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The study of starch nano-unit chains in the gelatinization process

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Abstract

The change of starch nano-unit chains during a gelatinization process has been observed using Atomic Force Microscopy (AFM) with a view to pinpointing the process from the point that starch granules break down to the total vanishing of crystallinity in the gelatinization process. This study puts forward a model of the gelatinization process for starch nano-unit chains and completes the gelatinization model of starch. The results also prove that the nano-unit chains contain crystalline areas and amorphous areas. Furthermore, it deduces that the blocklets of starch granules are formed by the twist or distortion of nano-chains.

Keywords: Starch nano-units chains; Blocklets; Gelatinization process

1. Introduction

1.1. The classical gelatinization model for starch granule

Gelatinization is one of the important properties of starch. The starch granules can absorb water and irreversible swelling takes place in this process. The data for this process, such as gelatinization temperature, viscosity and enthalpy are important parameters for starch in industry. It can reflect starch characteristics and play an important role in the application of starch.

Former researchers have reported many studies on the gelatinization process of starch and have put forward the classical gelatinization model of starch (Fennema Owen, 1985). Starch granules are insoluble in cold water and only form suspensions. When the suspension is heated, starch granules can swell slightly. With the increase of suspension temperature, some pores begin to appear on the surface of starch granules and some soluble components (primarily amylose) can dissociate and diffuse out of the starch granules. At a certain temperature (the gelatinization temperature), starch granules begin to swell rapidly and the viscosity of the suspension rises very fast. When the suspension is heated continuously, the volume of starch granules reaches a maximum and the viscosity of the suspension reaches a peak. At higher temperatures, starch granules break down and crystalline areas vanish.

This gelatinization model can generally be illustrated by a viscosity curve, which is measured by a Brabender Amylograph (Fig. 1). Furthermore, with the utilization of Scanning Electron Microscopy (SEM), researchers have directly seen this process (Gallant Daniel, Bouchet, & Baldwin Paul, 1997; Zhongdong, Yunchuang, & Hongjie, 2003) (Fig. 2).

Obviously, the final situation of starch gelatinization should be that the order of starch macromolecules is disrupted and the crystalline area of starch vanishes. But the above gelatinization model doses not describe the process clearly, which from the point that starch granules break down to the vanishing of crystalline. This paper focuses on this process. It uses Atomic Force Microscopy (AFM) to observe the change of starch nano-unit chains in gelatinization process.

1.2. The classical model of starch structure

The study on starch structure has been going for a long time and former researchers have accumulated lots of

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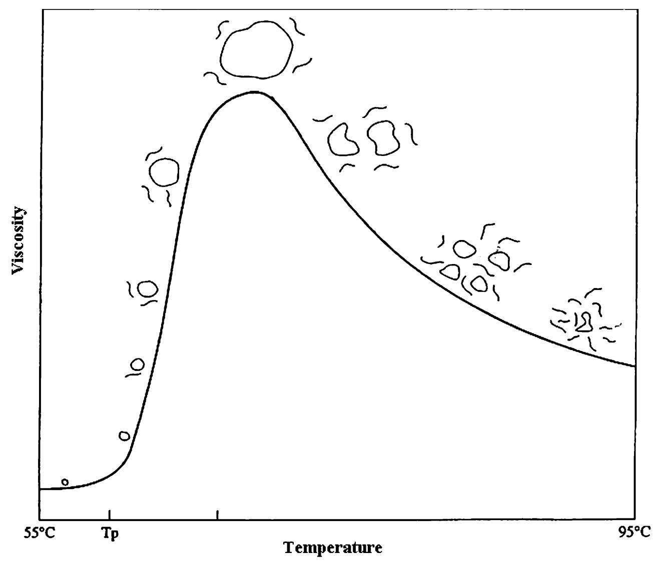

Fig. 1. The viscosity curve, which is measured by a Brabender Amylograph.

data. On the bases of these data, Gallant Daniel et al. (1997) put forward the classical model of starch structure in 1997. In their model, the starch granule is composed of crystalline hard shell and semi-crystalline soft shell. There are pores on the surface of starch granules and these pores stretch into the inner parts of starch granules, which are the route for soluble components to dissociate out of granules when swelling. Both crystalline hard shell and semi-crystalline soft shell are made up of blocklets. Blocklets are formed by crystalline amorphous layers (Fig. 3). When large amounts of amylopectin macromolecules are assembled together, their side chains twist with each other to form a crystalline layer and their branch points (1,6-α-D-glucosidic bonds) form amorphous layer.

