Synthesis of Precursors of Chitin Oligosaccharides by Electrochemical Glycosylation Polymerization

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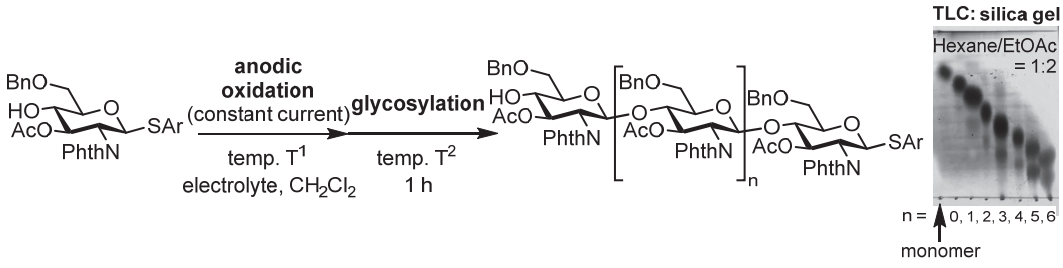
A convenient method to synthesize linear oligosaccharides using electrochemical glycosylation polymerization has been developed in this study. We have already reported automated electrochemical assembly for oligosaccharides synthesis.[1,2] This method is useful to prepare structurally well-defined oligosaccharides; however, this one-pot multiple-step synthesis is time-consuming and too sophisticated to prepare linear oligosaccharides with a single repeating unit. Therefore, we envisioned that glycosylation polymerization of a thioglycoside monomer under the electrochemical conditions might be an alternative method for oligosaccharide synthesis.

We investigated electrochemical glycosylation polymerization to synthesize chitin oligosaccharides containing β-1,4-glycosidic linkages of glucosamine as a model reaction. Various reaction parameters such as temperature, electrolyte, amount of electricity, current, anomeric leaving group, were optimized and oligosaccharides up to octasaccharide (n = 6) have been detected by MALDI-TOF MS. Although higher conversion of a thioglycoside monomer was observed with more electricity and higher reaction temperature, the condition of excess amount of electricity (>0.6 F/mol) was not appropriate to keep the anomeric thioaryl (SAr) leaving group and protecting groups of oligosaccharides intact. Oligosaccharides with different chain length and by-products such as hydroxy sugars can be easily separated by preparative GPC and silica gel column chromatography, respectively. We also examined synthesis of oligosaccharides longer than hexasaccharide (n = 4) by repeating the same procedure in one pot. This method can be applicable to synthesis of other oligosaccharides containing glucose.



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