

# A Novel Aggregation State of Amphiphile: Spherular Crystal

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Received December 30, 1997. Revised Manuscript Received March 10, 1998

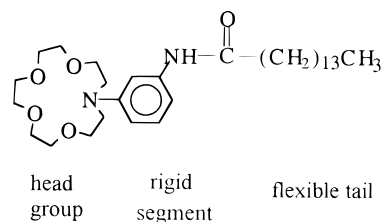
When the amphiphile single-chain aza crown ethers crystallize from its melt, a novel aggregation state—spherulite—is observed. Distinguished from the others, this spherulite has hierarchical structures: the spherulite consists of the solid cylinders, and the cylinder is composed of the bilayer of the amphiphilic molecules. This is a good example of molecular architecture, and the discovery will promote study on self-assembly and self-organization of amphiphile in the future.

As the use of molecular self-assembly and self-organization may be possible to engineer various special microscopic structures, it has the potential to enable the fabrication of technologically useful microstructures.<sup>1,2</sup> Therefore, the research on molecular tectonics has received considerable attention and has developed very rapidly in recent years.

Unlike other compounds, amphiphiles consist of two elemental structural segments at least: a polar hydrophilic headgroup and an unpolar flexible tail. As a result, they always display several kinds of aggregation states which result in different molecular orientations.<sup>3</sup> In general, amphiphilic molecules can form various aggregation states such as the following: micelles, reversed micelles, microemulsions, monolayers, bilayers, unilamellar or multilamellar vesicles, Langmuir–Blodgett films, cast films, liquid crystals and crystals.<sup>2–4</sup> Subsequently, the lipid tubule, which is formed by a membrane wrapped in a hollow cylinder, is reported as a special aggregation state of some single-chain amphiphiles.<sup>5</sup>

However, in our present work, we found the single-chain aza crown ether **I**, (Scheme 1) a typical amphiphilic compound we synthesized, can form a novel aggregation state: a spherular crystal (spherulite, a kind of solid state). Although the structure of inorganic, organic, and finally polymeric spherulites are extensively studied<sup>6</sup> and much of the information on spheru-

**Scheme 1. Chemical Structure of Single-Chain Aza Crown Ether I**



lites is described by many works, the spherular crystal of amphiphile **I** is unusual not only because it is the first one but also because it has some peculiar features that are quite different from the ordinary ones.

## Experimental Section

**Material.** The amphiphile single-chain aza crown ether **I** was synthesized by our laboratory according to the procedure described previously.<sup>7</sup> The product was purified and recrystallized from ethanol twice. The purity of the compound **I** was >99.8%, and the structure was confirmed by spectroscopic and chemical analysis.

**Preparation of the Spherular Crystal.** The thermal and optical properties of the single-chain aza crown ether **I** were studied using a differential scanning calorimeter (Setaram Micro-DSC, France) and a polarizing microscope (Leitz, Germany) with a heating stage. The differential scanning calorimetry (DSC) study showed that the melting point of the compound was 94.8 °C. Therefore, we put the compound on the heating stage and raised the temperature to 96 °C. After the compound was melted completely, the temperature was decreased to 45 °C and then dropped to the room temperature (18 °C) at the rate of 0.5 °C min<sup>-1</sup>. Under the microscope, it was observed that a novel aggregation state of the amphiphile—spherular crystal—was nucleated and grown during the cooling (the nucleation occurred at the temperature of ≈40 °C). At room temperature, the formed spherulite of amphiphile **I** was a very stable solid.

## Results and Discussion

When the spherulite crystallized from the melting state of compound **I**, as the principles of crystallization

