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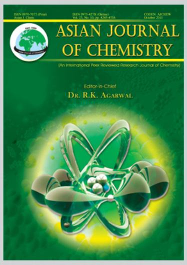

Optimization of Synthetic Conditions of Graft Copolymerization of Alginate-*g*-Poly(methacrylamide)

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In this study, we synthesized a novel graft copolymer based on sodium alginate (NaAlg) and polymethacrylamide (PMAAm) *via* a free radical polymerization method. The graft copolymerization reaction was carried out in a homogeneous medium. The graft copolymer structures were confirmed by FTIR spectroscopy and solubility characteristics of the products. The effect of grafting variables, *i.e.* concentration of ammonium persulfate, methacrylamide, sodium alginate and temperature was systematically optimized to achieve a highest per cent grafting possible.

Key Words: Sodium alginate, Methacrylamide, Grafting, Copolymerization, Optimization.

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 super absorbent polymers or modified properties of natural polymers, is graft polymerization of vinylic monomers (hydrophobic and hydrophilic) onto their backbones in presence of the crosslinkers. Free radical graft copolymerization with various monomers can carried out with different initiator systems[1-4].

The literature survey, reveals that few of the modifications deal with chemical grafting such as sodium alginate. Alginate (Alg) is a collective term for naturally derived polysaccharides, *i.e.* alginic acid, its salts and its derivatives. Alginates are composed of (1→4)-linked β-D-mannuronic acid and α-L-guluronic acid in a non-regular, block-wise pattern along the linear chain, which varied in amount and sequential distribution along the polymer chain depending principally upon the seaweed species. These polysaccharides are widely used in various applications such as chelating and thickening agents, emulsifiers, stabilizers, encapsulation, swelling and suspending agents, or used to form gels, films and membranes[5-7]. Most studies of alginate chemistry have focused on structural characterization such as conformation, ion selectively or mechanical and rheological properties[8] but among unique properties of alginates, gelation in presence of multivalent metal cations is important.

Infact, ammonium persulfate-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate, AN/methyl methacrylate mixture, acrylamide and 4-vinylpyridine onto protein and other polysaccharides has been reported. However, to the best of our knowledge, no report has been published on the optimization graft polymerization of methacrylamide (MAAm) onto sodium alginate chains using ammonium persulfate-Alg initiating system[9]. In the present report, to modify the sodium alginate, the grafting of methacrylamide onto sodium alginate chains in the presence of ammonium persulfate as an initiator was performed in a homogeneous system. The effect of reaction variables affecting on percent grafting was investigated.

EXPERIMENTAL

Sodium alginate (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Potassium persulfate (KPS, from Fluka) and methacrylamide were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for graft copolymer preparation.

Synthesis of graft copolymer : A general procedure was conducted as follows. Sodium alginate (0.50 g) was dissolved in 25 mL degassed distilled water in a three-neck reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm). The reactor was placed in a water bath preset at 65 ºC. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.20-0.6 g in 5 mL H_2O) was added into the mixture and was allowed to stir for 10 min. Then certain amounts of methacrylamide monomer

(1.5-4.0 g in 10 mL H_2O) was added to the reaction mixture. After 1 h, the reaction product was allowed to cool to ambient temperature. The obtained copolymer was then poured into ethanol (200 mL). After complete dewatering for 24 h, the hardened copolymer dried at 50 ºC and stored away from moisture, heat and light[4].

Homopolymer extraction: The graft copolymer, namely NaAlg-*g*-PMAAm, was freed from poly methacrylamide and homopolymer, by pouring 0.50 g of the product in 50 mL of ethanol solution. The mixture was stirred gently at room temperature for 44 h. After complete removal of the homopolymer, the NaAlg-*g*-PMAAm copolymer was filtered, washed with methanol and dried in oven at 50 ºC to reach a constant weight[4].

