

ORIGINAL ARTICLE

Studies on Effective Parameters onto Graft Copolymerization of Acrylic Acid onto Alginate

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ABSTRACT

The polysaccharide, alginate, has been chemically modified by graft copolymerization of acrylic acid in an aqueous medium using ammonium persulfate (APS) as an initiator under argon atmosphere. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, AcA monomer and alginate substrate.

Key words: graft copolymer, alginate, modification, acrylic acid monomer.

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INTRODUCTION

The modification of natural polymers is a promising method for the preparation of new materials. An efficient approach to modify of natural polymers, in order to synthesis of natural-based SAPs, is graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers. Free radical graft copolymerization with various monomers can carried out with different initiator systems [1-2].

The literature survey, however, reveals that few of the modifications deal with chemical grafting of a pre-modified protein such as gelatin. Ceric-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate, A/methyl methacrylate mixture, acrylamide (AAM), and 4-vinylpyridine onto gelatin has been reported. However, to the best of our knowledge, no report has been published on the optimization graft polymerization of Acrylamide (AAM) and 2-Acrylamido-2-methyl propan sulfonic acid (AMPS) together onto Gelatin chains using APS-Protein initiating system [3]. The present investigation deals with the detailed study of some major factors which affect graft copolymerization of acrylic acid onto alginate, initiated by APS in aqueous medium with a view to elucidate the grafting mechanism.

MATERIALS AND METHODS

Materials

Sodium alginate (chemical grade, MW 50000), ammonium persulfate (APS, from Fluka), acrylic acid (AcA, from Merck), were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for the hydrogel preparation and swelling measurements.

Procedure to Graft Copolymerization:

Synthesis of the graft copolymer, alginate-g-poly (acrylic acid), was carried out using APS as an initiator in an aqueous medium. A general procedure for graft copolymerization of acrylic acid onto alginate was conducted as follows. Alginate (0.50-1.20 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 40 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature

(30-75 °C). After complete dissolution of alginate, various amounts of the initiator solution (0.01-0.40 g APS in 5 mL H₂O) were added to the mixture. After stirring for 10 min, certain amounts of monomer (2.0-6.5 mL) were added to the reaction mixture. After 60 min, the produced copolymer was poured to excess non-solvent ethanol (200 mL) and remained for 3 h to dewater. Finally, the filtered composite is dried in oven at 60 °C for 10 h.

Homopolymer extraction

The graft copolymer, alginate-g-poly (acrylic acid), was freed from poly (acrylic acid) homopolymer, by pouring 0.50 g of the product in 50 mL of ethanol-aceton. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer by filtration of the alginate-g-poly (AcA), copolymer, the product was washed with ethanol and dried in oven at 50°C to reach a constant weight.

Grafting parameters

Grafting parameters

The grafting parameters, i.e. grafting ratio (Gr %), add-on value (Ad %), and homopolymer content (Hp %), used to characterize the nature of the copolymer are defined and calculated using the following equations [6] :

$$\text{Gr \%} = 100 (W_2 - W_0) / W_0 \quad (1)$$

$$\text{Ad \%} = 100 (W_2 - W_0) / W_2 \quad (2)$$

$$\text{Hp \%} = 100 (W_1 - W_2) / W_1 \quad (3)$$

Where W_0 , W_1 , and W_2 are the weight of the initial substrate, total product (copolymer and homopolymer), and pure graft copolymer (after ethanol-aceton extraction), respectively.

RESULTS AND DISCUSSION

OPTIMIZATION OF COPOLYMERIZATION REACTION

Since polymerization variables determine the extent of grafting and homopolymer amount, certain factors affecting the grafting parameters were investigated to achieve the optimum condition of polymerization.

Effect of monomer concentration

The acrylic acid concentration was varied from 0.17 to 0.85 mol/L to study its effects on grafting parameters (Figure1). These parameters were found to be increased by enhancement of AcA concentration from 0.17 up to 0.7 mol/L. This behavior can be attributed to the increase of monomer concentration in the vicinity of the alginate backbone and consequent greater availability and enhancement chances for molecular collisions of the reactants. The decrease in %Gr and %Ad after a certain level of AcA (0.7 mol/L) is probably due to preferential homopolymerization over graft copolymerization as well as increasing the viscosity of reaction medium, which hinders the movement of free radicals[5]. Needless to say, the increase in the chain transfer to monomer molecules may be other possible reason for the diminished grafting at higher AcA concentrations. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose and methyl acrylate onto starch [4].