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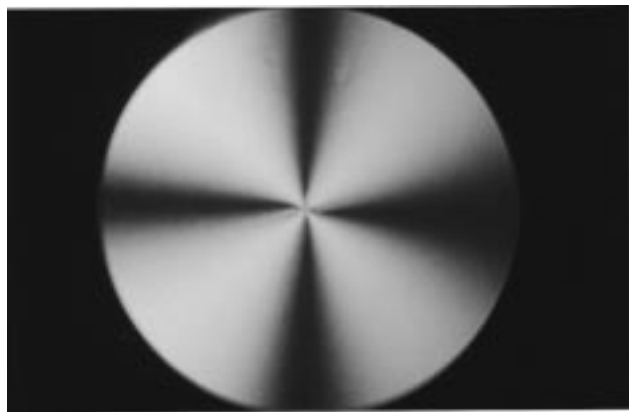
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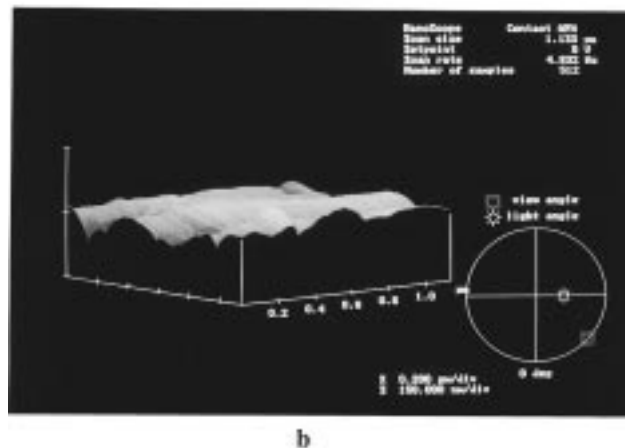
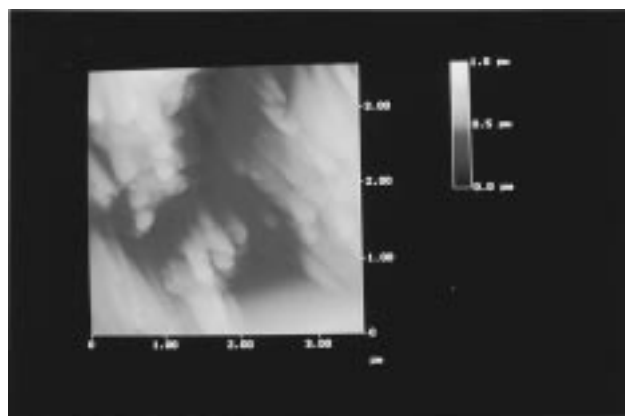


**Figure 1.** Microscope image of spherulite I taken under crossed polarizers ( $\times 40$ ).

kinetics,<sup>8,9</sup> its spherulitic crystallization was nucleated at the center and followed by radial growth during the formation. Its size could be controlled easily by regulating the rate of temperature drop after the nucleation. The morphology of the formed spherulite was a perfect sphere, as shown in Figure 1. Under the optical microscope with cross polarizers, a black cross named the Maltese cross, which was a peculiar characteristic of most spherulites, appeared. The cross was brought about by the zero amplitude extinction of birefringence in the spherulite.<sup>9</sup> When the specimen was rotated in its own plane, the cross remained stationary. According to the past studies, these phenomena implied that all radii were crystallographically equivalent to within the resolution employed and also meant that the major refractive index (molecular chain) in the spherulite was either parallel or perpendicular to a radius.<sup>9</sup> Besides the Maltese cross, however, the banded structure with close concentric bright-dark stripes that can often be observed in other spherulites<sup>9,10</sup> did not exist in this spherulite.

The spherulite was examined by the FTIR method, and its results confirmed that the chemical structure of the amphiphile I was not changed during its formation. Nevertheless, compared with the pattern of the polycrystals powder of amphiphile I, the intensities and widths of the IR absorption peaks of its spherulite were obviously increased, and the bathochromic shift occurred simultaneously. This fact suggested that the spherulite had significantly more order aggregation and that molecular interaction was enhanced internally. As a result, the DSC study also showed that the melting point of the spherulite was raised to 95.3 °C, and it was a sharp peak in the thermogram.

The most interesting phenomenon was not only the spherulite itself, but also the uncommon hierarchical structure of the spherulite. In the past, people had realized that spherulites (most of polymers) always have substructures, and fibrous, needlelike, and lamellae



**Figure 2.** Contact mode AFM images of spherulite I. Panel a shows that the spherulite is made up of many cylinders and their long axes parallel to the radii of the bulk spherulite; Panel b is the detailed image of the cylinders.

morphology are certified.<sup>6,9</sup> To make meaningful progress in the understanding of this novel aggregation state, it was necessary to study the microstructures presented in the spherulite of amphiphile I. Since atomic force microscopy (AFM) is a most powerful instrument in the investigation of microstructures, we studied the spherulite by means of the Nanoscope III multimode AFM (Digital Instruments). It was revealed that the substructure of the spherulite was complex, and its morphology was cylindrical with a diameter of ca. 300 nm (generally, the length is more than 20  $\mu\text{m}$ ). In fact, the spherulite structure was composed of innumerable cylinders, as shown in Figure 2. These cylinders were always densely and orientedly packed, and their long axes lay just along the spherulite's radii. Therefore, the spherulite might be considered as an organized assembly of the cylinders with nearly spherical symmetry in macroscopic view. As a large-scope scanning on the spherulite crystal by AFM did not find any tube branching, it was suggested that the number of cylinders must be very small in the center of the spherulite and increase radially to incorporate the condensed structure of the solid state.

