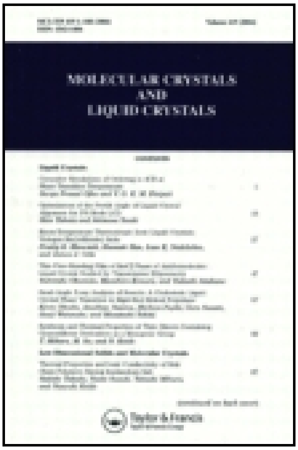

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Self-Organization in the Growth of Azotic Crown Ether

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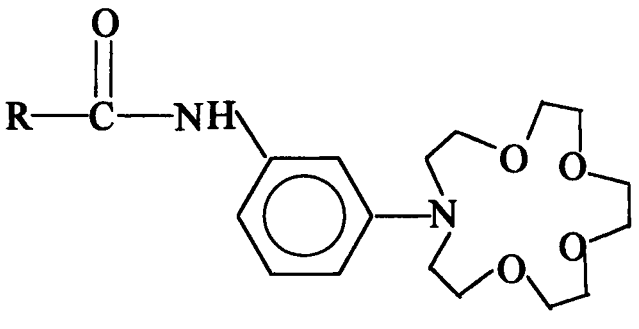
We present here observations on the growth habits of a crown ether from the melt. Two spherulites A and B are obtained. It is established that spherulite A has bimolecular layered structure and spherulite B has net-like structure. Atomic force microscopy (AFM) is used to observe the surface morphology X-ray diffraction and IR spectroscopy are used to analyze crystal structure and hydrogen bonding formation. This is the first time to find the molecular self-organization of bimolecular-layered structure and the net-like structure when crystals grow from melt.

Keywords: Self-organization; crown ether; melt growth

The study of the self-organization has been greatly progressed in the last years (1–8). Many supramolecular structures have been obtained in solution (2), monolayer (3,4) and solid (5–8). The impetus for these are: 1) the self-organization occuring in biological systems through networks of cooperative noncovalent interaction; 2) the advance of material science in the nanostructures. Self-organization often exists in systems of amphiphilic molecules. It is usually caused by weak forces, such as hydrogen bonds, polar interactions and hydrophobic interactions of alkyl chains. It is also studied in semiconductive materials for its possible application in energy conversion, transport and storage (9,10). When the crystals of amphiphilic molecules grow from the melt, the self-organization is not studied, yet the self-organization is reasonably expected. In this letter, we have investigated the growth habits of azotic crown ethers, and have elucidated their self-organization structures through a series of physical methods when they grow from the melt, and have depicted the crystal structures of different phases.

A series of monoalkyl azotic crown ethers containing the phenyl group as a rigid segment were synthesized (11). Their molecular formulae are shown in Figure 1. The molecules are amphiphilic, having a long alkyl chain and a polar head.

A sample with $n = 14$ was placed into a glass cell with the space 10 μm separated by two lamella mica. The cell was introduced into an oven. The temperature was raised to 100°C, then decreased at different temperatures and finally kept constant. We observed the sample using Leitz polarized microscope. Figure 2a–d are the micrographs at different temperatures. We have found that, when $T = 70°C$, a disk-like phase appears which is growing (Fig. 2a). It is birefrigent and its birefrigent pattern is characteristic of a spherulite. Its edges are quite rough. We call it spherulite B. When $T = 65°C$, another kind of spherulite begins to form (Fig. 2b). Its birefringence is strong and its edges are quite flat. We call it spherulite A. It begins to nucleate primarily at the edges of spherulite B and it may also nucleate in the bulk of isotrophic phase. Its growing rate is much faster than that of the spherulite B. There are several nuclei in the field of veiw. They grow-up quickly to cover all the cell. After spherulites have covered all the cell, we continue to decrease temperature down to 32°C and keep it constant. We have found that some concentric dark lines appear in spherulite A (Fig. 2c).