When observing the surface of starch granule by AFM, Baldwin found some protrusions (Baldwin, Adler, Davies, & Melia, 1996). So in Gallant's model (Gallant Daniel et al., 1997), researchers deduced that blocklets is ellipsoid. In Fig. 3, the left egg-shaped matter is blocklets. The rectangular block in the right side is an amplificatory image from

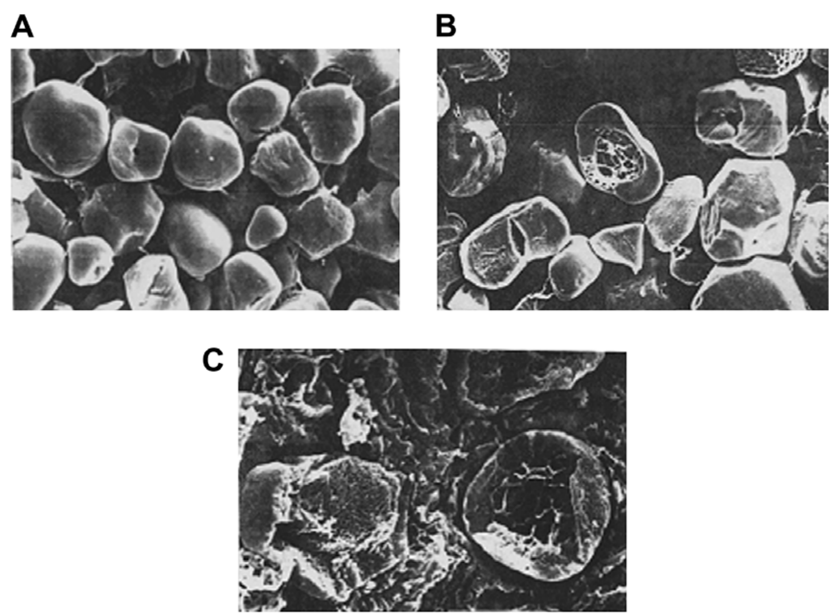

Fig. 2. The SEM images of cornstarch granules in swelling process. The suspension temperature of these images is that: A is 40 °C (60 min), B is 60 °C (20 min), and C is 70 °C (5 min). The gelatinization temperature of corn starch granules is 71 °C (Zhongdong et al., 2003).

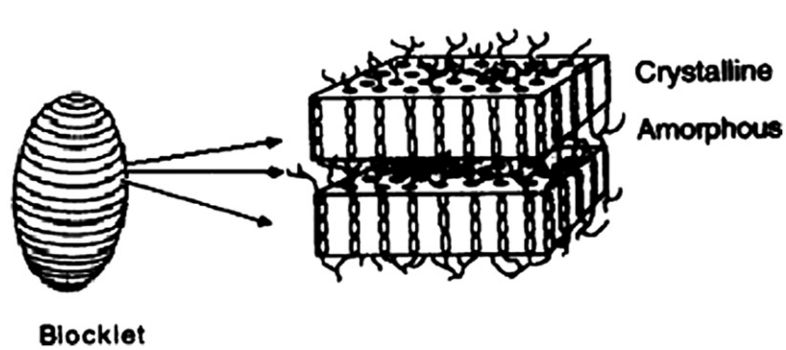

Fig. 3. The model of blocklets.

blocklet (left side). The middle arrowhead in Fig. 3 comes from a line in blocklet (left image) and points to amorphous area in left image. The neighbor two arrowheads of it come from the adjacent areas of the line in blocklet (left image) and point to crystalline areas in left image. So the lines in blocklet (left side) stand for amorphous areas and the areas between lines stands for crystalline areas. The meaning of Fig. 3 is that a blocklet is divided into crystalline and amorphous layers and these two layers alternate with each other. This is just a model. However, in our experiment, we could not find layer structure in any process of collapse and gelatinization of blocklets. Only nano-chains were found, so it was deduced that a blocklet should not be composed by crystalline layer and amorphous layer. It should be formed by the twist or distortion of nano-chains.

