

P.psyllium-g-polyacrylamide: Synthesis and characterization

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Summary

To graft acylamide (AM) onto the backbone of natural water-soluble polysaccharide of P.psyllium mucilage (PSY), ceric ion initiated solution polymerization technique was reported for the first time. This technique was found to be beneficial. The effects of varying concentration of AM and ceric ammonium nitrate (CAN) on graft copolymerization have been studied. The prepared copolymers were characterized by FTIR. The % grafting and the intrinsic viscosity of this water-soluble copolymer were found to be affected by the concentration of AM and CAN in the reaction mixture.

Introduction

Modification of natural polymers to improve their chemical and physical properties, using various techniques is gaining much importance. As the interest in graft polymers has increased over the years owing to their multifaceted application in many domains. A large variety of methods have been developed for their synthesis. Graft copolymers of AM have received much attention because of their immense industrial potential. Its water-soluble tendency in nearly all conditions has made it possible to form graft copolymers with other monomers easily. By further reaction at the amide function one can convert many of the polymers into polyelectrolyte or thermosetting resins. The most important applications of AM grafted copolymers are those associated with flocculation and settling of aqueous suspensions, paper treating resins and as gelling and stabilizing agents for soils and muds [1,2].

Grafting techniques have received considerable attention from scientists all over the world, especially regarding those systems in which a natural polymer is polysaccharide, probably due to its abundant availability and low cost. Numerous methods have been reported in the literature for initiating graft copolymerization [3,4]. When polyol type of polymers such as polysaccharides, are the substrates, the ceric ion initiated method has been used extensively [5,6,7].

A number of investigations of graft polymerization onto starch have been made using ceric ion initiator [8]. Singh et al. has prepared a large number of graft copolymers of AM with polysaccharides such as guar gum, xanthan gum, sodium alginate, carboxylic methyl cellulose and starch using ceric ion/ HNO₃ acid as redox initiator [9].

The present research is concerned specifically with ceric ammonium nitrate (CAN) induced grafting of AM with PSY mucilage (an anionic polysaccharide) consisting of

pentosan and uronic acid and is directed towards understanding the influence of concentrations of AM and CAN in the reaction mixture, on % grafting by preparing different samples. The prepared samples were characterized by FTIR.

Experimental

P.psyllium mucilage was obtained from its husk (The Sidhpur Sat-Isabgol Factory, Gujrat, India) and was used after purification. It was purified by precipitation from aqueous solution with alcohol and finally washed with acetone. Acrylamide (AM), ceric ammonium nitrate (CAN) (extra pure, Merck chemical co.) and nitric acid (analar grade, BDH), were used as received. The FTIR spectra of purified PSY and the copolymers prepared were recorded on Bruker-vector-22 spectrometer. The intrinsic viscosity of the aqueous solution of PSY-g-PAM was measured using the method given in our previous publication [10,11,12].

The (PSY-g-PAM) graft copolymers have been synthesized by grafting acrylamide onto purified P.psyllium mucilage by radical polymerization method in aqueous system using ceric ion, nitric acid redox initiator [13]. The following procedure has been adopted in carrying out the reactions. One gram of P.psyllium was dissolved in distilled water (200mL) in an Erlenmeyer flask. Required amount of acrylamide monomer was dissolved in distilled water (100mL) in another flask and the solution was added to the P.psyllium mucilage solution in the Erlenmeyer flask. The mixture of the solution was stirred with magnetic stirrer. The flask was then sealed with septum stopper. Nitrogen gas was then flushed into the solution through hypodermic needle. The solution was stirred for 30 minutes while being bubbled with nitrogen. Required amount of ceric ion solution (ceric ammonium nitrate dissolved in 1M HNO₃ solution) was then injected through the stopper by hypodermic syringe. The nitrogen flushing was continued for another 20 minutes; then the needles were taken out, and flasks were further sealed with teflon tape. The reaction temperature was maintained at 30°C by immersing the flask in constant temperature bath. The reaction mixture was stirred occasionally. The reaction was continued for 24 hours and then terminated by injecting 0.5 mL of saturated aqueous hydroquinone solution.

The reaction product was precipitated in excess of isopropanol and filtered through scintered glass filter. The precipitate was again slurried in acetone followed by filtration and finally the precipitate was dried in vacuum oven at 40°C.

