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Optimized Graft Copolymerization of Gelatin-g-Poly (Acrylamide-co-2-Acrylamido-2-methyl Propan Sulfonic Acid

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ABSTRACT

In this article, we synthesized of a novel graft copolymer of gelatin-based via radical polymerization mixtures of Acrylamide (AAm) and 2-Acrylamido-2-methyl propan solfonic acid (AMPS) onto gelatin backbones. The polymerization reaction was carried out in an aqueous medium and in the presence of ammonium persulfate (APS) as an initiator. The graft copolymer structures were confirmed by FTIR spectroscopy Gelatin and the graft copolymer as well as solubility characteristics of the products.. The effect of grafting variables, i.e. AAm/AMPS weight ratio and concentration of APS, and Gelatin and temperature was systematically optimized to achieve a highest percent grafting possible.

Key words: gelatin; graft copolymerization; Acrylamide; 2-Acrylamido-2-methyl propan sulfonic acid.

INTRODUCTION

The modification of natural polymers is a promising method for the preparation of new materials[1]. 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[2,3].

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[7,8], AN/methyl methacrylate mixture[9], acrylamide (AAm)[10,11], and 4-vinylpyridine[12,13] 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) togather onto Gelatin chains using APS-Protein initiating system. In the present report, to modify the Gelatin, the grafting of Acrylamide (AAm) and 2-Acrylamido-2-methyl propan solfonic acid (AMPS) onto Gelatin chains in the presence of ammonium persulfate (APS) as an initiator was performed in a homogeneous system. The effect of reaction variables affecting on percent grafting was investigated.

EXPERIMENTAL

Materials

Gelatin (from Parvar Novin-E Tehran Co.), potassium persulfate (KPS, from Fluka), Acrylamide and 2-Acrylamido-2-methyl propan Sulfonic acid (Merck) were used without further purification. All other chemicals were also analytical grade. Double distilled water was used for graft copolymer preparation.

Preparation of Graft CoPolymer

A general procedure for chemically graft copolymerization of Acrylamide (AAm) and 2-Acrylamido-2-methyl propan sulfonic acid (AMPS) onto gelatin backbones was conducted as follows. Gelatin (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at a desired temperature (70°C). Then 0.10 g of APS as an initiator was added to gelatin solution and was allowed to stir for 10 min. After adding APS, variable amounts of AAm and AMPS (AAm 0.40–1.60 g, AMPS 0.40–1.60 g) were added simultaneously to the gelatin solution. After 60 min, the reaction product was allowed to cool to ambient temperature. The graft copolymer was poured to excess non solvent ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted and the product scissored to small pieces (diameter ~ 5 mm). Again, 100 mL fresh ethanol was added and the graft copolymer was remained for 24 h. A brief proposed mechanism for APS-induced grafting of AAm and AMPS onto Gelatin showed in Scheme 1 .

Instrumental Analysis

The Gelatin-*g*-poly(acrylamide-co-AMPS) samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer.

Grafting parameters

The grafting parameters, i.e. grafting rati (Gr%), grafting efficiancy(Ge%), add-on value (Ad%), and homopolymer content (Hp%), used to characterize the nature of the copolymer are defined and calculated using the following equations(14):