But how do the amphiphiles make up the cylinder? As mentioned above, the recent research work on lipid tubules is one of the active topics in the study of molecularly engineered structures. Is the structure of the cylinder formed in the spherulite the same as that

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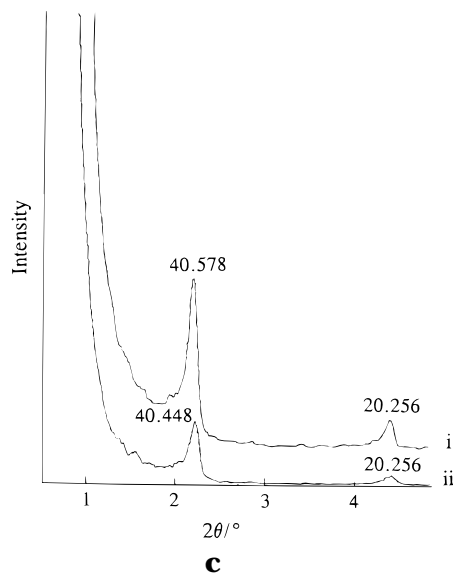
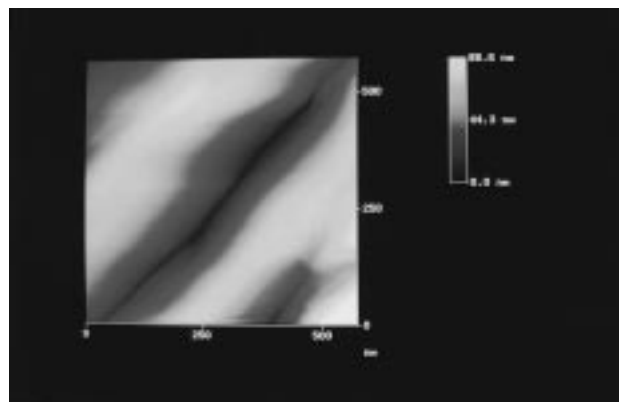
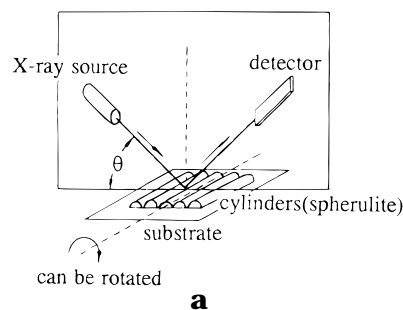
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of tubules? Our answer is no. One of the proofs was that the densities of the spherulite were the same as that of the polycrystals powder **I**. So, the cylinders in this spherulite must be solid, but the feature of these mentioned lipid tubules is hollow.<sup>5</sup>

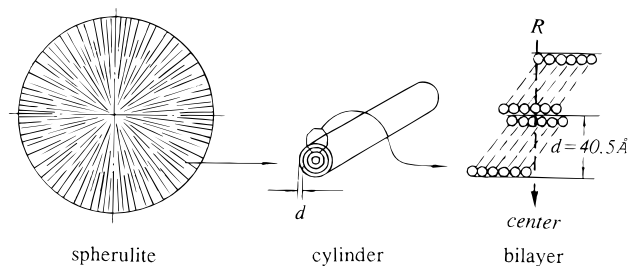
To understand the microstructure of the cylinder well, X-ray diffraction (XRD) was applied on the samples. In this experiment, we prepared the spherulite between two pieces of glass with less than  $0.5\ \mu\text{m}$  spacing so that the growth of spherulite was limited on a plane. Under such circumstances, nearly all the cylinders in the "plane-spherulite" were parallel to the substrate plane. The details of the experiment and the AFM image of the cylinders are described in parts a and b of Figure 3, respectively. The obtained results were related to the structure of the cylinder at vertical direction. In the diffraction pattern (Figure 3c), only one set of Bragg peaks was observed and the derived long spacing ( $d$ ) was about  $40\ \text{\AA}$ . These two peaks did not exist in the XRD pattern of the polycrystals of compound **I**, which had a lot of peaks but the largest  $d$  was about  $27\ \text{\AA}$ . This was another experimental evidence that showed the structural difference between the spherulite and the polycrystals of the amphiphile. However, the value ( $40\ \text{\AA}$ ) was in close agreement with the thickness of the bilayer with *J*-like aggregation of amphiphile **I**.<sup>7</sup> When the substrate, together with the cylinders, was rotated with varying angles as in the illustration, the diffraction pattern reflected the information of the cylinder at different directions which were still perpendicular to the cylinder. It was interesting that the pattern remained stationary except for the intensities of both peaks which decreased. This phenomenon meant that the structural regularity in the cylinder was axially symmetrical. Clearly, the above results denoted that the basic structural unit of the cylinder was bilayer, and the units were stacked just along with the radius of cylinder. To some extent, the morphology of the cross section of the cylinder was similar to that of the multilayer vesicle. With this suggested model, lacking of the banded structure, the spherulite **I** could be explained well. The banded structure had been studied thoroughly, and the accepted explanation was that it was a result of the lamellae twisting of the substructure around the radial direction in spherulites.<sup>9</sup> However, the substructure of our spherulite was the cylinder, which was axially symmetrical, and each cross section of cylinder was the same. Therefore, even if it was "twisted" around the long axis of the cylinder, its shape and structure remained stationary and there was no change at all. So, the characteristic of birefringence along the axis directions in the spherulite was the same too, and the banded structure would disappear accordingly. Besides, we also noticed that the molecular chains (the major refractive index of the amphiphilic molecule) were perpendicular to the spherulite radius in our model, which was in agreement with the mentioned experimental result of the Maltese cross, and this feature was similar to that of the other spherulites.

