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### Chemoenzymatic synthesis of polysaccharide-grafted polymeric materials

Biological macromolecules, such as polysaccharide and protein (peptide), are vital materials in living systems. Such functions are appeared by their controlled primary and higher-ordered structures. Furthermore, branched or grafted biological polymers are often appeared in nature and such complicated structures contribute to exhibiting important in vivo functions. Accordingly, synthetic method for combining several biological macromolecules into branching or grafting is expected to produce new functional polymers. On the basis of the viewpoint, we have reported the synthesis of amylose-grafted polymeric materials by chemoenzymatic approach, which is a combined method of phosphorylase, catalyzed enzymatic polymerization of  $\alpha$ -D-glucose 1-phosphate (G-1-P) monomer for the amylose production with appropriate chemical reactions. The phosphorylase-catalyzed enzymatic polymerization using G-1-P as a monomer proceeds with the construction of  $\alpha$ -glycosidic bond under mild conditions, leading to the direct formation of  $\alpha$ -(1,4)-glucan chain, i.e., amylose, in the aqueous media. To initiate the polymerization, a maltooligosaccharide is required as a primer in the initial reaction media. The synthesis of amylose-grafted heteropolysaccharides has been performed by combining the phosphorylase-catalyzed enzymatic polymerization with the appropriate chemical reaction (chemoenzymatic method). For example, amylose-grafted carboxymethyl cellulose (CMC) was synthesized as the following chemoenzymatic method. A maltooligosaccharide having an amino group was first introduced to the CMC by using condensing agent. Then, the phosphorylase-catalyzed enzymatic polymerization of G-1-P from the maltooligosaccharide chain ends on the product was performed to obtain the desired amylose-grafted CMC. The product had the rigid CMC main chain, which further assembled, leading to nanobers by the formation of double helix between the long amylose graft chains in the intermolecular CMC chains. The chemoenzymatic synthesis of amylose-grafted poly-L-glutamic acid (PGA) as a new artificial polysaccharide-polypeptide conjugate was also investigated. The product formed a robust hydrogel, which could be converted into a regularly controlled porous material.

### Biography

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