$R = C_nH_{2n+1}$, $n = 6, 8, 10, 12, 14, 16, 18$

FIGURE 1 Molecular structures of monoalkyl azotic crown ethers.

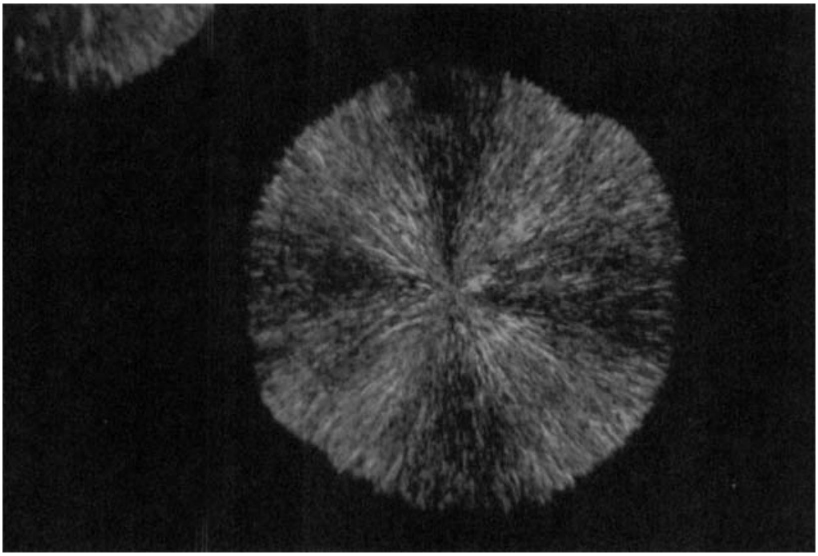


FIGURE 2 Micrographs of the spherulites under polarized microscope: a) spherulite A; b) spherulite B; c) concentric dark lines appear in spherulite A; d) spherulite A and spherulite B co-exist, the weaker birefrigent spherulites are spherulite B. The magnification is 40. (See Color Plate IX).