In conclusion, the hierarchical structure of the spherulite of amphiphile **I** could be derived as in Figure 4: the spherulite consisted of innumerable cylinders and had center symmetry in macroscopic view, and the cylinder was composed of the bilayer and had axial



**Figure 3.** Panel a is a scheme of the XRD study on the spherulite prepared between two pieces of glass. As a result, the cylinders in the spherulite lie on the plane of the substrate just as in the AFM image (b) shown. The direction of the substrate placed in the diffractometer can be regulated by rotating. (c) No matter the substrate's directions are changed, its diffraction patterns (i and ii) are unchanged, and there is only a set of Bragg peaks in the pattern.

symmetry. Thus, the formation of the bilayer structure was a most important factor for the formation of spherulite **I**. In 1994, we had reported that the synthetic aza crown ethers with single-chains containing more than 10 carbons could form stable bilayer membranes.<sup>7</sup> Coincidentally, we found that all these aza crown ethers whose alkyl chain contained 10, 12, 14, or 16 carbons could also form spherulites, and **I** (14 carbons) was only the typical one chosen among them

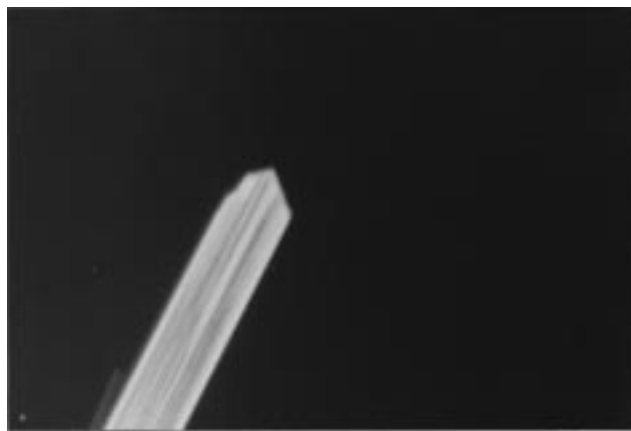


**Figure 4.** Hierarchical structure of the spherulite.

in this paper. On the other hand, when carbons in the long chains were numbered than 10, both the stable bilayer membrane and the spherulite could not form. In general, the needle-shaped crystals were always formed during cooling, and their characteristics of FTIR, DSC, and XRD studies are the same as those of the polycrystals powder. For instance, the morphology of the synthetic aza crown ether with a single chain containing six carbons is shown in Figure 5.

### Conclusions

In this paper, we have found and demonstrated that the amphiphile single-chain aza crown ether **I** can form a novel aggregation state, which is spherular crystal. Different from the normal ones, the spherular crystal formed from the amphiphile has special hierarchical structures, and it is a good example of molecular architecture. As for the other aggregation states of the



**Figure 5.** Morphology of the derived compound of **I** whose alkyl chain contains 6 carbon atoms crystallized from the melting state.

amphiphile, the formation of the spherular amphiphiles is also related to their chain length. These discoveries will not only extend the study of polymorphology of amphiphiles but also promote the further research on spherular crystals.

**Acknowledgment.** We thank National Natural Science Foundation of China for financial support.

CM9708224