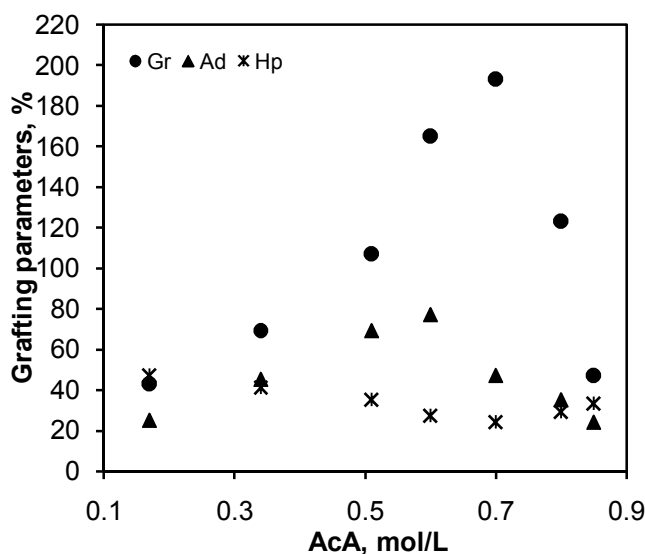


Figure 1. Effect of the monomer concentration on the grafting parameters.

Effect of Initiator Concentration

The grafting dependence on APS concentration can be concluded Figure 2. The highest grafting ratio (197%) was achieved at 0.0006 mol/L of APS where homopolymer content was 16 %. Increased APS concentration resulted in more radical sites on the alginate backbone that intern led to higher Gr and add-on values and lower photopolymers formation. As a result, increased free radicals on alginate are compensated by partial termination of the macro radicals [6, 10]. Thus Gr and add-on values were diminished at higher amounts of the initiator.

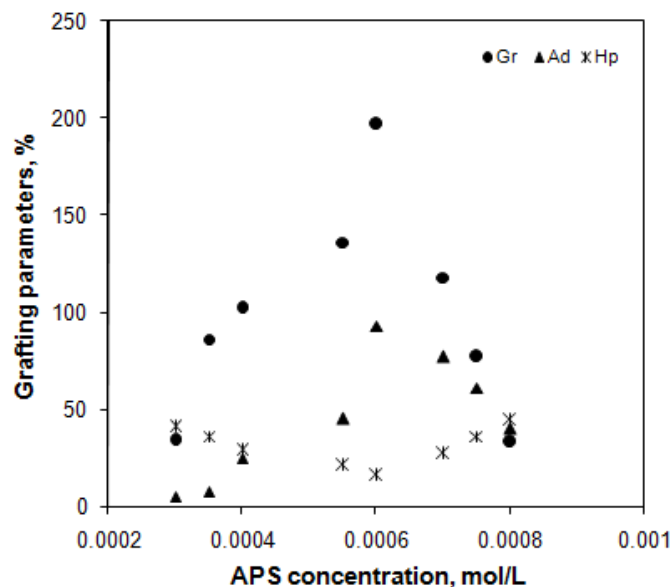


Figure 2. Effect of initiator concentration on the grafting parameters.

Effect of reaction time

Grafting of acrylic acid onto alginate backbones was carried out at various polymerization times as shown in Figure 3. The %Gr and %Ad increased with increase in the reaction time up to 70 min and thereafter, these parameters gradually decreased. It is obvious that the longer the reaction time, the better the graft copolymerization yield. The grafting loss may be attributed to decrease of all the consuming reactants. In addition, the decreased number of available active free radical sites for grafting and the retardation of diffusion of reactants, because of the long grafted chains at the alginate surface, may be other possible reasons for the diminished grafting at longer reaction times. Similar time dependency of grafting parameters was reported by others [7, 9].