$$Gr\ \% = 100\ (W_2 - W_0) / W_0 \quad ...(1)$$

$$Ad\ \% = 100\ (W_2 - W_0) / W_2 \quad ...(2)$$

$$Hp\ \% = 100\ (W_1 - W_2) / W_1 \quad ...(3)$$

$$Ge\ \% = 100\ (W_2) / W_1 \quad ...(4)$$

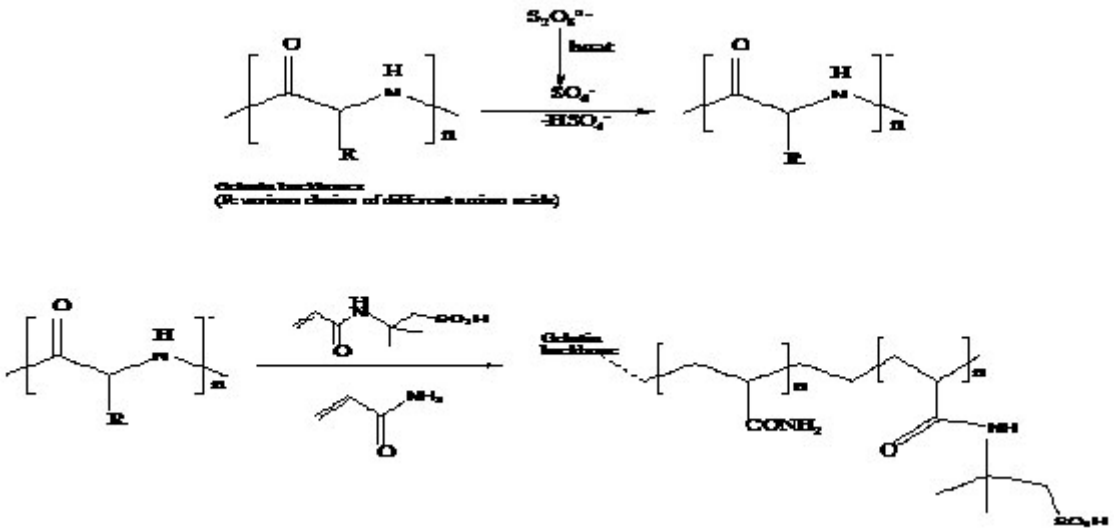
where W_0, W_1, and W_2 are the weight of the initial substrate, total product (copolymer and homopolymer), and pure graft copolymer (after DMF extraction), respectively.

RESULTS AND DISCUSSION

Grafting Evidences

The simplest method to prove the formation of Gelatin-*g*-poly(acrylamide-co-AMPS) is based on the solubility difference of the graft copolymer and the homopolymers, PAAm and PAMPS. Gelatin and homopolymers are soluble in water and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with water for 24h, an insoluble solid was still remained[15]. A Gelatin /PAAm-PAMPS physical mixture was dissolved completely when it was treated in the same was. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between the Gelatin substrate and PAAm-PAMPS macromolecules.

The PAAm-PAMPS grafting was also confirmed by the differences between FTIR spectra of the gelatin and that of the graft copolymer. Figure 1 shows the FTIR spectra of the Gelatin substrate, polyacrylamide, and poly 2-Acrylamido-2-methyl propan Sulfonic acid and the Gelatin-g-PAAm-AMPS graft copolymer freed from homopolymers. The existence of a rather sharp intense peak at 1215 cm^{-1} (Sulfonic groups) and 1653 cm^{-1} (carboxamide groups) in IR spectra of the graft copolymers is a certain evidence of grafting . This absorption band arises from stretching vibration mode of the sulfonic groups related to 2-Acrylamido-2-methyl propan Sulfonic acid monomers. Most of the other peaks are related to the protein backbone. Since PAAm-AMPS could be extracted nearly completely from a physical mixture of PAAm, PAMPS and Gelatin by DMF, the presence of appreciable amounts of sulfonic and carboxamide groups in our reaction products after extraction is an additional proof for grafting of PAAm and PAMPS onto the Gelatin.



Scheme 1: A brief proposed mechanism for APS-induced grafting of polyacrylamid and poly 2-Acrylamido-2-methyl propan sulfonic acid onto gelatin

