Kinetics of conformational change of multiple helical polysaccharides

Department of Macromolecular Science, Graduate School of Science

Professor Ken Terao

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Abstract

Xanthan is a double helical polysaccharide. It is widely used for food additives because the dilute solution has significantly high viscosity. Circular dichroism (CD) and small-angle X-ray scattering (SAXS) measurements were made for three xanthan samples in aqueous NaCl after rapid temperature change to investigate the kinetics of the conformational change between the ordered and disordered states. After the rapid heating, the CD signal mainly regarding the carbonyl groups on the side chains quickly changed within 150 s while the SAXS intensity reflecting the main-chain conformation decreased more gradually. This shows the intermediate conformation (loose double helix). The SAXS profile in the rapid cooling process showed that the loose double helical structure was formed within 150 s, but the CD signal slowly changed with around 2 days to recover the native local conformation.

Background & Results

DNA, collagen, and polysaccharides have multiple helix structure with high rigidity in water. In recent years, multiple helices consisting of polysaccharides and DNA were developed for gene delivery materials. However, since multiple helical polysaccharides are simple homopolymers with the equivalent repeating units, branched and hairpin like superstructures can be found for renatured samples. In order to control the renatured conformations, it is important to investigate their kinetics to form the multiple helices. We thus made time-resolved small-angle X-ray scattering measurements for double helical xanthan whose chemical structure is shown in Figure 3 to observe the conformational change processes by using the synchrotron radiation at SPring-8. Considering the CD signal reflects the chiral structure of the chromophores, temperature change of the CD signal of xanthan shows the conformational change of side groups. While this is consistent with the double helix content at the equilibrium state, we found that clear differences were found just after the temperature change. Carbonyl side chains immediately became more fluctuating after rapid heating, whereas the rodlike double helical conformation observed from SAXS was maintained at least several minutes. On the other hand, while the rodlike double helix formed in a short time range after the rapid cooling, it took more than one day to recover the CD signal. In the near future, we would like to clarify the relationship between this intermediate structure and the obtained hairpin/hyperbranching structures.

Significance of the research and Future perspective

The melting and refolding of the multiple helical structures are usually studied using spectroscopic methods such as CD. We showed that SAXS profile is a more direct measure of the double helix contents. Significantly different kinetics between CD and SAXS clearly indicated that the existence of the intermediate conformation. It is known that xanthan can form specific superstructures, such as hairpin-like or hyperbranched structures, during their refolding process. Considering the functionalities can be related to the superstructures, elucidating the kinetics of molecular morphology changes, including intermediate structures, will provide useful information to develop the new functionalities of xanthan.

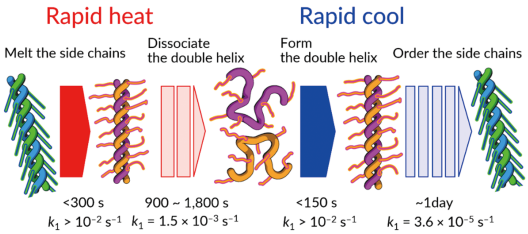

Figure 1. Schematic representation of conformational change after rapid heating and cooloing processes and the time constants.

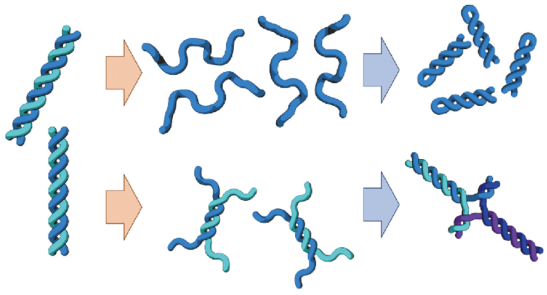

Figure 2. Possible conformations of xanthan through denature and renature processes.

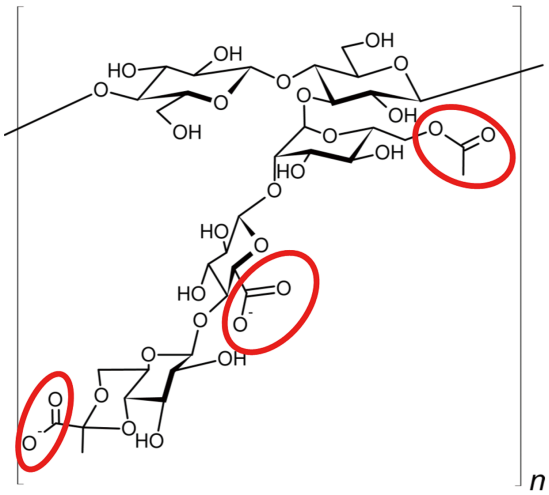

Figure 3. Chemical structure of xanthan.

Patent

Treatise Tomofuji, Yu; Matsuo, Koichi; Terao, Ken. Kinetics of denaturation and renaturation processes of double-stranded helical polysaccharide, xanthan in aqueous sodium chloride. Carbohydr. Polym., 275, 118681. doi: 10.1016/j.carbpol.2021.118681

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Keyword multiple helical polymers, polysaccharides, molecular conformations, food additives