



Synthesis and characterization of photo-crosslinkable 4-styryl-pyridine modified alginate



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ABSTRACT

In this article photo-crosslinkable styryl-pyridine modified alginate (ASP-Alg) was prepared and entirely investigated utilizing different instrumental techniques such as Elemental analysis, Fourier transform infrared (FTIR), ¹³C and ¹H nuclear magnetic resonance (NMR), ultraviolet-visible light (UV-vis), X-ray diffraction (XRD) spectra and scanning electron microscope (SEM). Upon irradiation in the UV region, the casted ASP-Alg membranes were cross-linked through the [2π + 2π] cycloaddition reaction of the inserted photo-active styryl pyridine moieties. Both cross-linking density and kinetics were monitored by examining the UV-vis light spectra of the irradiated membrane at predetermined time intervals and the obtained results were found to fit with the second order mathematical kinetic model, revealing the performance of the cross-linking via bimolecular [2π + 2π] cycloaddition reaction. Also, the swelling behaviors along with biodegradability were also studied, and the results indicated the decrease of the swelling ratio and degradation rate by increasing the cross-linking density. Moreover, the mechanical properties were also examined under both wet and dry conditions.

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1. Introduction

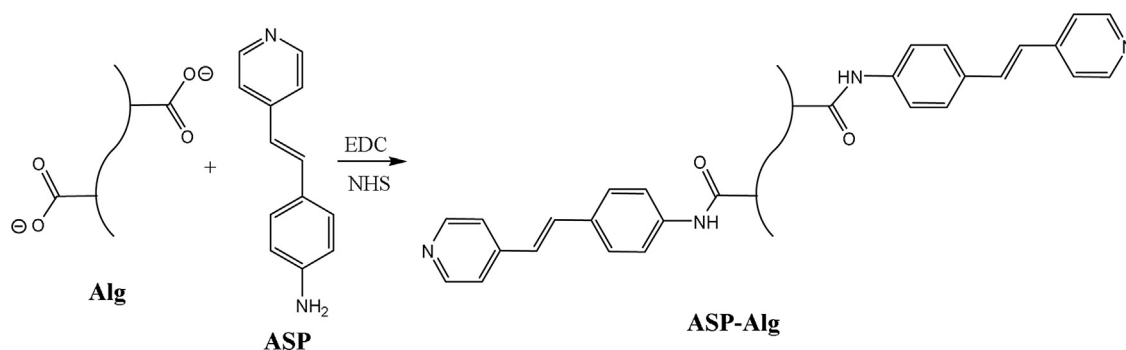
Alginate is a natural carbohydrate that mainly extracted from brown algae as a copolymer containing both β-D-mannuronate (M) and α-L-guluronate (G) units in block pattern *i.e.* MMM-GGG or alternating pattern *i.e.* MGMGM (Chiang & Chu, 2015; Bruchet & Melman, 2015; García-González, Alnaief, & Smirnova, 2011; Gong et al., 2011; Goh, Heng, & Chan, 2012). Due to the presence of the carboxyl functional groups within these monomeric sugar units, alginate are able to bind with di or tri valent metal ions such as Ca²⁺ or Al³⁺ to create ionically cross-linked network structures (Jang et al., 2014; Monier, Abdel-Latif, & Mohammed, 2015). Upon treatment with Ca²⁺, the cross-linked alginate hydrogel is formed by aggregation of the carboxylate groups, which exist mainly in the GG units resulting in egg-box formatting structure (Graulus et al., 2015). Because of its high biocompatible and non-immunogenic properties (Bubenikova et al., 2012), ionically cross-linked alginate hydrogels had been employed in various pharmaceutical and biomedical applications such as drug delivery systems (Yang, Shi,

Zhou, & Shaokui Cao, 2015; Agarwal et al., 2015; Wu, Wang, Zhuo, & Cheng, 2014), wound dressing (Peng, Lin, Wang, & Wu, 2012; Han, Dong, Song, Yin, & Li, 2014; Sweeney, Mirafteb, & Collyer, 2014), tissue engineering (Qiao et al., 2013; Tang, Chen, Weir, Thein-Han, & Xu, 2012; Lee, Park, Shin, & Kim, 2011), enzymes and cell immobilization (Dong, Zhang, Tu, & Miao, 2014; Abd Rahima et al., 2013; Abd El-Ghaffar & Hashem, 2013; Wang, Chen, Wang, & Xing, 2014) etc. However, the difficulty to control the ionic gelation mechanism in addition to the formation of heterogeneous network structure could sometimes limit its application in these biomedical areas (Bruchet & Melman, 2015).

