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Enzymes as powerful biocatalysts for precision synthesis of oligo and polysaccharides

Oligo- and polysaccharides have complicated structures because of the structurally different monosaccharide units and differences in stereo- and rearrangements of glycosidic bonds. Various structures of such substances in nature exhibit several functions in host organisms, and a subtle change in the monosaccharide structure and the type of glycosidic linkage exerts a profound effect on their properties and functions. Accordingly, the synthesis of well-defined non-natural oligo- and polysaccharides has attracted significant attention. Enzymes are identified as powerful biocatalysts to precisely synthesize oligo- and polysaccharides because enzymatic reactions using glycosyl substrates are progressed with regio- and stereocontrolled fashions in glycosidic linkage formation without the use of protective groups. Phosphorylase, which catalyzes phosphorolysis of α-(1→4)-glucans at a non-reducing end in the presence of inorganic phosphate, producing α-D-glucose 1-phosphate (Glc-1-P), is one of the enzymes that are practically used as the catalyst for synthesis of oligo- and polysaccharides with a well-defined structure. Because by means of the reversibility of the phosphorolytic reaction, phosphorylase catalyzes successive glucosylation using Glc-1-P as a glycosyl donor (monomer) and a maltooligosaccharide as a glycosyl acceptor (primer) as the polymerization to produce -(1→4)-glucans, that is, amylose with liberating inorganic phosphate (Fig1). As this enzyme shows loose specificity for the recognition of substrates, it recognizes several analogue substrates of Glc-1-P as glycosyl donors in glycosylations to give non-natural oligo- and polysaccharides. For example, α-D-glucosamine (GlcN-1-P) and α-D-glucuronic acid 1-phosphates have been used as glycosyl donors in phosphorylase-catalyzed enzymatic glucosaminylation and glucuronidation to give non-natural basic and acidic oligosaccharides having glucosamine and glucuronic acid residues at the non-reducing end, respectively. Phosphorylase isolated from thermophilic bacteria, *Aquifex aerolicus* VF5, catalyzes enzymatic polymerization of GlcN-1-P as a monomer from maltotriose primer. The enzymatic reaction was accelerated in ammonia buffer containing Mg2+ ion, owing to the precipitation of inorganic phosphate, giving non-natural amino polysaccharide, which corresponded to chitosan stereoisomer.

Biography

Jun-ichi Kadokawa received his Ph.D. in 1992. He then joined Yamagata University as a Research Associate. From 1996 to 1997, he worked as a visiting scientist at the Max-Planck-Institute for Polymer Research in Germany. In 1999, he became an Associate Professor at Yamagata University and moved to Tohoku University in 2002. He was appointed as a Professor of Kagoshima University in 2004. His research interests focus on polysaccharide materials. He received the Award for Encouragement of Research in Polymer Science (1997) and the Cellulose Society of Japan Award (2009). He has published more than 200 papers in academic journals.

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