1.3. The technology of molecular combing

In 1994, with the flowing and evaporation effect of water, Bensimon drew out DNA chains of molecules from helixes to parallels on a microscopy glass slide (Bensimon & Simon, 1994). That was the technology of molecular combing. The destination of this technology is to stretch the bio- and poly-macromolecules from the clew or the leptospira to the straight chains in order to directly observe their fine structure by some special instruments such as AFM (Kechuan, 2001; Lijuan & Yingge, 2004). In this study, this technology it also used to stretch starch nano-unit chains (Zhongdong, Peng, & John, 2005).

2. Experimental

2.1. Reagents and apparatus

Cornstarch (Henan Shangshui Starch Factory, Shangshui, PR China, ash < 0.4%, protein < 0.6%, cellulose < 0.1%); double distilled water (quartz evaporator, conductivity $< 1.0 \times 10^{-7}\,\Omega\,cm^{-1}$); Atomic Force Microscope (AFM) (Digital Instruments Co., St. Barbara, USA).

2.2. Methods

1. Gelatinization (Hongxiu & Zhaotan, 1996): a starch sample (0.1–0.3 mg) was placed into a 2.5 ml covered vial and double distilled water (2 ml) added. Then the vial was placed in a water bath 100 °C for 5, 10, 15, 20, 30, 40 min, respectively.
2. The technology of molecule combing (Zhongdong, Shenfu, & Zhenqian, 2001): starch solution (2 μl) was deposited instantly onto the surface of newly cleaved natural mica. Then the mica surface was promptly dried with a blast of air from a blastball (a normal tool in lab with high elasticity that is made of rubber, so the air in it can be squeezed out as a strong airflow) in a certain single direction. It should be noted that this step must be finished within 5 s.
3. Testing: all samples ready to be tested are observed using the AFM, working in tapping mode in air.

3. Results and discussions

In this study, it uses AFM to observe the chains of starch nano-units in gelatinization process. The AFM images can be seen in Figs. 4–9.

From Figs. 4 to 9, one can observe the changes of starch nano-unit chains in the gelatinization process after these chains have dissociated out of starch granules.

Fig. 4 (Zhongdong et al., 2005) illustrates the moment that the starch granule is just collapsing and the nano-chains are just flowing out of granules. In this figure, the nano-unit chains have the uniform height and width and no parts of chains react with water. However, when comparing Fig. 5 with Fig. 4, it can be observed that although the whole nano-unit chain can still be identified in Fig. 5, some parts of it are different from other places. The height and width of these parts are impaired and the whole nano-unit chain is divided into salient points and conjunction areas. In Fig. 6, the distance between salient points becomes farther and the conjunction areas are not very clear. In Fig. 7, one only can observe the salient points of nano-unit chains and the conjunction areas can hardly be found out. In Fig. 8, the whole nano-unit chains nearly completes gelatinization process, so the height and width of nano-unit chains become uniform again. In Fig. 9, the height of nano-chains becomes much lower and the AFM image of whole nano-unit chains becomes faint and blurred.

These six figures reveal the whole gelatinization process of starch nano-chains. Before describing the gelatinization process from these six figures, it should be made clear what the nano-unit chains are and what the salient points and conjunction areas are. Through the analysis of starch nano-unit chains, it can be deduced from the vertical bars; the height of starch nano-unit chains of in these figures cannot be higher than 3.0 nm. From the present data, the diameter of blocklets should be 20–500 nm (Baker, Miles, & Helbert, 2001; Gallant Daniel et al., 1997; Ridout, Paker, Hedley, Bogracheva, & Morris, 2003; Szymonska & Krok, 2003), which are larger than these nano-unit chains. On the other hand, the height of starch nano-unit chains (Fig. 4) and salient points (Figs. 5–7) are bigger than the helix diameter of VH-amylopectin. So these nano-unit chains should not be glucose monochains. As a result, it is deduced that the starch nano-unit chains in these figures should be the configuration of blocklets that are stretched by molecular combing technology. In other words, blocklets should be formed by the twist and distortion of these nano-unit chains. This is different from the former classical models of starch blocklets, which are made by crystalline layers and amorphous layers.