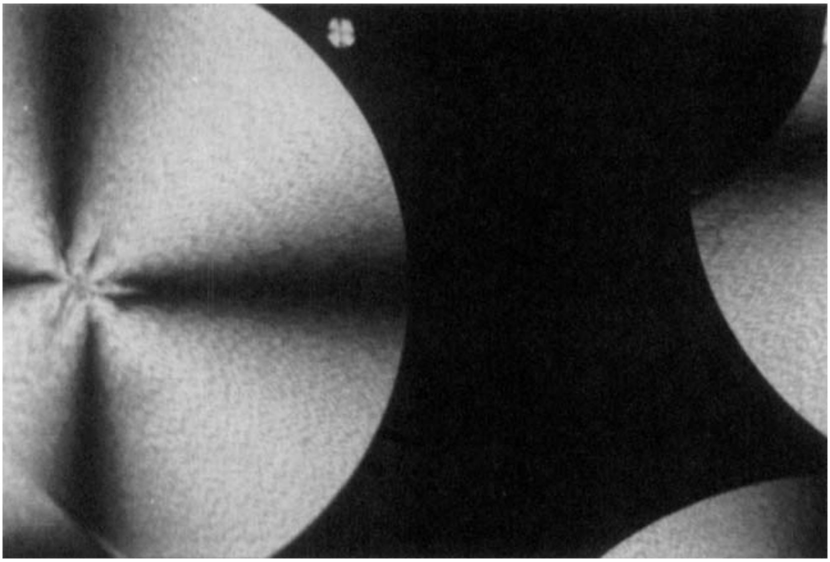
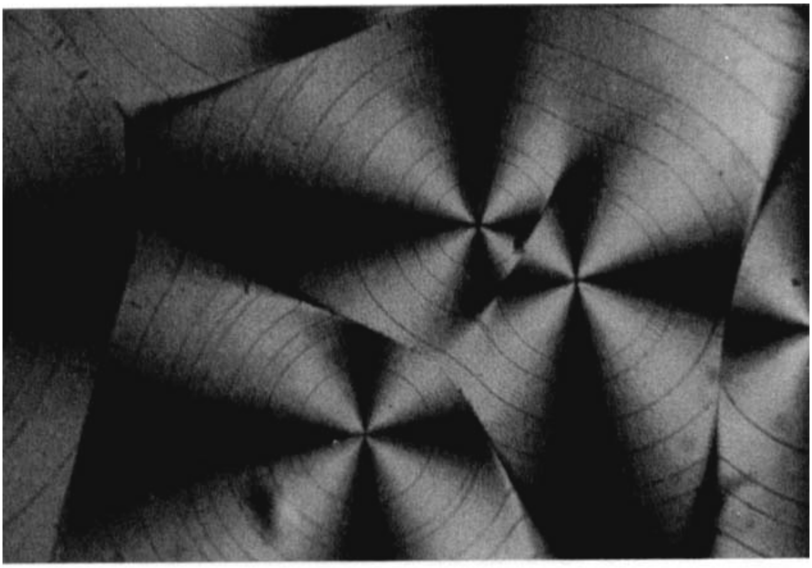
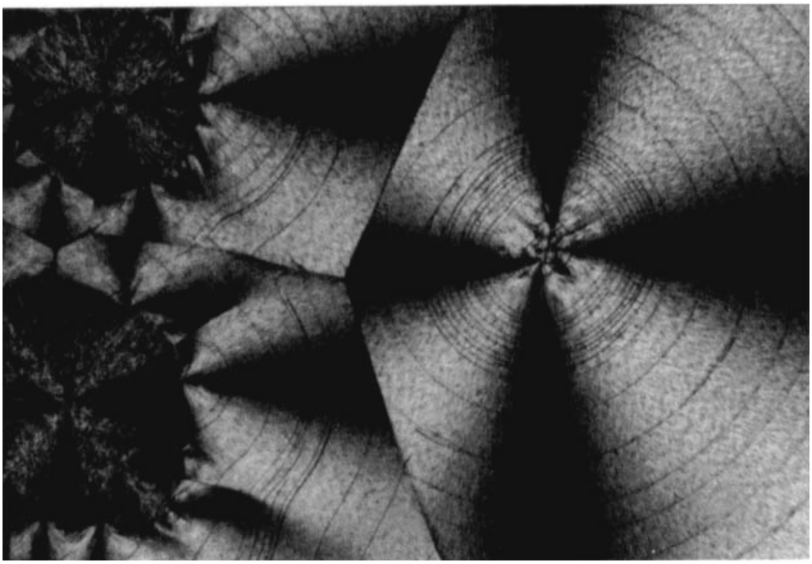


FIGURE 2 (Continued).



(c)



(d)

FIGURE 2 (Continued).

They appear very quickly. A circle appears almost at the same time to the naked eye. The intervals are very long more than 10 minutes. Sometime they stop at defects or the interfaces of two spherulites. If the circles of two adjacent spherulites are both at wide angles and almost perpendicular to the interface, they can be cojointed. Further studies with $n = 6-18$ show that, when $n = 6-12$, spherulite B will form; when $n = 14-18$ both spherulites A and B can be observed at different supercooling; and for some time they coexists (Fig. 2d). When we decrease the temperature continuously, the spherulites B appear first and grow to a certain size, then spherulites A begin to appear at the edges of spherulites B and in the bulk of isotropic phase.