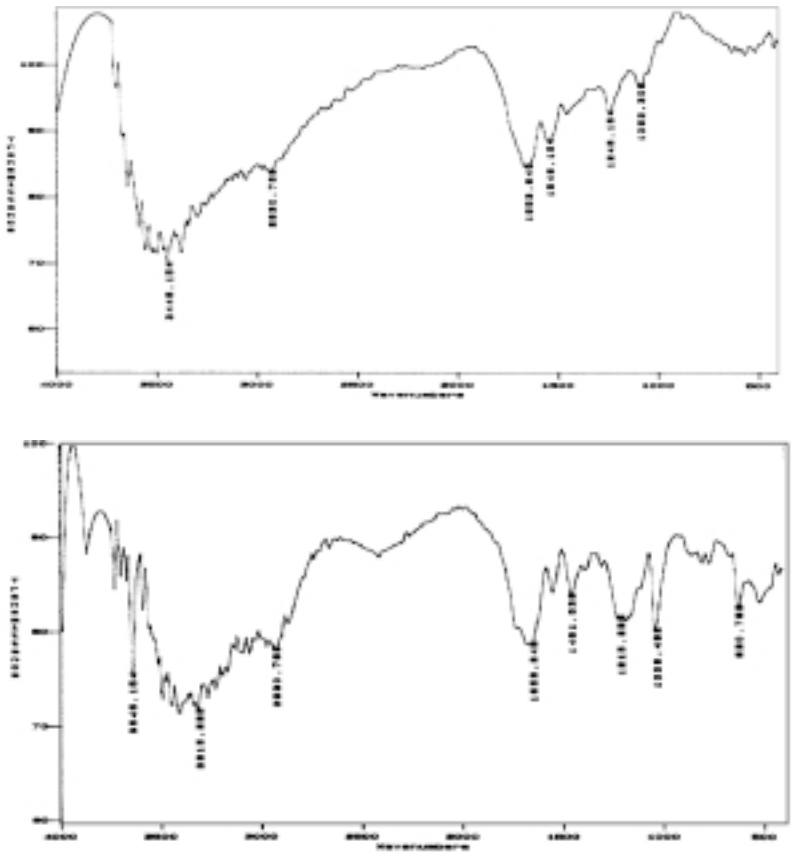


Fig. 1: FT–IR spectra of (a) Gelatin (b) optimum Gelatin-g-PAAm-AMPS copolymer

Thermogravimetric behavior

The grafting was also supported by thermogravimetric analysis (Fig. 2). TGA of Gelatin (Fig. 2a) shows a weight loss in two distinct stages. The first stage ranges between 15 and 120 °C and shows about 17% loss in weight. This may correspond to the loss of adsorbed and bound water[17]. No such inflexion was observed in the TGA curve of gelatin-*g*-P(AAm-co-AMPS). This indicated that the grafted copolymers were resistant to moisture absorption. The second stage of weight loss starts at 330 °C and continues up to 440 °C during which there was 60% weight loss due to the degradation of Gelatin. Grafted samples, however, show almost different behavior of weight loss between 15 and 550 °C (Fig. 2b). The first stage of weight loss starts at 205 °C and continues up to 330 °C due to the degradation of Gelatin. The second stage from 370 to 480 °C may contribute to the decomposition of different structure of the graft copolymer. The appearance of these stages indicates the structure of Gelatin chains has been changed, which might be due to the grafting of poly(AAm-co-AMPS) chains. In general, the

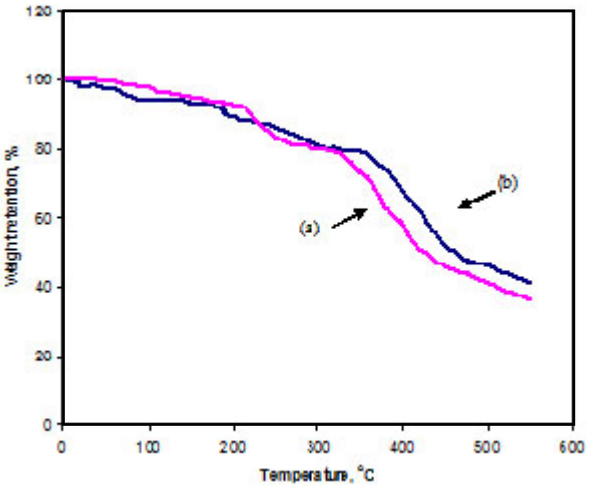


Fig. 2: TGA curves of (a) gelatin and (b) gelatin-*g*-P(AAm-co-AMPS)