The salient points of starch nano-unit chains should be the crystalline areas, which are formed by the helixes of

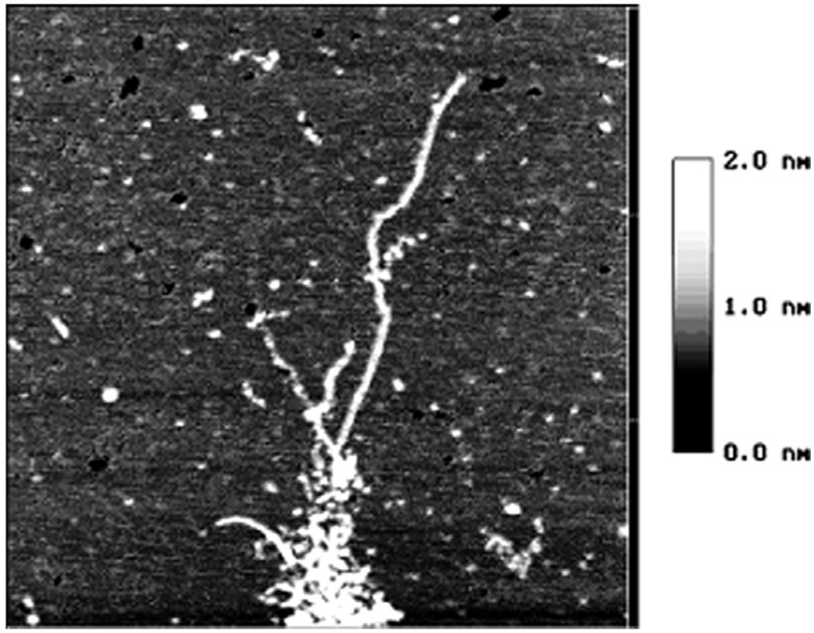

Fig. 4. The AFM image of starch nano-chains when heated in 90 °C water bath for 5 min (Zhongdong et al., 2005), size 1.5 × 1.5 μm.

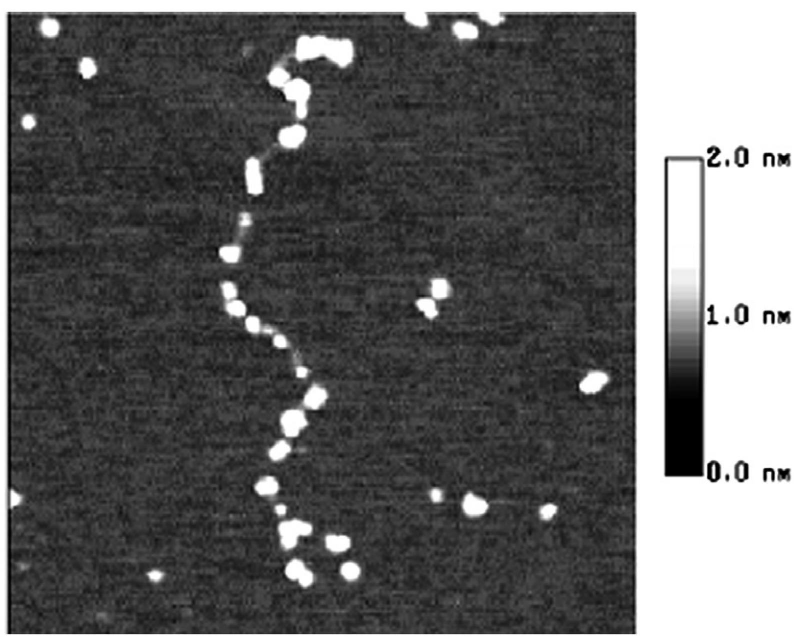

Fig. 5. The AFM image of starch nano-chains when heated in 100 °C water bath for 10 min, size 600 × 600 nm.

side chains of amylopectin macromolecules. The conjunction areas of starch nano-chains should be amorphous areas, which are formed by the branch points (α-1,6-glucoside bond) of amylopectin macromolecules. So it proves that starch nano-unit chains contain crystalline areas and amorphous areas, which are alternated with each other.

From the above analysis, it can be deduced that the gelatinization process of starch nano-unit chains should be that: first of all, the structure of starch nano-unit chains that are just flowing out of granules are very tight, just likes an impacted spring. The amorphous areas could not be observed by AFM and the whole nano-unit chain has the uniform height and width. Next, when the nano-unit chains contact with hot water, they can begin swelling, just like the swelling process of starch granules. As a result, the structure of the nano-unit chains becomes loose, just like the untying of an impacted spring, and the amorphous areas can be observed by AFM. Then, gelatinization begins to happen in amorphous areas.