The effect of AM and CAN concentration on % grafting has been given in Table 1. The % grafting was calculated by the equation

$$\% \text{ grafting} = \frac{W_0 - W_1}{W_2} \times 100$$

Where

W_0 = weight of resulting polymer

W_1 = weight of added PSY

W_2 = weight of AM

Table 1. Details of graft reaction

Sample No.	Moles in the reaction mixture		P.psyllium (PSY) (g)	Grafting Efficiency (%)	Intrinsic viscosity $[\eta]$ (dL/g)
	Acrylamide (AM)	Ce IV ion ($\times 10^3$)			
1	0.00	0.00	1.0	0.00	1.29
2	0.07	0.05	1.0	50.00	3.60
3	0.07	0.10	1.0	52.76	3.51
4	0.07	0.15	1.0	55.82	3.23
5	0.14	0.05	1.0	78.00	5.60
6	0.14	0.10	1.0	79.57	5.12
7	0.14	0.15	1.0	82.15	5.01
8	0.21	0.05	1.0	87.73	5.73
9	0.21	0.10	1.0	91.00	5.45
10	0.21	0.15	1.0	95.19	5.41

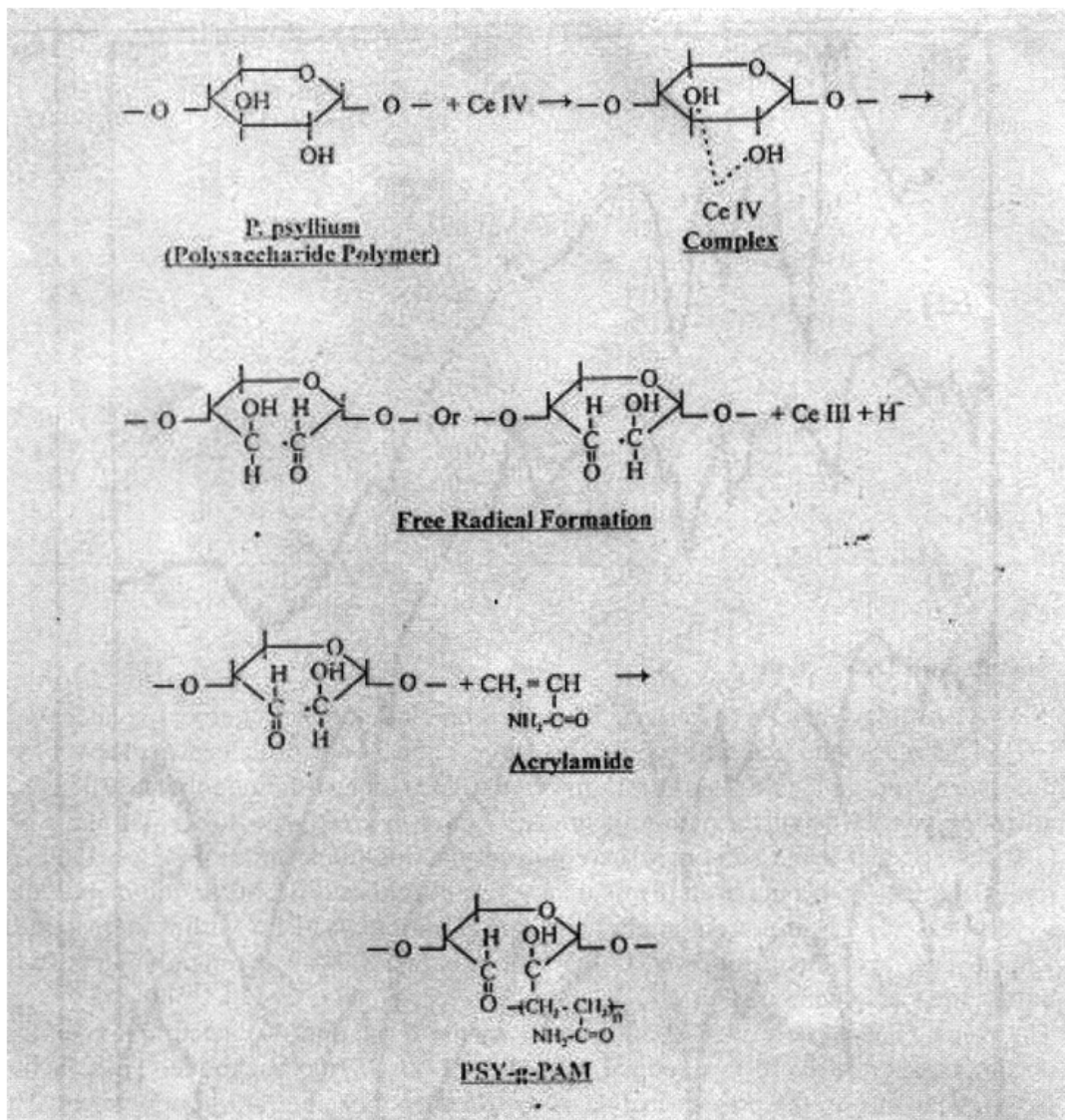
Results and Discussion

PSY-g-PAM has been synthesized by ceric ion initiated polymerization technique [13]. This technique was utilized because free radicals are produced exclusively on polysaccharide molecules and it minimizes the formation of homopolymers. There is always a possibility of formation of homopolymer in grafting. But Owen and Shen [14] showed that if the monomer (here polyacrylamide) concentration is less than 2.0 moles and CAN concentration is less than 0.1 mole, chances of forming homopolymer is very less. Here, in present study their concentration was kept within these critical values. The mechanism followed in the synthesis of PSY-g-PAM copolymer may be represented as Scheme I.

The mechanism of ceric ion reaction involves the formation of chelate complex that decomposes to generate free radical sites on polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers. The number of free radical sites so generated should be proportional to the concentration of ceric ions. In other words, the length of the grafted chains at a fixed monomer concentration should be largest in case of low ceric ion concentration and vice-versa. This trend is clearly observed in case of graft copolymers prepared in this study.