In this case the dark concentric lines can be cleavages. Yet, they may also be caused by the linear defects, which are due to the changes of the refractive rate. In order to clarify the origin of these cleavages, we have used AFM to observe the surface morphology of the spheurlite A. A sample cell with spherulite A phase was prepared. We cooled the sample cell to room temperature. The cell was not sealed with glue so as that we could shear the cell and separate the up and down plates. Under polarized microscope, we found that the spherulites are still on the glass substrate and most of them were not damaged. We observed the spherulite's surfaces using AFM. Figure 3 shows that there is arc cleavage in the crystal surface. Its width is about 0.5 μm. According to the gray scale bar on the right-hand side of the figure, the surface is quite rough. This is due to the shearing when we seperate the up and down glass plate of the cell. Changing the scanning field, we can find similar cleavages which are concentric. This indicates that they are not caused by shearing. Their widths are different even in the same spherulite and the distance between two adjacent cleavages changes significantly. From microscopic results, we can.draw conclusion that the dark lines in the spherulite A, seen under polarized microscope, are cleavages.

X-ray diffraction (XRD) shows that the spherulite A perfectly crystallizes. Figure 4 shows the XRD spectra of spherulite A at different temperature in the cooling process. There are two major peaks at 4.92° and 21.28° corresponding to 17947 Å and 4.172 Å. We can find that, when the temperature is down to 32°C, the peaks are shifted to higher angles. 4.940° and 21.500° respectively, corresponding to 17.874 Å and 4.130 Å. It means that the cell of the crystal becomes smaller. This will cause tension in the sample. The concentration of the tension will lead to cleavages in the sample. If the crystal has layered periodic structure, then the cleavages will appear along the plane of the layer. Further, if the layers are concentric, the cleavages will be also concentric. So the AFM results are reasonable.

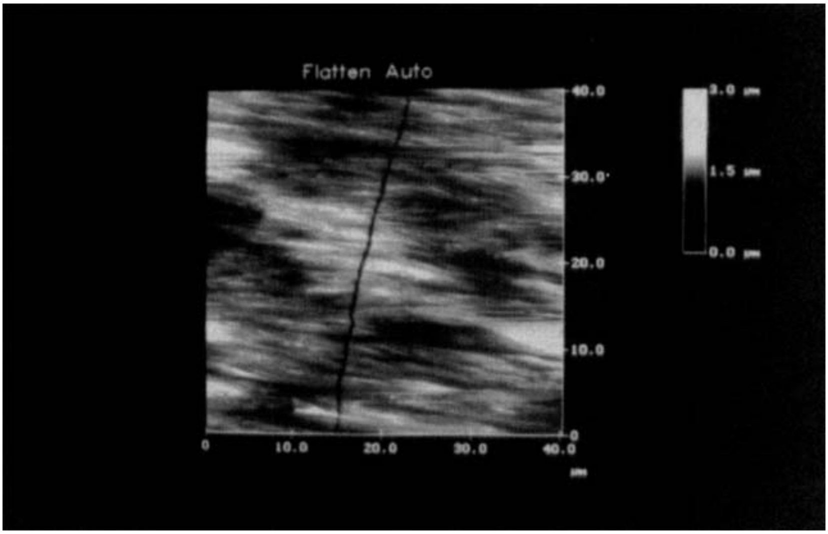


FIGURE 3 AFM photo of the morphology of the surface of the crown ether $n = 14$. The force between the AFM tip and the sample surface is of the order of 10 nN. (See Color Plate X).

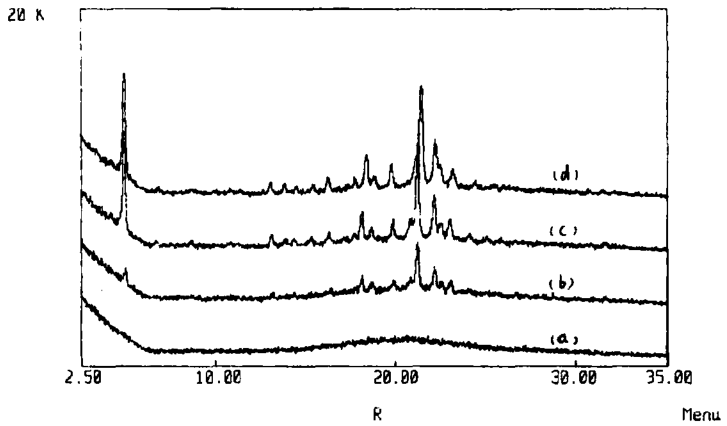


FIGURE 4 X-ray diffractive spectrums of the crown ether $n = 14$ at different temperatures: a: $T = 100°$, b: $T = 65°$, c: $T = 50°$, d: $T = 25°$.