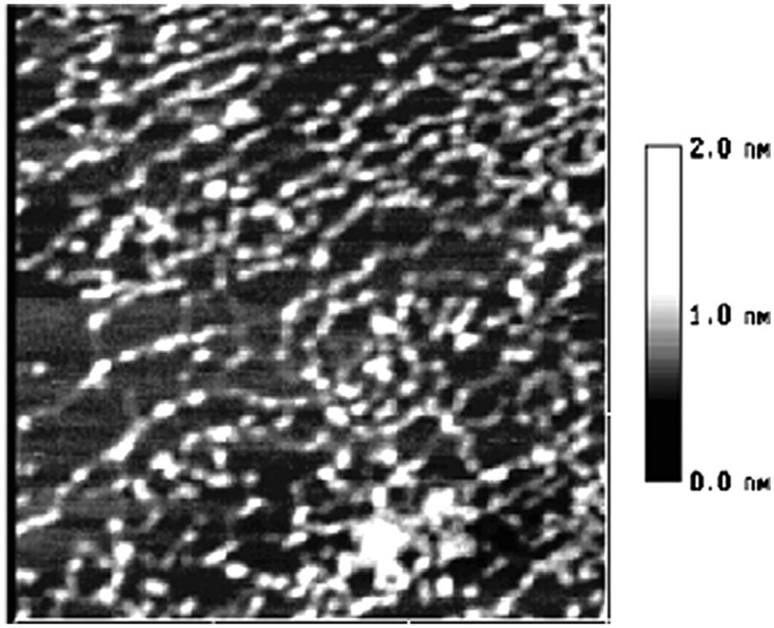

Fig. 6. The AFM image of starch nano-chains when heated in 100 °C water bath for 15 min, size 600 × 600 nm.

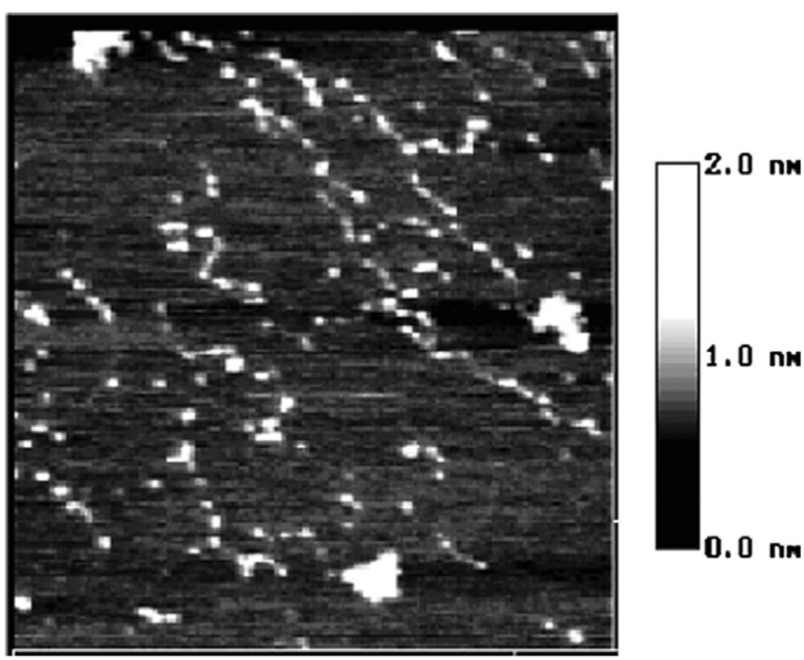

Fig. 7. The AFM image of starch nano-chains when heated in 100 °C water bath for 20 min, size 1.0 × 1.0 μm.

Water molecules penetrate slowly into crystalline areas from amorphous areas and untie the helixes in the crystalline locations. As a result, the crystalline areas disorganize slowly and its structure becomes loose. This can explain why the height of salient points becomes lower and lower from Figs. 6 to 9. Finally, water molecules untie the helixes of amylopectin side chains in crystalline areas completely and the crystalline areas vanish. The amylopectin and amylose exist in water solution as the state of macromolecules or the distortion between a few macromolecules.