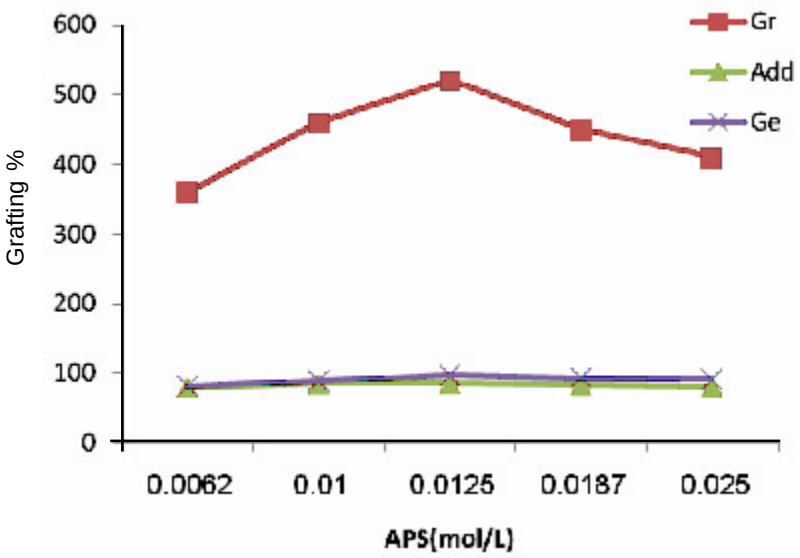


Fig. 3: Grafting percent variances with concentration of ammonium persulfate variance

copolymer had lower weight loss than Gelatin. This means that the grafting of Gelatin increases the thermal stability of Gelatin in some extent.

Optimization of Polymerization

Since polymerization variables determine the extent of grafting and homopolymers amount, certain factors affecting the grafting parameters were investigated to achieve the optimum condition of polymerization. Therefore, we optimized the grafting of PAAm, PAMPS onto Gelatin in homogenous aqueous media by changing temperature, the initial concentration of monomers, initiator, and the relative amount of the substrate. Within the range of the amount of the reactants used, our preliminary studies showed no considerable dependence between the reaction time and the grafting extent[16].