Subsequently we have tried to establish the structures of the spherulites A and B. The observations with polarized microscopy showed that the azotic crown ethers from spherulites. So the molecules are oriented radially. AFM and XRD show that the spherulite A has a layered periodic structure and the spherulite can break along the layer plane. This indicates that the interactions between layers are weak and the molecules in adjacent layers are not in a network. We propose that the spherulite A has bimolecular-layered structure (Fig. 5a). There are two molecular chains in each layer. In every chain, the molecules are linked through hydrogen bonds between the group C=O and the group N—H of the neighbouring molecules to form molecular chain structure. Another molecular chain like this is formed the alkyl chains of the molecules in two molecular chains are cross-linked. This is somewhat like polymer structure. Another kind of monomolecular-layered structure is excluded. It is expected that, in this monomolecular layered structure, some of the alkyl chains in one layer will penetrate into the adjacent layer. So it is not easy for spherulite to break along the layer plane when the cell of the crystal becomes smaller with the decrease of the temperature. Also, in this structure, the alkyl chain will be holded because the width of the polar head is bigger than that of the alkyl chain. So the birefringence will be weak. In Figure 5a, the alkyl chains in the two molecular chain of the same layer are cross-linked and occupy the room between the two molecular chains. The alkyl chains needn't be holded, then the birefrigence is quite strong.

The other kind of spherulite (B) is also studied. Its crystal structure is shown in Figure 5b. Here the molecules form the net-like structure through the hydrogen bonds (C=O···H—N). In its formation, there is no layer structure. The alkyl chain of the next neighboring molecules net together.

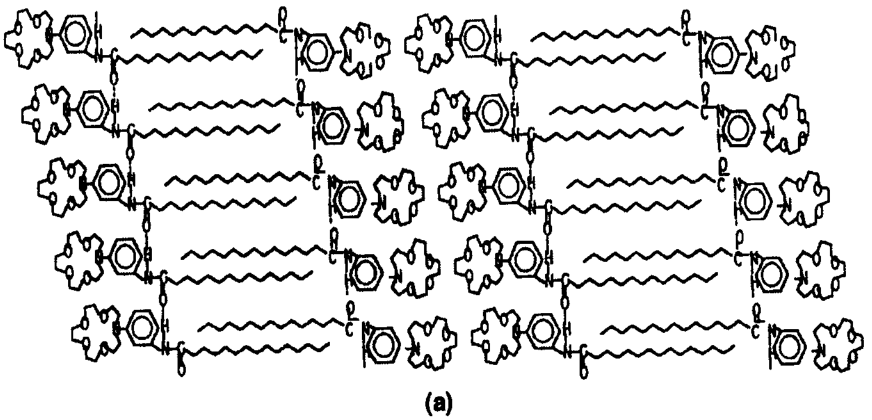
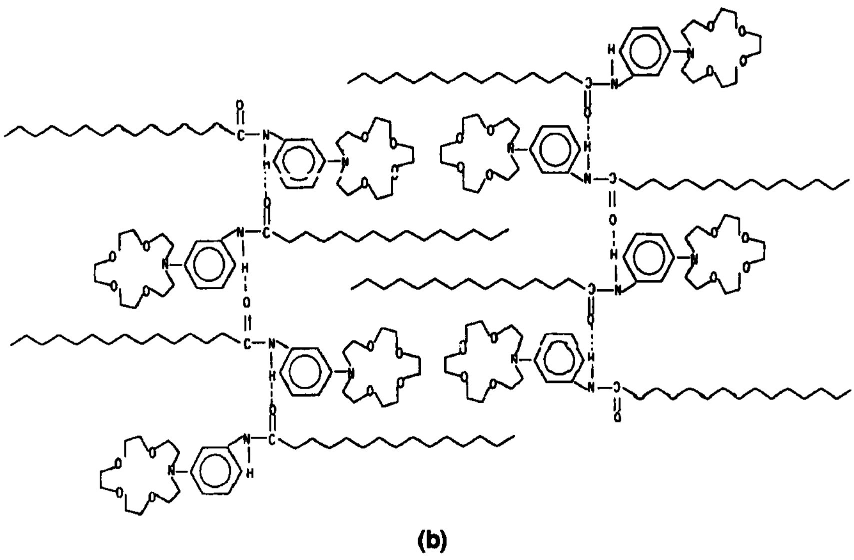


