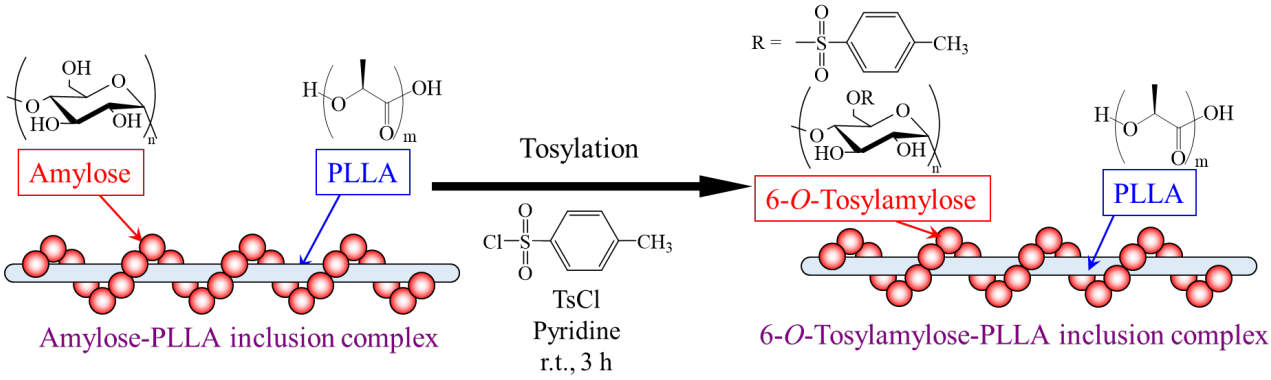
2018 年度セルロース学会西部支部セミナー：Joint Seminar at Tainan: the Department of Chemical Engineering, National Cheng Kung University and the Seibu-branch, the Cellulose Society of Japan, 30 November-1 December 2018, Tainan, Taiwan

Preparation of Supramolecular Materials by Regioselective Derivatization of Amylose-polylactide Inclusion Complexes

Kohei Shimomura[1], Kazuya Yamamoto[1], and Jun-ichi Kadokawa[1]

Abstract

Amylose is a linear natural polysaccharide with helical conformation, which is composed of glucose residues linked through α(1→4)-glycosidic linkages. It is an energy polysaccharide in nature, which, therefore, shows difficulty in applying to materials having high strength compared with structural polysaccharides such as chitin and cellulose. On the other hand, we have found that supramolecular inclusion complexes of amylose with various hydrophobic polymers, such as poly(L-lactide) (PLLA), are formed in phosphorylase-catalyzed enzymatic polymerization field in hydrophobic polymer dispersions[1-3]. However, the inclusion complexes have not exhibited sufficient properties for material application as same as a pure amylose. In this study, we found that regioselective derivatization of the amylose-PLLA inclusion complex at C-6 position with *p*-toluenesulfonyl chloride (TsCl) produced a supramolecular material with better material property. Tosylation of the inclusion complex, which was prepared by the vine-twining polymerization using PLLA, was carried out using TsCl in the presence of pyridine at room temperature for 3 h **(Scheme 1)**. The product was isolated by centrifugation and dried under reduced pressure. When the powdery product was immersed in methanol and then pressed at 60℃, it could be processed to a plate-like shape. In the XRD measurement of the product, a diffraction peak assignable to parallel alignment of the complex was diminished compared to that assignable to pitch of the helicity. This indicated irregulary arrangement of the complexes with retaining the inclusion structure resulting in the property of the plate formation.



Scheme 1. Preparation of 6-*O*-tosylamylose-PLLA inclusion complex.

References

1) S. Shoda, H. Uyama, J. Kadokawa, S. Kimura, S. Kobayashi, *Chem. Rev.*, **2016**, *116*, 2307.
2) S. Orio, S. K. Yamamoto, J. Kadokawa, *Polymers.*, **2017**, *9*, DOI:10.3390/polym9120729.
3) J. Kadokawa et al., *Macromol. Biosci.*, **2011**, *11*, 1407.

[1] Department of Chemistry, Biotechnology, and Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan