論文の内容の要旨

論文題目　**Studies on Hierarchical Formation and Characterization of Polymeric Nano-assemblies**
（高分子ナノ組織体の階層的な構造制御とキャラクタリゼーションに関する研究）

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1. Introduction

Over the past decade, nanostructured materials, one of the most hotting and also promising fields of research in materials, have attracted a great deal of attention because of both fundamental science and their potential applications in areas such as electronics, catalysis, optics, ceramics, magnetic data storage, drug releases, sensors. The development of methods to construct small polymeric nano-assemblies would be interdisciplinary, combining fields such as physics, chemistry and biology, and remains a challenge that limits advances in many fields of nanoscience and nanotechnology. This thesis is focus on the studies of hierarchical formation and characterization of polymeric nano-assemblies. The research is done using the stereoregular poly(methyl methacrylate)s (PMMAs), with the same chemical structure but different configurations, as the model polymers. In this research, a facile and stepwise method to fabricate hierarchically grown nanostructures composed of polymeric crystals was firstly developed. It gives some new insight for nanoscale structure formation of crystalline polymer systems.

2. Experiments, results and discussion

2.1 Preparation and characterization of surfactant-free nanoparticles composed of stereoregular poly (methyl methacrylate)s

Surfactant-free nanoparticles composed of it, st, and at PMMAs with fairly narrow size distributions were prepared by adding water into freshly prepared PMMA solutions, and subsequently evaporating THF. A schematic illumination of the route to prepare surfactant-free PMMA nanoparticles is shown in Figure 1. The morphologies and particle sizes of obtained PMMA nanoparticles were characterized by scanning electron microscopy (SEM) and dynamic light

scattering (DLS). As their SEM images (Figure 2) shown, the obtained particles were spherical in shape and fairly mondisperse, and their sizes were unexpectedly dependent on PMMA stereoregularity. Under the same preparation conditions, the at-PMMA nanoparticle showed the largest size, while the it-PMMA showed the smallest. The particle size generally increased with increasing the initial PMMA concentration and the THF/water volume ratio. Attenuated total reflection infrared (ATR-IR) and wide-angle X-ray diffraction (WAXD) measurements revealed that it- and st-PMMAs formed characteristic helical structures in nanoparticles. These observations suggested that formation of helical nanostructures can enhance in the dynamic THF evaporation process. As a novel finding, I show herein that the formation of helical nanostructures during particle preparation results in a decrease in particle size.

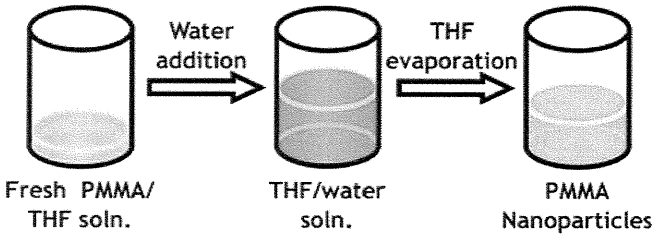

Figure 1. A schematic illumination of the preparation of PMMA nanoparticles.

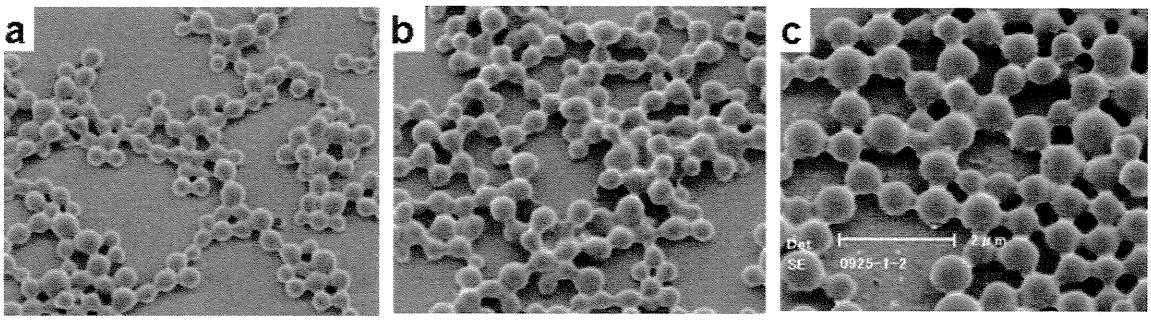

Figure 2. SEM images of (a) it-PMMA (*mm* : *mr*:*rr*=95.5:2.3:2.2, M_w=21000), (b) st-PMMA (*mm*:*mr*:*rr*=0.6:12.6:86.8, M_w=23000) and (c) at-PMMA(*mm*:*mr*:*rr*=4.5:36.5:59.0, M_w= 23000) nanoparticles.

2.2 Nanoribbon networks composed of hierarchically grown polymer crystals

As above results shown, nanoparticles could be prepared using fresh PMMA solutions with the method illuminated in Figure 1. However, it was found that no nanoparticle but bulk precipitates were observed by aforementioned method, when the long time stock it-PMMA solutions, instead of freshly-prepared solutions, were used. The ATR-IR and WAXD measurements showed transitions of it-PMMA chains from the nonhelical states to the helical states with energetically favorable *tt* conformations in their backbones and crystalline states of precipitated it-PMMAs. These observations suggested formation of helices in stock THF solutions and further crystallization of them with adding water and evaporating THF.