Grafting parameters: The percentage of graft yield (G %) and graft efficiency (GE %) and homopolymer (% Hp) were evaluated with the following weight-basis expressions as reported by Fanta:

$$\text{Graft yield (\%)} = 100\ (W_3\text{-}W_0)/W_0 \qquad (1)$$

$$\text{Grafting efficiency (\%)} = 100\ (W_3\text{-}W_0)/(W_2\text{-}W_0) \qquad (2)$$

or

$$\text{Grafting efficiency (\%)} = 100\ (W_3\text{-}W_0)/(W_4 + W_3\text{-}W_0) \qquad (3)$$

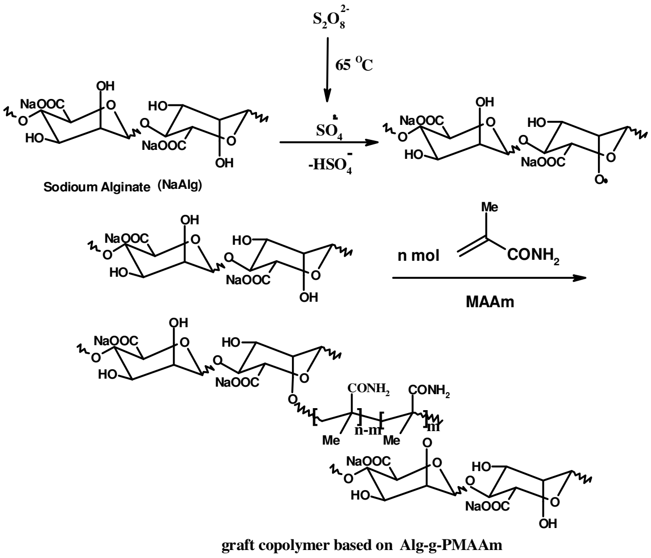
$$\text{Homopolymer (\%)} = 100\ (W_4\text{-}W_3)/W_4 \qquad (4)$$

where, W_0 and W_1 are the weight of sodium alginate substrate and methacrylamide monomer in feed, respectively. W_3 and W_4 are also the dried weight of grafted sodium alginate after extraction and poly(methacrylamide) homopolymer, respectively. Ethanol is a good solvent for poly(methacrylamide) as well as a precipitant for pure sodium alginate or grafted sodium alginate, so the poly(methacrylamide) homopolymer could be easily separated from the rough products. However, it seemed to be difficult to further separate the unreacted sodium alginate from the products and the right separation methods are still in progress in my research. In view of the modification intention, the unreacted sodium alginate is not very necessary to be separated from the products, so the blends of unreacted sodium alginate and the graft copolymer NaAlg-*g*-poly(MAAm) were actually obtained in this research and their compositions were unknown. In several studies on the grafting modification of polymer, the unreacted substrate polymer and graft copolymer were also not sep- arated from the products[7]. If the unreacted sodium alginate could be separated from the products, the graft copolymer NaAlg-*g*-poly(MAAm) with higher G % could be obtained, but the values of PC % and GE % would not be affected.

RESULTS AND DISCUSSION

Mechanism and spectral characterization of copolymer: As shown in the **Scheme-I**, at the first step, the thermally dissociating initiator, *i.e.* ammonium persulfate, is decomposed under heating (65 ºC) to produce sulfate anion-radical. Then the anion-radical abstracts hydrogen from the hydroxyl group of the Alg substrate to form corresponding alkoxy radicals. So, these macroradicals initiate poly(methacrylamide) grafting onto NaAlg backbones led to a graft copolymer so called NaAlg-*g*-PMAAm[7].

Infrared spectroscopy was carried out to confirm the chemical structure of the copolymer. Fig. 1 shows the FTIR spectra of pure NaAlg, NaAlg-*g*-PMAAm. The graft copolymer, Alg-*g*-PMAAm, comprise a pure Alg backbone with side chains that carry carboxamide functional groups that are evidenced by a new peak at 1678 cm^{-1} (Fig. 1b). This peak attributed to C=O stretching in carboxamide functional groups of poly(methacrylamide). The stretching band of NH overlapped with the -OH stretching band of the alginate portion of the copolymer.



