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Self-Assembling of an Amphiphilic Polyacetylene Carrying L-Leucine Pendants: A Homopolymer Case

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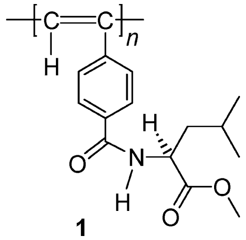
Introduction. Hierarchical organization of biological polymers such as proteins plays a critical role in the construction of living machineries,[1] and self-assembly of synthetic polymers is under enthusiastic investigation. A wealth of efforts has been devoted to the research on self-organization of copolymers, especially amphiphilic block copolymers;[2,3] as a result, a variety of morphological structures have been generated from the copolymers, and their involved assembling mechanisms have been well studied.[4,5] Self-assembling of homopolymers has, however, been much less investigated, and little is known about their organizational behaviors.[6,7]

While amphiphilic block copolymers are versatile components for morphofabrication, their syntheses often require nontrivial efforts. A widely used technique for the preparations of the copolymers is ionic living polymerization,[8,9] which has to, however, be carried out using extremely pure reagents (initiators, monomers, solvents, etc.) under stringently dry conditions in rigorously clean reactors, in addition to its high demands on synthetic skills. Many homopolymers, on the other hand, can be easily prepared under ordinary reaction conditions, which makes it an attractive proposition to utilize the homopolymers as building blocks for morphofabrications.

We have succeeded in creating a group of novel amphiphilic homopolymers, amino acid-containing polyacetylenes.[10,11] The polymers are synthesized by "simple" polymerization reactions that can even be conducted in open air using tap water as solvent.[12] The polymers possess a unique molecular structure, comprising hydrophilic amino acid pendants and hydrophobic conjugated polyacetylene backbones. In this work we studied self-assembling of one such homopolymer, poly(4-ethynylbenzolyl-L-leucine methyl ester) (**1**; Chart 1), a poly(phenylacetylene) (PPA) derivative containing L-leucine (Leu) moieties.[11b,d] We examined how the polymer chains would associate under different environmental conditions and tried to capture intermediate or transit morphological structures in an effort to understand the self-assembling behaviors of the amphiphilic homopolymer.

Chart 1



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Experimental Section. Concentrated solutions of polymer **1** in pure methanol and THF were initially prepared, which were diluted with methanol and/or THF to desired concentrations (~10−50 μg/mL).[13] Tiny drops (~2−4 μL) of the polymer solutions were deposited onto newly cleaved mica. The solvents of the deposited polymer solutions were allowed to naturally evaporate without exercising any external engineering controls to ensure that the polymer chains were self-assembling under the particular sets of environmental conditions. The resultant morphological structures were imaged on a Nano IIIa atomic force microscope (Digital Instruments, Santa Barbara, CA) operating in a tapping mode using hard silicon cantilever tips with a spring constant of ~40 N/m.

Results and Discussion. Upon natural evaporation of a methanol solution of **1** dropped on mica, pearl-shaped nanospheres are formed (Figure 1A). The nanospheres have a wide size distribution, with their diameters ranging from several tens to hundreds of nanometers. However, when a THF solution of **1** is evaporated under similar conditions, nanofibers are formed (Figure 1B). The heights and widths of the nanofibers are in the ranges ~5−12 and ~68−136 nm, respectively, and their lengths can be as long as several tens of micrometers. It is remarkable that such a small variation in solvent has brought about such a big change in morphology.

For amphiphilic block copolymers, their hydrophilic and hydrophobic blocks have distinct affinities with surrounding solvent molecules, which drives the different blocks to associate according to attraction and aversion in order to minimize the contact between immiscible components.[3] In homopolymer **1**, there exists, however, no such blocks. How do the homopolymer chains change their morphological structure when the solvent is changed from methanol to THF? Methanol is a very polar solvent with a high Debye solvent polarizability ($P_s = 0.91$),[14] while THF is less polar and has a moderate P_s (0.68).[15] Methanol is thus a good solvent of the polar Leu pendant of **1** but a nonsolvent of its nonpolar PPA backbone, while THF is a good solvent of both of the Leu pendant and the PPA backbone.[12] Although **1** is soluble in both methanol and THF at low concentrations (thanks to its chain amphiphilicity), the polymer chains should aggregate in different ways according to their different affinities with the solvent molecules when the solution thickens accompanying solvent evaporation.

