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## Preparation of Amylose Supramolecular Gel Materials by Vine-Twining Polymerization

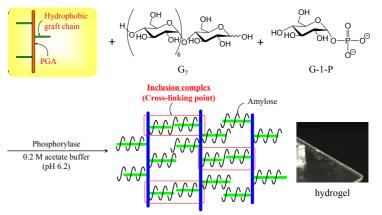
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#### Abstract

Amylose is a natural glucose polymer linked through  $\alpha$ -(1→4)-glycosidic linkages. It acts as a host molecule and forms polysaccharide supramolecules by inclusion complexation with various guest molecules of relatively low molecular weight owing to the helical conformation. However, only limited studies have been reported regarding the direct construction of inclusion complexes composed of amylose and polymeric molecules. We have already reported the polymerization method for the architecture of amylose-polymer supramolecular inclusion complexes be named "vine-twining polymerization". In this method, amylose-polymer inclusion complexes were obtained with the progress of phosphorylase-catalyzed enzymatic polymerization, which was conducted using  $\alpha$ -D-glucose1-phosphate (G-1-P) as a monomer from a maltoheptaose (G<sub>7</sub>) primer in the presence of the guest polymers [1-3]. In this study, we performed the preparation of supramolecular gel materials by the vine-twining polymerization using poly( $\gamma$ -glutamic acid-*graft-ε*-caprolactone) (PGA-*g*-PCL) as a new guest polymer. When the enzymatic polymerization of G-1-P from G<sub>7</sub> primer was performed using the graft copolymer, a supramolecular hydrogel was obtained (Scheme 1) [4]. The resulting hydrogel, purified by immersing in water, had a self-standing property. The XRD result of a cryogel obtained by lyophilization of the hydrogel indicated the presence of inclusion complexes of amylose with the PCL graft-chains between intermolecular (PGA-*g*-PCL)s, which acted as

supramolecular cross-linking points for the hydrogelation. Macroscopic healing of two hydrogel pieces was achieved by the formation of inclusion complexes at their interfaces through the enzymatic polymerization. Furthermore, an ion gel was fabricated by immersing the hydrogel into an ionic liquid, 1-butyl-3-methylimidazolium chloride.



*Scheme 1.* Preparation of hydrogel by vine-twining polymerization using graft copolymer.

#### References

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