Scheme-I: Proposed mechanistic pathway for synthesis of NaAlg-*g*-PMAAm copolymer

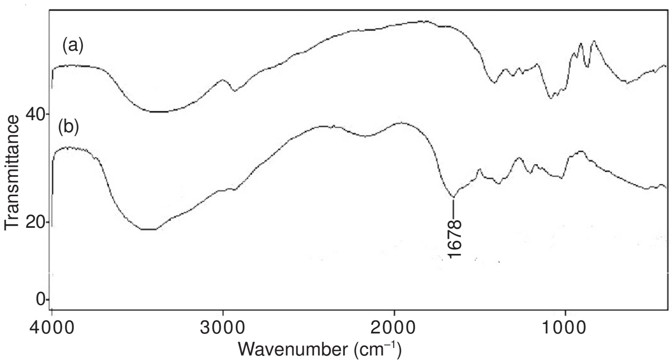


Fig. 1. FTIR spectra of pure NaAlg (a), NaAlg-*g*-PMAAm (b)

Optimization of the reaction conditions: In the present investigation, the effect of concentration of sodium alginate, ammonium persulfate and methacrylamide, along with reaction temperature was studied, to optimize the reaction conditions.

Effect of initiator concentration: The grafting dependence on ammonium persulfate concentration can be concluded (Fig. 2). The highest grafting ratio (398 %) was achieved at 0.03 mol/L of ammonium persulfate where homopolymer content was 14 %. Increased ammonium persulfate concentration resulted in more radical sites on the sodium alginate backbone that inturn led to higher graft yield (Gr %) and graft efficiency (GE %) values and lower homopolymers formation. As a result, increased free radicals on gelatin are compensated by partial termination of the macroradicals[8]. Thus grafting and grafting efficiency values were diminished at higher amounts of the initiator.

Effect of temperature: Fig. 3 exhibits the effect of polymerization temperature on the grafting parameters. In fact, an increase in temperature upto 60 ºC increases the grafting parameters. This behaviour may be related to the mobility of reactive free radical sites. Moreover, higher temperatures increase the solubility of the reactants. Temperatures higher than 60 ºC disfavour the grafting parameters. At higher temperatures, the rate of termination of the growing chain is increased and the monomer is volatilized out to some extent[8].

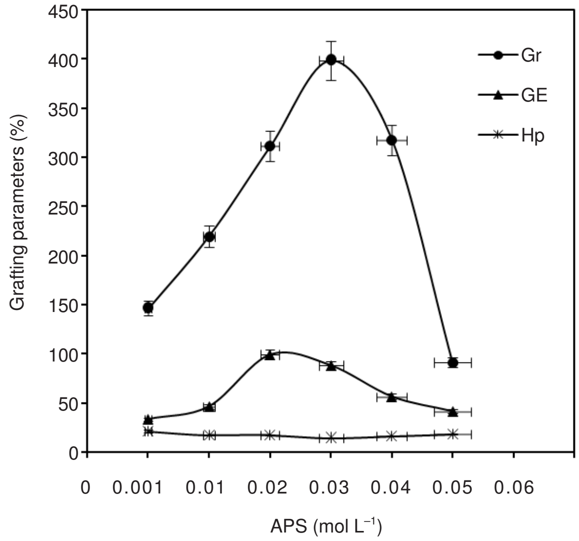


Fig. 2. Grafting per cent variances with concentration of ammonium persulfate variance

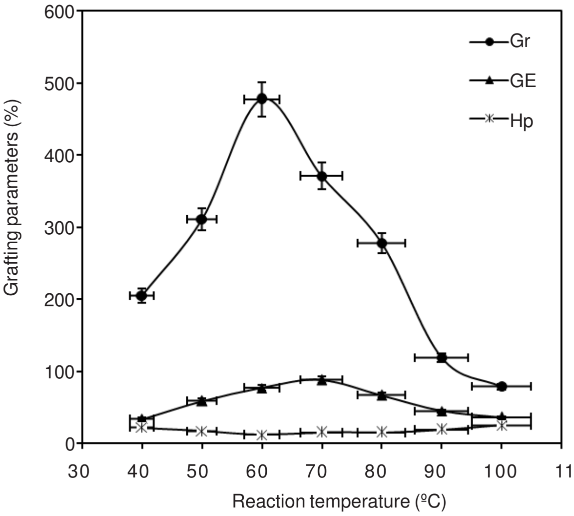


Fig. 3. Grafting per cent variances with temperature variance

Effect of methacrylamide concentration: The effect of monomer amount on the grafting reaction was studied at various concentrations of methacrylamide while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer (Fig. 4). The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain grafting % value, *i.e.*, 326 % at methacrylamide 0.75 molL^{-1}, the trend is inversed. The conversion and the graft efficiency (Ge %) are decreased and homopolymer content is increased noticeably from 14 to 33 percent. Thus, methacrylamide in an amount of MAAm 0.75 molL^{-1}, was recognized as an optimum monomer concentration. Once the monomer units are added, an excess of monomer can only increase the optimum volume of the reaction mixture[9].