When methanol evaporates, the solution concentration effectively increases and the polymer chains undergo interstrand association. Because the hydrophilic methanol solvent and the hydrophobic PPA backbone do not have an attraction for each other, the amphiphilic

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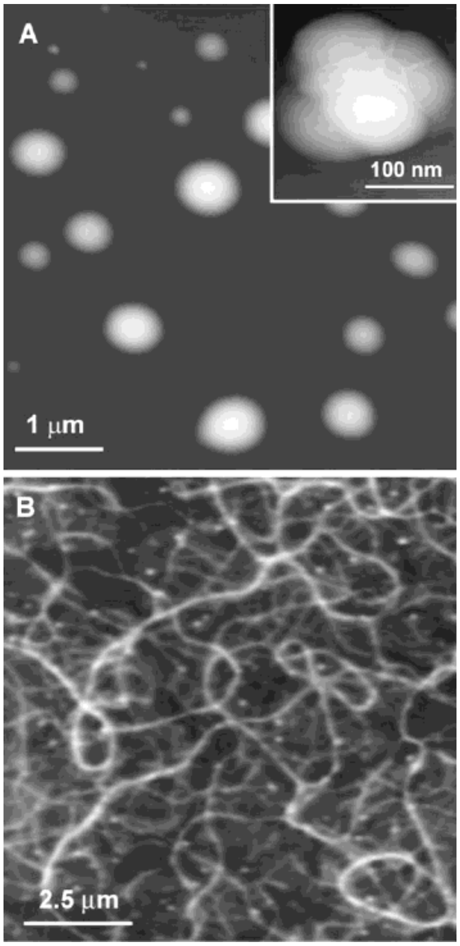
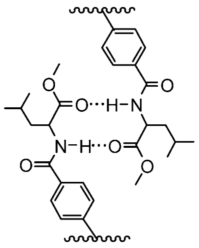


Figure 1. (A) Nanospheres and (B) nanofibers formed by polymer **1** upon natural evaporation of its (A) methanol and (B) THF solutions. Inset in panel A: zooming-in image of a nanocluster of the polymer.

Chart 2



polymer chains may form micelle-like structures with the PPA backbones located in the cores and the Leu pendants positioned outward on the shells. The micellar coronas are thus decorated with numerous amino acid moieties, and many small micelles may stick together through intermicellar hydrogen bonding, an example of which is shown in Chart 2, to form large micelles to minimize the interfacial surface areas. Similarly, the large micelles can further merge into pearl-like nanospheres, again with the aid of the intermicellar hydrogen bonding. We occasionally capture the images of some intermediate nanoclusters, an example of which is given in the inset of Figure 1A. The surface contour clearly indicates that the "large" nanocluster is formed by agglomeration of many small micelles of different diameters.

As THF can solvate both the PPA backbone and the Leu pendant, the polymer chains of **1** may take an extended conformation in the dilute THF solution. Accompanying the solvent evaporation, the extended polymer chains may intertwine with each other via interstrand hydrogen bonding (Chart 2) to form nanofibers. While the side-by-side hydrogen bonding of the polymer chains facilitates the formation of thick nanofibers, their head-to-tail hydrogen bonding assists the extension of nanofibers in length. The bundling of the macromolecular chains during the solvent evaporation is, however, a statistic but not a synchronic process, hence the observed coexistence of the nanofibers of various sizes. Some small dots are also formed, probably due to the self-coiling of isolated polymer chains and their small mismatched aggregates.

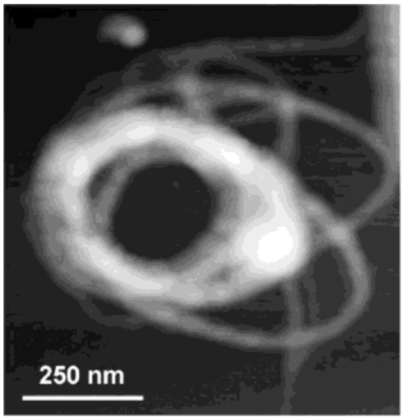


Figure 2. Doughnut ornamented with coiling nanofibers formed by polymer **1** upon natural evaporation of its solution in a mixture with a THF/methanol ratio of 1:2.5.