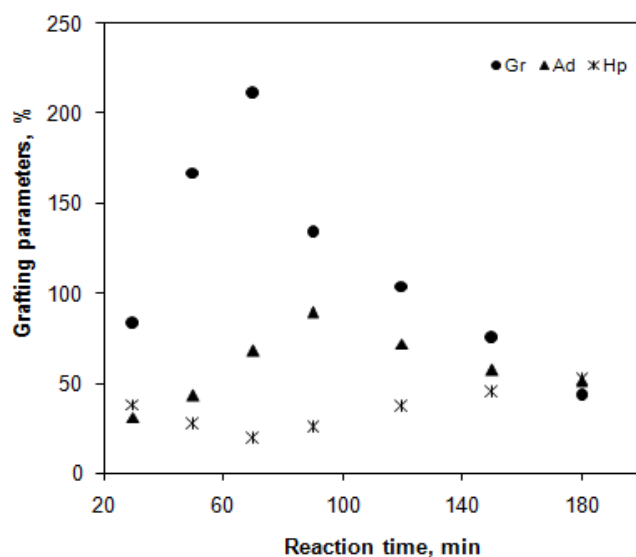


Figure 3. Effect of the reaction time on the grafting parameters

Effect of polysaccharide concentration

The results obtained by changing the alginate concentration for the graft polymerization are presented in Figure 4. It is evident from the figure that the %Gr and %Ad increase with increase in AcA concentration up to 4.0 wt% and then decrease with further increment of polysaccharide level. The initial increase may be due to the availability of more grafting sites, where AcA can be grafted. Subsequent decrease in grafting parameters, %Gr and %Ad, in increasing AcA content more than 4.0 wt% , can be explained on the basis of increase in viscosity of the medium and a decrease in the diffusion of monomers to active sites to produce graft copolymer. This observation is in close agreement with the results obtained by Zhang [8].

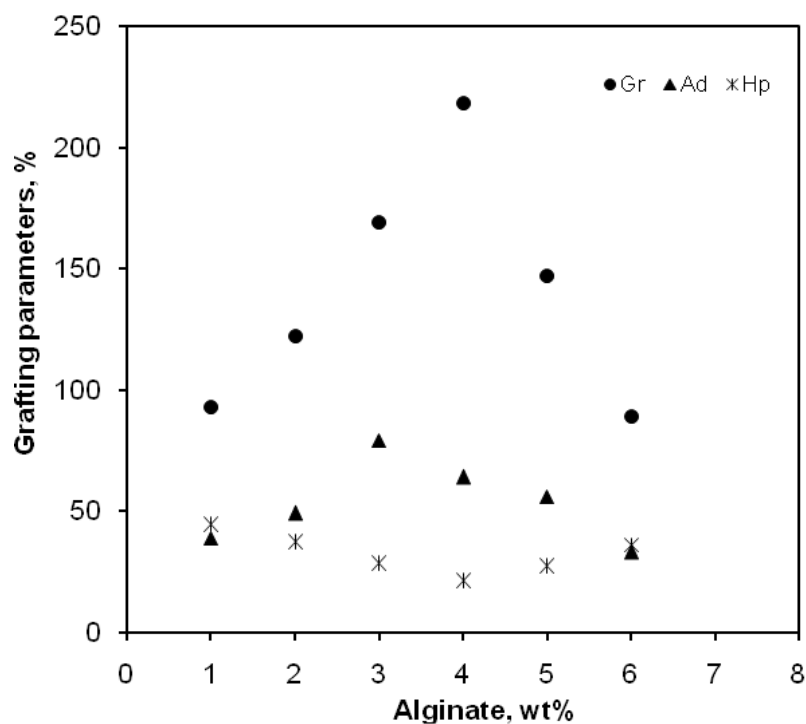


Figure 4. Grafting parameters as functions of alginate concentration

CONCLUSIONS

A doubly modified alginate, alginate-g-poly (acrylic acid), was prepared using APS-initiated graft polymerization of acrylic acid onto alginate. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, the acrylic acid monomer and the substrate alginate. The effect of the individual factors was investigated by calculating the grafting parameters, *i.e.*, grafting ratio (Gr %), add-on value and homopolymer content (Hp). Under optimum conditions (alginate 4wt%, AcA 0.7 molL⁻¹, APS 0.0006 molL⁻¹, reaction time 70 min), the grafting parameters were achieved as 218%, 64 % and 21% respectively.

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