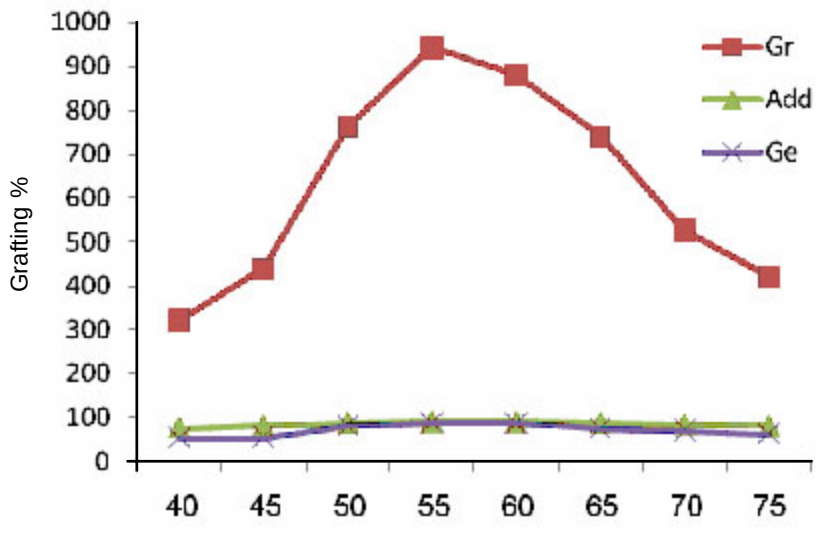


Fig. 4: Grafting percent variances with temperature variance

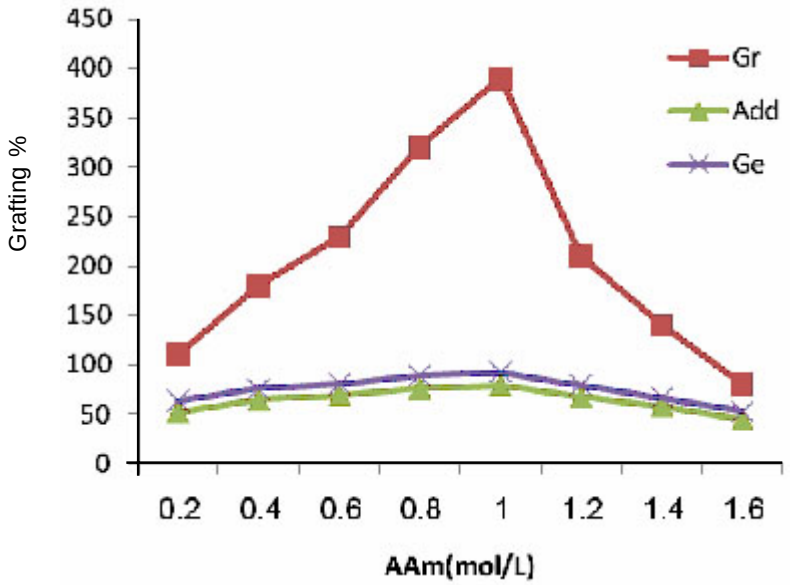


Fig. 5: Grafting percent variances with amount of acrylamide monomer variance

Effect of Initiator Concentration

The grafting dependence on APS concentration can be concluded Figure 3. The highest grafting ratio (520%) was achieved at 0.125 mol/L of APS where homopolymer content was 1.3 %. Increased APS concentration resulted in more radical sites on the Gelatin backbone that inturn led to higher Gr and add-on values and lower homopolymers formation. As a result, increased free radicals on Gelatin are compensated by partial termination of the macroradicals[17]. Thus Gr and add-on values were diminished at higher amounts of the initiator.

Effect of Temperature

To study the influence of the reaction bath temperature on the grafting parameters, the grafting of AAm, AMPS onto Gelatin was carried out at six