We are intrigued to follow the transition process from the nanospheres to the nanofibers and to probe the intermediate structures to be formed by the polymer chains when mixtures of methanol and THF are used. We prepared polymer solutions in methanol/THF mixtures with varying solvent compositions.[13] Upon natural evaporation of a solution of **1** in a mixture with a THF/methanol ratio of 2:5 (or ~29% THF), a doughnut adorned with entwining fibrils is formed (Figure 2).[16] This morphological structure is of intermediate feature, for the doughnut seems to be evolved from the nanospheres formed by the pure methanol solution, while the fibrils clearly resemble the nanofibers formed by the pure THF solution. Increasing the THF ratio in the solvent mixture populates the fibrous morphology; as can be seen from Figure 3, most of the structures formed by a solution in a mixture with a high THF/methanol ratio of 3:4 (or ~43% THF) are nanofibers.[16] The nanofibers are ~34−99 nm in width, ~2−20 nm in height, and a few tens of micrometers in length; that is, their dimensionality is comparable to that of the nanofibers shown in Figure 1B. Interestingly, all the fibrous nanostructures are ring-shaped. When the solvents evaporate, methanol tends to encourage the polymer chains to coil into micellar spheres, but THF is inclined to induce the polymer chains to twist into extended fibrils. The balance of these two different force fields leads to the formation of the mesomorphic structure, the ring-shaped nanofibers. When THF becomes a major component in the solvent mixture, the extended fibers become dominant structures; for example, upon natural evaporation of a polymer solution in a mixture with a THF/methanol ratio of 6:1 (or ~86% THF), morphological structures almost identical to those shown in Figure 1B are formed.

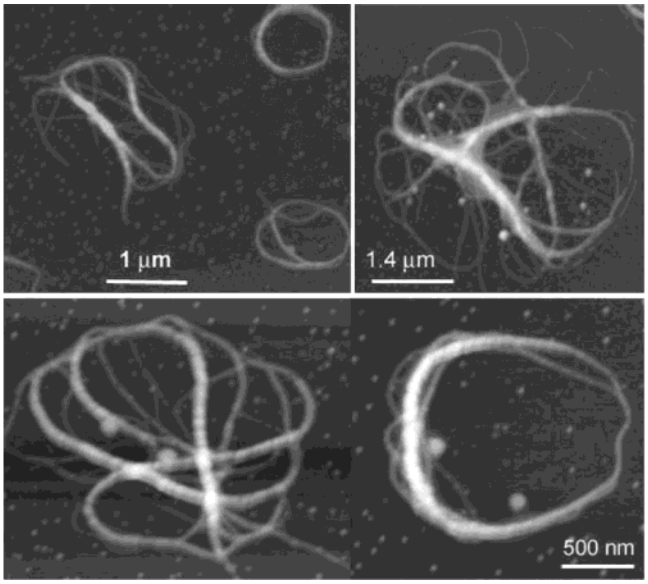


Figure 3. Loops and cages of nanofibers formed by polymer **1** upon natural evaporation of its solution in a solvent mixture with a THF/methanol ratio of 1:1.3.

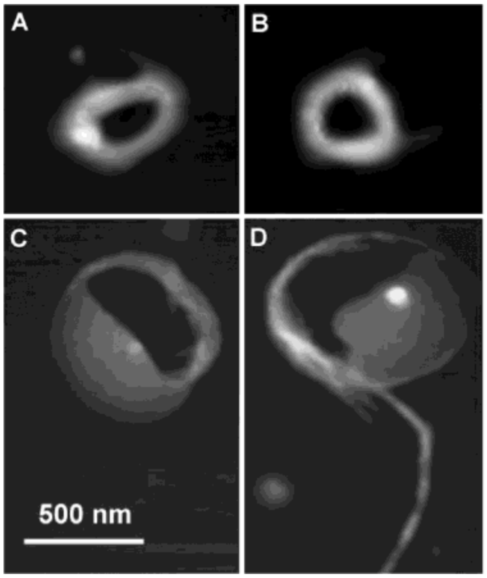


Figure 4. (A, B) Doughnuts and (C, D) globules formed by polymer **1** upon natural evaporation of its solution in a solvent mixture with a THF/methanol ratio of 1:3. The morphological structures shown in the upper (A, B) and lower panels (C, D) are respectively imaged ~0−1 and ~4 min after a small amount of THF has been added into a dilute methanol solution of **1**.