4. Conclusions

In this paper, AFM has been used to observe the change of starch nano-unit chains, after they dissociate from granules, in the gelatinization process. From the analysis, it puts forward the gelatinization model of starch

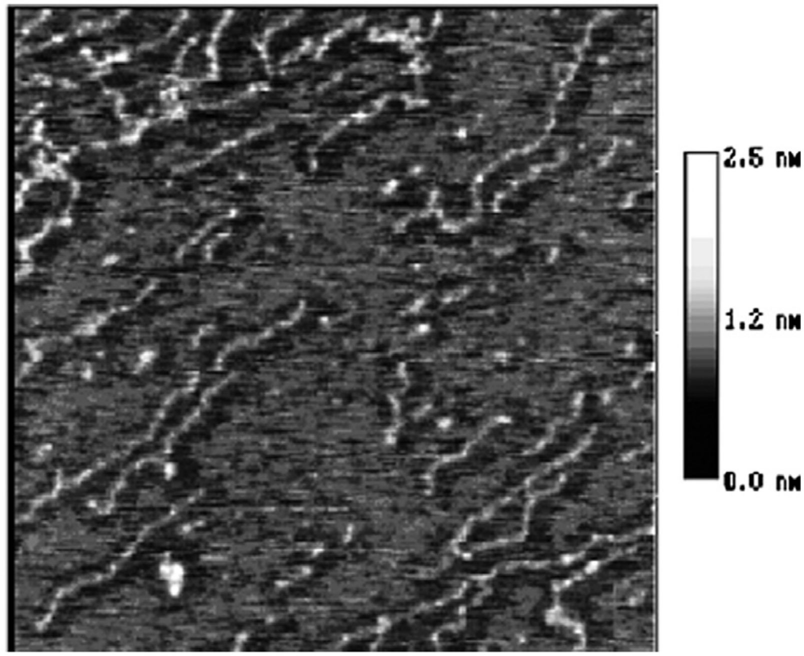

Fig. 8. The AFM image of starch nano-chains when heated in 100 °C water bath for 30 min, size 800 × 800 nm.

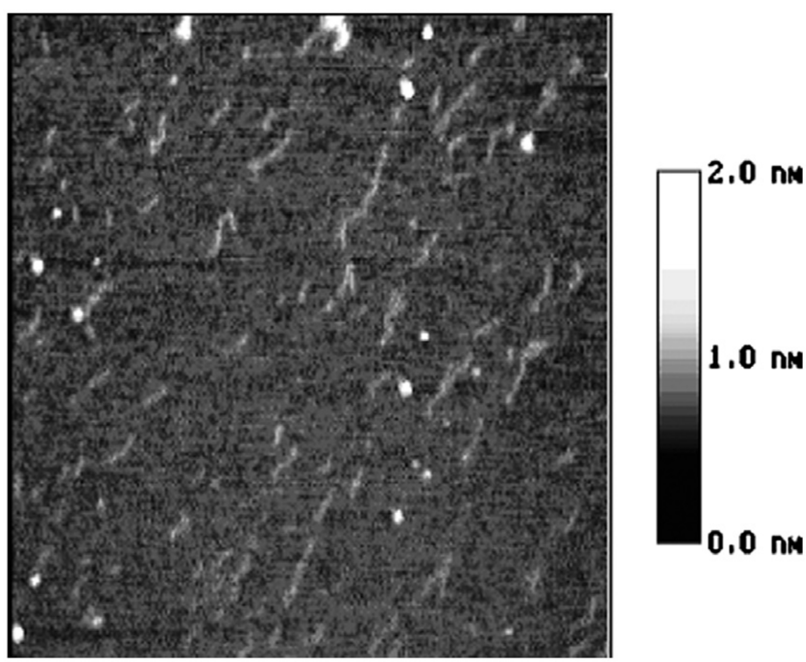

Fig. 9. The AFM image of starch nano-chains when heated in 100 °C water bath for 40 min, size 2.0 × 2.0μm.

nano-unit chains. This model completes the gelatinization model of starch. On the other hand, it proves that starch nano-unit chains contain crystalline areas and amorphous areas. Furthermore, it deduces that blocklets should be made up by the twist or distortion of nano-chains.

Acknowledgment

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