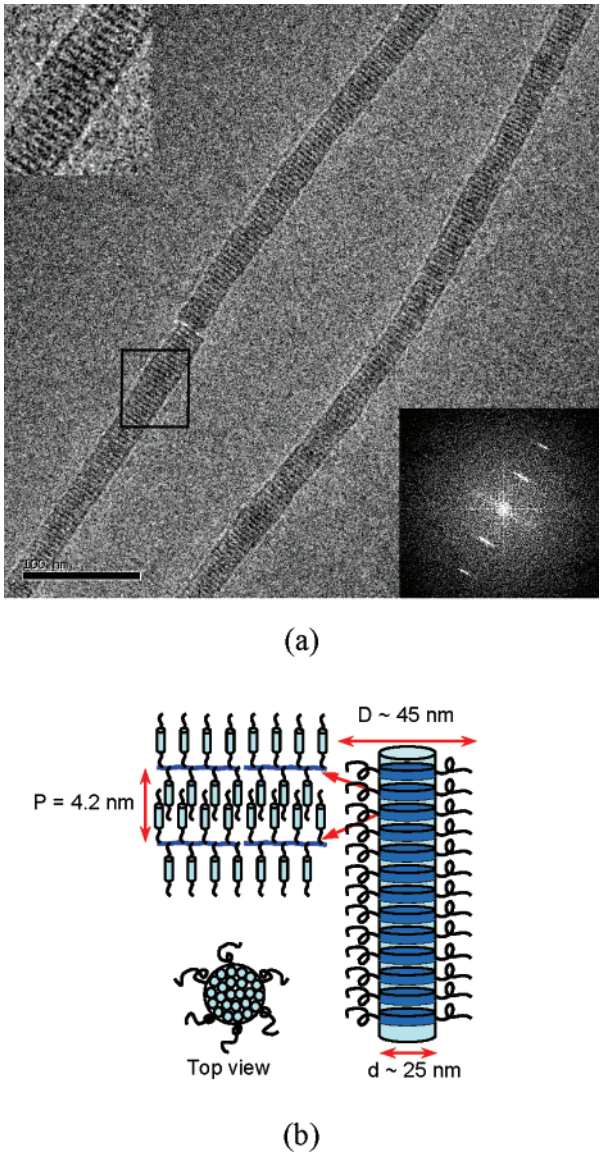

Figure 3. (a) Cryo-TEM image of nanofibers formed by PEG5000-*b*-PAChol(14/86) in water. The scale bar at lower left is 100 nm. The inset at higher left is an enlargement of the nanofiber in the selected rectangular area. The inset at lower right is the Fourier transformation of the image, which gives the period of the striated structure $P = 4.25$ nm. (b) Structural model of the nanofibers formed by PEG5000-*b*-PAChol(14/86) in water. The cholesteryl mesogens are represented by small cylinders.

Self-assembly of the amphiphilic block copolymers in water was performed using the procedure described previously.[10] Typically, the block copolymer was first dissolved in dioxane at 1 wt %. Deionized water was then added very slowly to the solution with slight shaking up to a water concentration of about 35 wt %. The mixture was then dialyzed against water for 3 days to remove dioxane, using a cellulose membrane with a

molecular weight cutoff of 3500. The morphological analysis of this turbid polymer solution was then performed by TEM on samples stained by uranyl acetate or by cryo-TEM on sample fast frozen in liquid ethane.

Nanoparticles of different morphologies were observed for the two block copolymers self-assembled in water: nanofibers for PEG5000-*b*-PAChol(14/86) and polymersomes for PEG2000-*b*-PAChol(28/72) (see Figure 2). Nanofibers observed by TEM have typical diameters of 40−50 nm. Larger diameters up to 100 nm are also observable (Figure 2a). The sizes of the polymersomes are estimated as 20−200 nm in diameter (Figure 2b). In order to get detailed structure of the nanofibers, we have studied them by cryo-TEM (Figure 3). A lamellar structure was observed, with layer normal parallel to the long axis of the nanofibers and a lamellar spacing of 4.25 nm. This value is in good agreement with the lamellar spacing of SmA phase for the LC block in bulk sample. By cryo-TEM, we measured precisely the diameter of the nanofibers, which is not homogeneous everywhere and is close to 25 nm for examples in Figure 3a. This value is smaller than that estimated by TEM with negative staining (compare Figure 2a with Figure 3a). The reason is that only the hydrophobic part is visible by cryo-TEM, the hydrophilic PEG swollen in water giving no contrast relative to the aqueous environment. However, by TEM with negative staining, the whole nanofiber is visible. Combining the cryo-TEM and TEM results of the nanofibers and the SAXS analysis on the bulk sample, we propose a structural model, as outlined in Figure 3b, for the nanofibers formed by PEG5000-*b*-PAChol-(14/86) in water. With this model, we can also explain why larger nanofibers of diameter up to 100 nm are observed. The copolymer PEG5000-*b*-PAChol(14/86) has a rather large polydispersity, $M_w/M_n = 1.5$, and an asymmetrical distribution with a larger population with long chains of LC block (PAChol). Block copolymers with long PAChol block form then nanofibers with larger diameters.

In conclusion, nanofibers with lamellar fine structure were formed in water by the block copolymer PEG5000-*b*-PAChol-(14/86). The lamellar structure in their hydrophobic core has the same origin as that of the SmA_d phase observed in the bulk sample. Both of them result from the interdigital smectic A self-organization of the cholesteryl-based mesogens. In contrary, polymer vesicles instead of nanofibers were formed by PEG2000-*b*-PAChol(28/72), in bulk sample of which only a nematic phase with smectic fluctuation was observed. (The actual in-plane order of the vesicle membrane needs to be studied further by cryo-TEM and will be discussed in a forthcoming paper.) Of course, the morphology of nanoparticles depends also on the balance of the amphiphilicity of the block copolymers.[3] In our previous studies,[10b] an amphiphilic block copolymer (PEG-*b*-PA444), in which the LC block is nematic, forms polymer vesicles in water when the hydrophilic/hydrophobic ratio is between 40/60 and 19/81. However, it does not self-assemble into nanofibers but only forms microsized spherical particles in water when the hydrophilic/hydrophobic ratio is 13/87. Therefore, it seems that the smectic organization in LC hydrophobic block is essential to realize self-assembly into nanofiber structure in the block copolymer PEG5000-*b*-PAChol-(14/86).

We can envision the use of this kind of nanofiber system in biomimetic mineralization.[7b] This study is also a part of our endeavor to understand the interplay between the LC mesophase and the self-assembly of the LC block copolymers in water. Here, the LC hydrophobic blocks, because of their mesomorphic properties, are responsive to various external stimuli[12] like temperature, light, magnetic field, and electric field. These new amphiphilic block copolymers thus pave the way for the production of new smart nanomaterials.

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Supporting Information Available: Details of the synthesis and characterization, SEC chromatograms, ^{1}H NMR spectra, DSC thermograms, POM images, and WAXS pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

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