We are also interested in learning the time course of morphological transition. To make the transition process slow enough to be followed, we used a solution in a mixture with a low THF/methanol ratio of 1:3 (or 25% THF). We focused our observations on the transit structures dominant at different time intervals. Obvious change in morphological structure immediately occurs once a small amount of THF has been added into a methanol solution.[13] The morphology formed by evaporation of the polymer solution ~0−1 min after the solvent mixing[17] is doughnut-like, with wall widths and heights in the ranges ~125−139 and ~41−51 nm, respectively (upper panel of Figure 4). Short nanofibers stretching from the doughnut loops are also found. The morphology changes with time: after THF has been added into the methanol solution for ~4 min, the walls of the doughnuts become thinner, the loops become larger, and the partial globules become major structure. The nanofibers extending from the broken globules also become longer and thicker, as shown by an example given in Figure 4D.

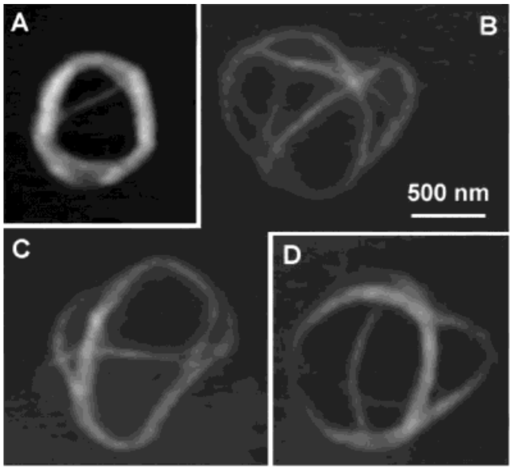


Figure 5. Rings and cages of nanofibers formed by polymer **1** upon natural evaporation of its solution in a solvent mixture with a THF/methanol ratio of 1:3. The morphological images are taken ~20 min after the solvent mixing.

After 20 min, the fibrous morphology becomes a dominant structure (Figure 5). The nanofibers have heights and widths in the ranges ~2−9.3 and ~18−40 nm, respectively, which coil around to form ring-shaped or cagelike structures. Incubation of the solution for longer times causes little change in the morphological structure formed by natural evaporation of the equilibrated polymer solutions, suggesting that the cage-shaped nanofibers are the final morphology at this solvent composition (25% THF) or that the morphological transition has finished in ~20 min after solvent mixing. This relatively slow process is probably associated with the polymeric nature of the amphiphile of **1**: it takes some time for the THF molecules to approach the polymer backbones and to solvate the polymer chains, especially when they have already been presolvated by the methanol molecules. This is not difficult to understand: we have experience in taking as long as about 1 week time to dissolve a high molecular weight polyacetylene, poly[1-(trimethylsilyl)-1-propyne], in its good solvent of toluene.[18] The very high molecular weight of polymer **1** ($M_w \sim 1.5 \times 10^6$)[19] may have also contributed to slowing down the transition process, making the intermediate morphological structures readily capturable by the AFM microscope.

In summary, homopolymer **1** is found to self-assemble into distinct morphological structures under different environmental conditions: its amphiphilic chains self-organize into nanospheres and nanofibers accompanying natural evaporation of its methanol and THF solutions, respectively. By adjusting the polarity or solvating power of the solvent mixture and by initiating the assembling process at different times, a series of intermediate structures are observed, revealing morphological transition processes from micellar nanopearls, via rings, globules, loops, and cages, to extended nanofibers, when the ratio of THF to methanol in the solvent mixture is increased. Interstrand hydrogen bonding is believed to be involved in the self-association processes of the polymer chains, and affinity or likeness of the solvent molecules with the hydrophobic PPA backbone or the hydrophilic Leu pendant may be responsible for the amphiphilic homopolymer chains to vary their assembly structures in response to the changes in their solvent surroundings. Unlike copolymers, homopolymers have been commonly believed to be difficult to self-assemble into well-defined morphological structures.[20] Our demonstration of the ready formation of the well-organized nanostructures by natural evaporation of the homopolymer solutions of **1** here may trigger new research efforts in using "simple" homopolymers as architectural units for nanostructural morphofabrications.

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(13) All the solutions in either the pure or the mixed solvents used in this work were kept in this narrow window of concentrations for the purpose of comparison.

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(17) Immediately deposited onto mica and imaged by AFM after admixing the added THF solvent with the methanol solution by quick and vigorous shaking.

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