FIGURE 5 The scheme of the crystal structures of the spherulites: a) scheme of spherulite A: b) scheme of spherulite B.



(b)

FIGURE 5 (Continued).

So the molecules form a structure with the head-chain arrangement of the molecules.

The study of the series using polarized microscopy also shows that the synthetic azotic crown ethers with hydrophobic chain length $n = 14, 16, 18$ can form bimolecular-layered structure when they grow from melt. It has been shown elsewhere that when dispersed in water, the azotic crown ethers can form stable bimolecular-layered membranes with the hydrophobic chain length more than 10 [3]. It is confirmed that the bimolecular-layered structure is a general phenomenon for the amphiphilic molecules in solution. Our experiments show that the investigated amphiphilic materials can also form bilayer structure when they grow from melt.

We have proposed above that there are hydrogen bonds ($C{=}O \cdots H{-}N$) in spherulite A and B and we have used IR spectroscopy to confirm this. Figure 6 are the IR spectra of the azotic crown ether $n = 16$. Spectrum in Figure 6a is in melt state. We have found that the C=O peak at 3302 cm^{-1} and the N—H peak at 1662 cm^{-1} are much broadened. This indicates that there exists hydrogen bonds between them. Spectrum in Figure 6b is in the crystalline state. The peaks become much more sharp indicating that the hydrogen bonds are much more stable than in melt.

Figure 7 shows the formation of the nuclei of the sample on the substrate. There are two interfaces: the liquid-solid interface and the solid-substrate

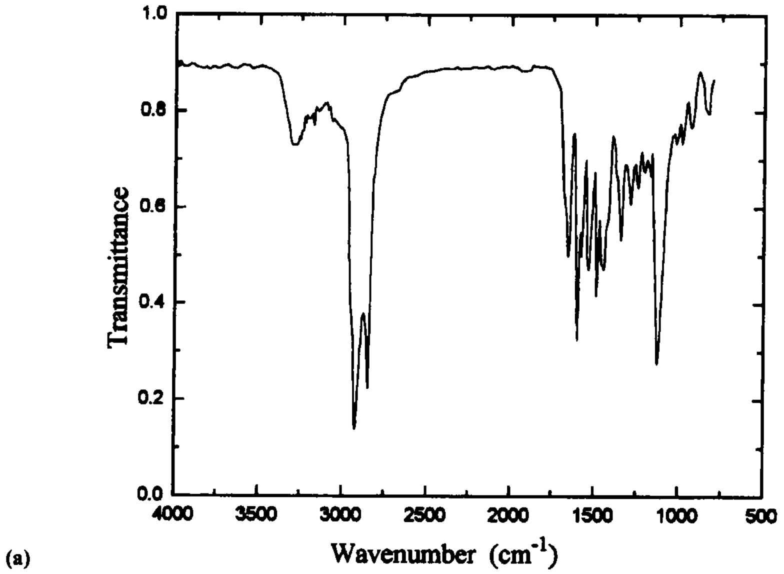


FIGURE 6 IR spectrums of the crown ether $n = 16$ at different temperatures: a: $T = 100°$, b: $T = 50°$.