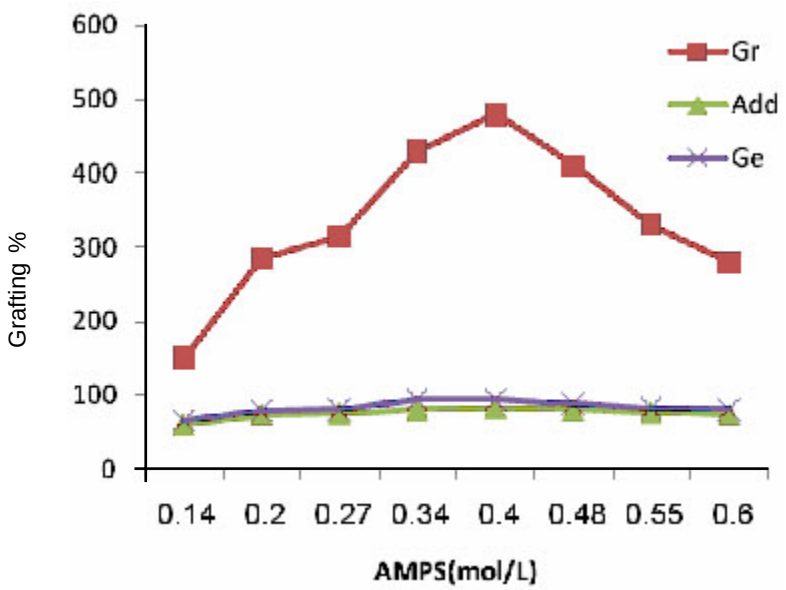


Fig. 6: Grafting percent variances with amount of AMPS monomer variance

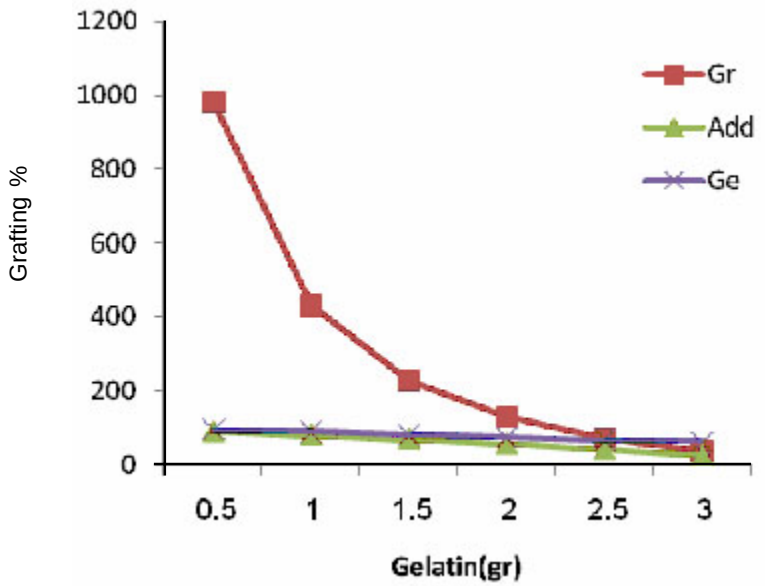


Fig. 7: Grafting percent variances with amount of gelatin variance

temperature ranging from 40 to 75 °C. The results are given in Figure 4. Grafting percentage (%Gr) is increased with increasing the temperature from 40 to 55 °C, and then decreased. At 55 °C, maximum grafting (Gr 942%), minimum homopolymers content (69.11%) and highest add-on value (40.90%) was obtained. Improvement of grafting up to 55 °C can be attributed to the following factors: increased the number of free radicals formed on the Gelatin backbone, increased propagation of the graft copolymerization onto Gelatin, enhanced diffusion of monomers and initiator into and onto backbone structure, and increased in mobility of the monomers molecules and their higher collision probability with the backbone macroradicals(18). However, Gr was decreased as the bath temperature was raised beyond 55 °C. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the APS-gelatin are presumably another reasons for reduced amount of grafting beyond 55 °C. The PAAm and PAMPS homopolymer formation is minimal at the bath temperature of 55 °C.

Effect of AAm Concentration

The effect of monomer amount on the grafting reaction was studied at various concentrations of AAm while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer[19]. The results are given in Figure 5. The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain Gr value, *i.e*., 390% at AAm 3.5 mL, the trend is inversed. The conversion and the grafting efficiency (Ge) are decreased, and homopolymer content is increased noticeably from 5.7 to 33.3 percent. Thus, acrylamid in an amount of AAm 3.5 mL 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.

Effect of AMPS Concentration

The 2-Acrylamido-2-methyl propan Sulfonic acid concentration was varied from 0.14 to 0.60 mol/L to study its effects on grafting parameters (Figure 6). These parameters were found to be increased by enhancement of AMPS concentration from 0.14 up to 0.4 0 mol/L. This behavior can be attributed to the increase of monomer concentration in the vicinity of the gelatin 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 AMPS (0.4 0 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[19,20]. Needless to say, the increase in the chain transfer to monomer molecules may be other possible reason for the diminished grafting at higher AMPS concentrations. Similar observations have been reported for the grafting of ethyl acrylate onto cellulose[22] and methyl acrylate onto starch[21].

Effect of Gelatin Concentration

The related to the grafting dependence on Gelatin amount is summarized in Figure 7. Maximum grafting and the lowest homopolymers formation was observed at 0.50 g Gelatin, while others reactants including, monomers, initiator, and temperature were kept constant. Beyond this value, both grafting ratio and add-on values are considerably reduced. This behavior is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (until 0.50 g Gelatin). 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 add-on values(24). 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[23].

CONCLUSION

A doubly modified Protein, Gelatin-g-PAAm-AMPS, was prepared using APS-initiated graft polymerization of acrylamide (AAm) and 2-Acrylamido-2-methyl propan Sulfonic acid onto Gelatin. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, the monomers AAm,AMPS and the substrate Gelatin. The effect of the individual factors was investigated by

calculating the grafting parameters, *i.e.*, grafting ratio (Gr), grafting efficiancy(Ge%), add-on value and homopolymer content (Hp). Under optimum conditions (Gelatin 0.50g, AAm 3.5 mL, AMPS 3.0 mL, APS 0.125 mol/L, reaction bath temperature 55 °C, reaction time 1h), the grafting parameters were achieved as 980%, 73,94 %, 74.90 and 26.50% respectively.

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