Motivated by this hierarchical process of the crystallization of it-PMMA, we developed

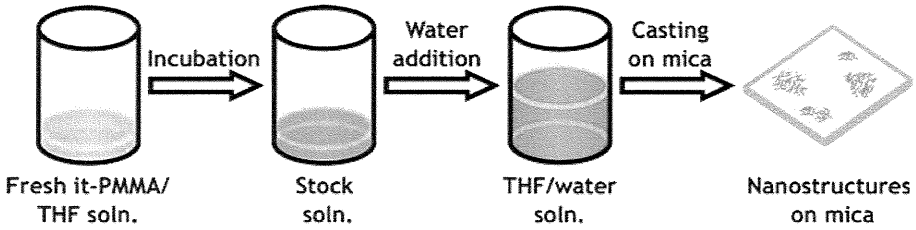

Figure 3. A schematic illumination of the preparation of nano-ribbon networks by solvent evaporation methods.

a facile and stepwise method to fabricate hierarchically grown nanoribbon networks composed of polymers by a solvent evaporation method on mica. As shown in Figure 3, the THF solution was firstly incubated for a certain time, then water was added into the incubated solution, finally the resultant THF/water solutions was casted on mica. The nanoribbon networks were observed after evaporation of solvents.

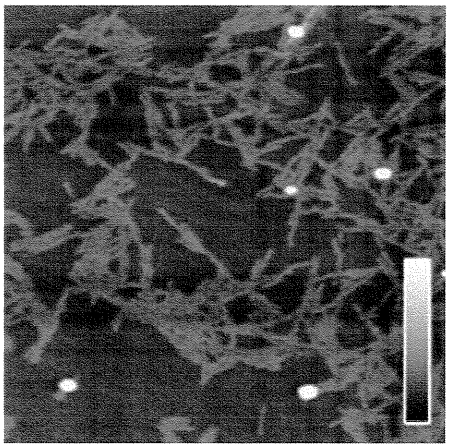

Figure 4. AFM height image of the it-PMMA film surface on mica. Scale: 2.5 × 2.5 μm. The Z-scale is 3 nm.

By this method, nanoribbon networks composed of it-PMMA crystals (Figure 4) were fabricated from THF/water solutions prepared using the 2 months incubated THF solutions. The control experiments, preparing samples using freshly prepared THF solution or directly casting the incubated THF solution on mica, showed that no nanoribbon networks were observed, thereby, suggesting that the incubation of THF solution and the addition of water were indispensable to successful fabrication of hierarchically grown nanoribbon networks.

When solutions with longer incubation time were used, multilayered nanoribbon networks and compact films composed of it-PMMA nanoribbons could be observed, indicating greater amounts of a precursor of it-PMMA crystals were formed with increasing incubation time. The investigations on the effect of the ratio of THF/water on the formation of nanoribbon networks revealed that the samples

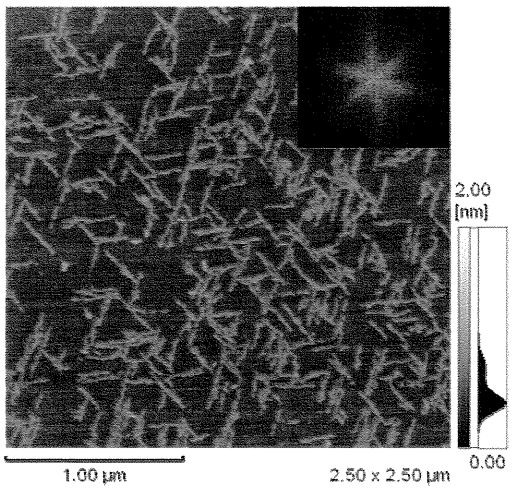

Figure 5. AFM height images of the it-PMMA nanoribbon networks on mica. The inset was the 2D Fourier transform of the image, showing preferential orientation of the nanoribbons.

prepared from THF/water solution with the THF/water from 1 : 2 to 1 : 4 shared similar nanoribbon networks composed of it-PMMA crystals. The most interesting observation (Figure 5) was that highly oriented nanoribbon networks formed by an epitaxial growth of nanoribbons according to the three-fold symmetry axes of the underlying mica surface could be fabricated when I allowed the THF/water solution, prepared by adding 3 mL water to 1 mL 2 months incubated THF solution, and then evaporated for 5 hrs before casting on mica. This observation suggested that the facile method could be used to control the epitaxial growth of crystalline polymers on mica surface.

3. Conclusions

Using the streoregular PMMAs as model polymers, a series of streoregular PMMA nanoparticles was prepared by evaporation of THF from its THF/water solution to study the effect of the formation of polymeric regular structures, such as helices, on the final sizes of obtained nanoparticles. It was found that the formation of helical structures during the particle preparation resulted in the acquisition of smaller-sized particles. However, when the THF/water solution was prepared using incubated it-PMMA solutions, in which helical structures were already formed, no nanoparticle but bulk precipitates with high crystallinity were observed. Motivated by this, we developed a facile and stepwise method to fabricate hierarchically grown nanoribbon networks composed of polymers by a solvent evaporation method on mica. With this method, nanoribbon networks, composed of it-PMMA crystals, with various morphologies, such as monolayer structures, multilayer structures, compacted films and epitaxial patterns, could be observed.

I believe that the present hierarchal method may be generally applicable to other crystalline polymers. The generality of this method will be investigated in the near future.