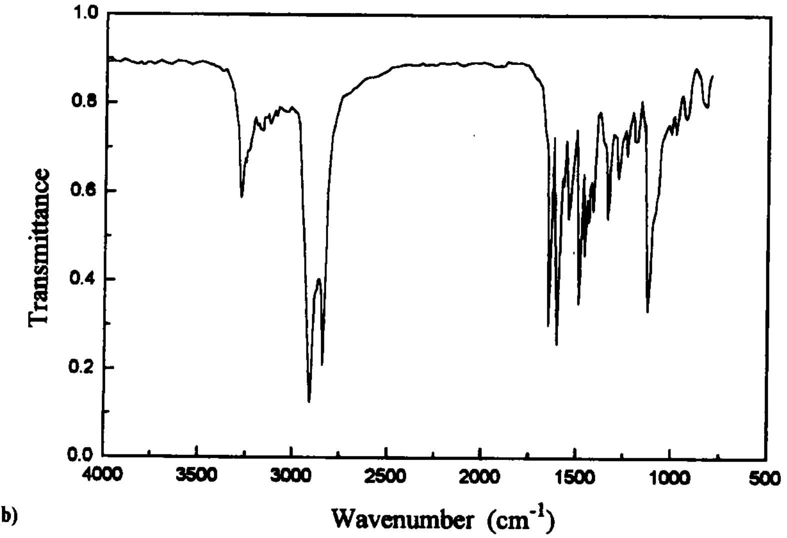


FIGURE 6 (Continued).

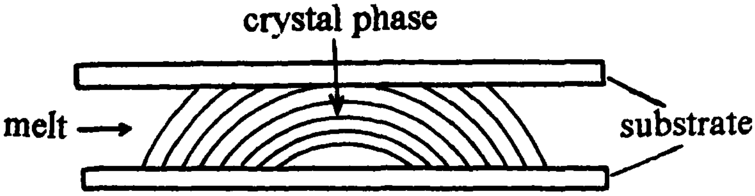


FIGURE 7 Picture of the nucleation of spherulite A from melt on the substrate.

interface. There is a cure angle between the two interfaces. This can be proved through observation under polarized microscope with the employed thick cell. We focus from the top surface of the sample to the bottom surface, and find the interface of the two phases is oblique. We propose that the layer plane is parallel to the interface of the two phases. So when temperature is decreased and the cleavages appear, the cleavages will oblique to the substrate surface.

With careful control of the temperature and careful clearing of the cell, we have obtained very great spherulites. They can grow-up covering all the cell with the size 1 cm × 1 cm. Yet, when temperature is decreased very quickly passing the phase transition point and keeping a great supercooling degree, many small spherulites will be formed. The greater is the decrease rate of temperature, the smaller are the spherulites.

Generally established in the crystal of inorganic materials, the square symmetry exists. So in phase transition, i.e., free energy, the elastic energy is not considered. Yet the square symmetry does not exist in the spherulite, so the elastic energy may be included in the free energy and it is especially big in the process of nuclei formation and the earlier stage of the growth. How the nuclei form is not known. Also, because the molecule of azotic crown ether is long and amphiphilic, and the molecules are oriented radially in the spherulitic crystals, the phase transition must include orientational free energy. This means that we can not simply use the nucleation theory of inorganic materials. Why does the azotic crown ether form the spherulite instead of square symmetry crystal? There is a lot of work to be done for finding the theory of the growth of the small molecules of organic materials. This will be discussed in subsequent work.

In summary, we have studied the growth habits of crown ethers from melt. AFM shows that the concentric dark lines of spherulite A are cleavages. X-ray diffraction shows that there is a shift of the peaks to wide angles corresponding to the two states before and after the cleavages appear. We have established the bimolecular-layered structure of spherulite A and the net-like structure of spherulite B. This is the first time that molecular self-organization of bimolecular-layered structure was found in crystal growing from the melt.

Acknowledgements

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