In order to overcome the drawbacks of the ionic cross-linking technique, various attempts were made to prepare covalently cross-linked alginate based hydrogels such as De Santis, Diociaiuti, Cametti, and Masci (2014) where alginate and Hyaluronic acid were cross-linked using l-lysine ethyl ester, Stone, Gosavi, Athauda, and Ozer (2013) where alginate/polyvinyl alcohol were cross-linked using citric acid and Mandal & Ray (2013) who cross-linked alginate in presence of acrylic acid (AA) and hydroxy ethyl methacrylate in aqueous solution. Despite the efficiency of these methods in minimizing the disadvantages of the ionic cross-linking, the use of some reagents such as initiators in addition to the formation of unfavorable and sometimes toxic products during the biodegradation still

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Scheme 1. Synthesis of ASP-Alg.

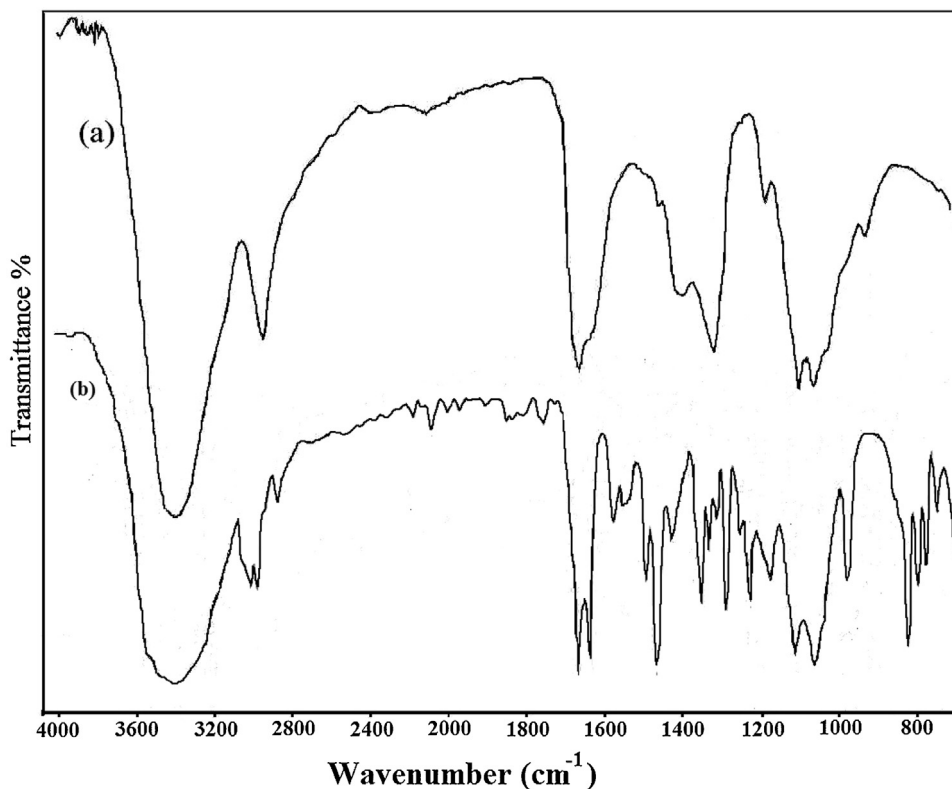


Fig. 1. FTIR spectra of (a) Alg and (b) ASP-Alg-2.

a serious drawback, which could still limit the pharmaceutical and biomedical application.

In this work, photo-crosslinkable alginate functionalized with styrylpyridine (ASP-Alg) had been synthesized and investigated utilizing Elemental analysis. Fourier transform infrared (FTIR), nuclear magnetic resonance (^{13}C and ^1H NMR) wide angle X-ray diffraction (XRD) spectra in addition to scanning electron microscope (SEM). The initiator-free photo-crosslinking process had been carried out by UV irradiation, through the $[2\pi + 2\pi]$ cycloaddition reaction of the inserted photo-active styryl pyridine moieties. Both extent and kinetics of the photo-crosslinking were monitored by UV–vis light spectra.

2. Materials and methods

2.1. Materials

Sodium alginate (Alg) ($M_w = 2 \times 10^5$ Da and viscosity 735 cps at 25°C) was purchased from Alfa Aesar (USA) and used with-

out further purification. The G/M ratio was determined by NMR to be 6.8. 1-Ethyl-(dimethylaminopropyl) carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS) were also obtained from Alfa Aesar (USA). Trans-4-[*p*-(amino)styryl]pyridine (ASP) was supplied from Hangzhou Chempro Tech Co. (China). All other chemicals and solvents were of analytical grade and used as provided.

2.2. Synthesis of photo-crosslinkable styrylpyridine-alginate (ASP-Alg)

The chemical modification of the alginate was performed by insertion of the photo-active (ASP) moieties through the amide bond formation between the Alg carboxyl and the ASP amino groups in presence EDC/NHS combined coupling agent as presented in Scheme 1. The formulation codes are collected in Table 1. Briefly, 0.5 g Alg was dissolved in 50 mL distilled water to get clear solution. Then a mixture of 0.14 g NHS and 1.16 g EDC was charged into the reaction flask and the mixture was magnetically stirred until homogeneous solution was obtained. In separate vials, aque-

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