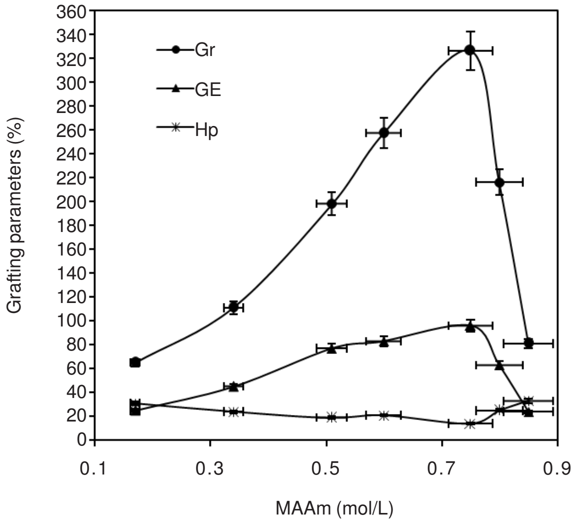


Fig. 4. Grafting per cent variances with amount of methacrylamide monomer variance

Effect of substrate concentration: The related to the grafting dependence on sodium alginate (NaAlg) amount is showed in Fig. 5. Maximum grafting and the lowest homopolymer formation was observed at 1.2g (4 wt %) sodium alginate, while others reactants including, monomer, initiator and temperature were kept constant. Beyond this value, both grafting yield and graft efficiency values are considerably reduced. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 1.0 to 4.0 wt % sodium alginate). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals leading to decreased grafting ratio and graft efficiency values. It also may be attributed to deactivation of the macroradical growing chains (*e.g.*, by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation. This observation is in close agreement with the results obtained by other investigators[10].

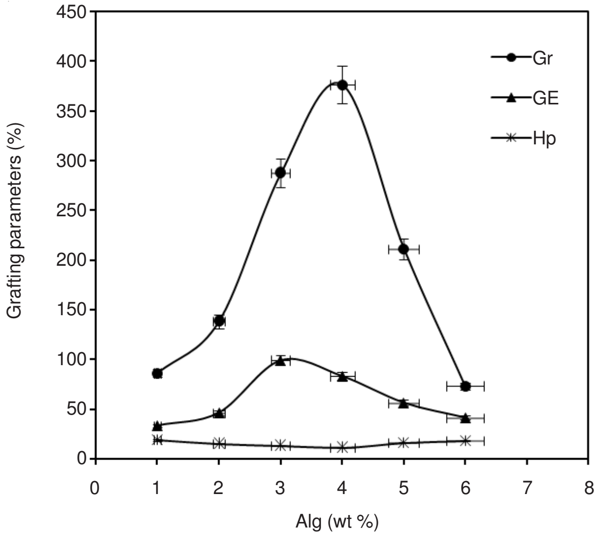


Fig. 5. Grafting per cent variances with amount of sodium alginate variance

Conclusion

The monomer, methacrylamide, can be easily graft copolymerized onto sodium alginate (NaAlg) using ammonium persulfate as an initiator in acidified aqueous medium. In order to prove that polyMAAm molecules were grafted, solubility test, FTIR spectroscopy were used. The reaction conditions were attempted to optimize for obtaining graft copolymers with higher grafting parameters. So, the reaction conditions for achieving the maximum Gr % (477) and GE % (99) were found to be as follows: ammonium persulfate 0.03 mol/L, MAAm 0.75 mol/L, NaAlg 4 wt %, reaction temperature 60 ºC. As an extension of this work, the NaAlg-*g*-PMAm copolymer is being subjected to further modification to prepare thickeners and flocculants for aqueous systems.

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