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Functional modification of agarose: Synthesis of nanosize half-esters of succinic, phthalic and maleic acids

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A facile synthetic method for preparing new half-esters of agarose (Ag) with succinic (SA), phthalic (PA) and maleic (MA) acids has been described. The half-esters (Ag-SA, Ag-PA and Ag-MA) wherein the acid moieties are attached to the backbone of the agarose are characterized. Dynamic light scattering measurements show that nano-sized polymeric vesicles (32-124 nm) are formed in aqueous solution. A series of Ag-SA, Ag-PA and Ag-MA derivatives have been prepared with degrees of substitution ranging from 0.36 to 0.89 using varying molar ratios of Ag/SA, Ag/PA and Ag/MA (1:1–1:5). The highest degrees of substitution are found to be 0.89, 0.69 and 0.39 for Ag-SA (1:4), Ag-PA (1:3) and Ag-MA (1:2) respectively. The aqueous solution of sodium salts of these esters exhibit enhanced electrical conductivity (*ca*. 17.5 mS/cm at 40 °C) as compared to those of the parent half-esters (*ca*. 0.3 mS/cm at 40 °C). These new agarose based nanosized materials may have potential applications in electrochemical devices, sensors and as drug carriers.

Keywords: Agarose, Polysaccharides, Functional modification, Succinoylation, Phthaloylation, Maleoylation

In recent years, polymers have been widely used in polymer therapy as carriers of small-molecular and protein or peptide drugs to increase the solubility, stability, and half-life activity *in vivo* through controlled release techniques.[1, 2] To comply with the environmental concerns, naturally occurring polymers are preferable to the synthetic ones for ingestible and other applications. In recent times, synthetic polymers especially polyethylene glycol have become more popular than the natural ones as drug carriers in clinical applications.[3, 4] Homogeneous modification of cellulose with succinic anhydride in ionic liquid using 4-dimethylaminopyridine as a catalyst was reported.[5] Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride have been reported.[6] Likewise, modification of cellulose and wood with dicarboxylic acid anhydrides such as succinic, maleic or phthalic anhydrides has been employed to effect new material properties.[7, 8] Chemical modification of dextran, pullulan and starch with succinic anhydride has been extensively studied under variable reaction conditions.[9-13] Synthesis and characterization of dextrin monosuccinate with high degree of substitution have been reported.[9, 14]

Agarose, the gelling red seaweed polysaccharide, is widely used in biomedical and bioengineering applications. The basic disaccharide repeating units of agarose consists of (1, 3) linked β-D-galactose (G) and (1, 4) linked α-L-3, 6-anhydrogalactose (A).[15] It was reported that polysaccharide activation could be achieved by succinoylation.[10,16] Preparation of starch-maleate ester derivative was also reported.[17-20] The succinoylation method was the most widely used one to activate polysaccharides. Microwave assisted esterification is one of the facile ways to modify agarose. This technique has been used to prepare polysaccharide based new materials.[21]

In a continued programme of functional modification of agarose in our laboratory, we report herein the syntheses of half-esters of agarose, viz., agarose-succinate (Ag-SA), agarose-phthalate (Ag-PA) and agarose-maleate (Ag-MA), where the free –COOH group of the half-ester would be available for further functionalization.