Referring the Table 1 two distinct observations can be made. First, a variation in the catalyst concentration affected the chain length of polyacrylamide [sample numbers 2,3,4; 5,6,7 and 8,9,10]. In each set, the increase in catalyst concentration increased the % conversion of acrylamide but gradually decreased the intrinsic viscosity of the samples. This can be explained in terms of increasing number and decreasing length of polyacrylamide chains. Second observation is that with an increase in acrylamide (AM) concentration, % grafting increased and the intrinsic viscosity of the samples also increased.

P. psyllium mucilage takes a longer time to be dissolved in water at room temperature as compared to their grafted copolymers. This observation with all the copolymers indicated that the solubility in water increased due to polyacrylamide chains.



Scheme 1. Mechanism of Reaction

FTIR Spectra

FTIR spectrum of purified PSY [Fig 1(a)] shows characteristic peaks of -OH between 3609 and 3288 cm^{-1} , -C=O of -COOH between 1635 and 1617 cm^{-1} and ether linkage at 1419 cm^{-1} . The most prominent peak is the -C=O peak of -COOH group present in PSY.

FTIR spectra (figures 1b-1d) of prepared PSY-g-PAM samples give characteristic peaks of -OH and -NH overlapping between 3609-3288 cm^{-1} of ether linkage between 1543-1438 cm^{-1} , C=O of amide at 1636 cm^{-1} , -CH₂ 2924 cm^{-1} , C-N stretching at 1261 cm^{-1} and out of plane NH band at 800-600 cm^{-1} .

The FTIR spectra of these samples are different from FTIR spectrum of pure PSY (Fig1a) by showing a strong band at 1636 cm^{-1} due to -C=O of amide group. The intensities of the absorption of -C=O have been compared to correlate the calculated % grafting in each sample. In the FTIR spectra, Fig 1(b) corresponds to PSY-g-PAM

with acrylamide content 0.07 mole, Fig 1(c) corresponds to PSY-g-PAM with AM content 0.14 mole and Fig 1(d) corresponds to PSY-g-PAM with AM content 0.21 mole in the reaction mixture. In each case, the concentration of CAN was constant (0.05×10^{-3} moles/L) Increase in the intensities of peaks especially $-C=O$ peak with increase in AM concentration supports that the % grafting increases with increase in mole fraction of AM in the reaction mixture [15].

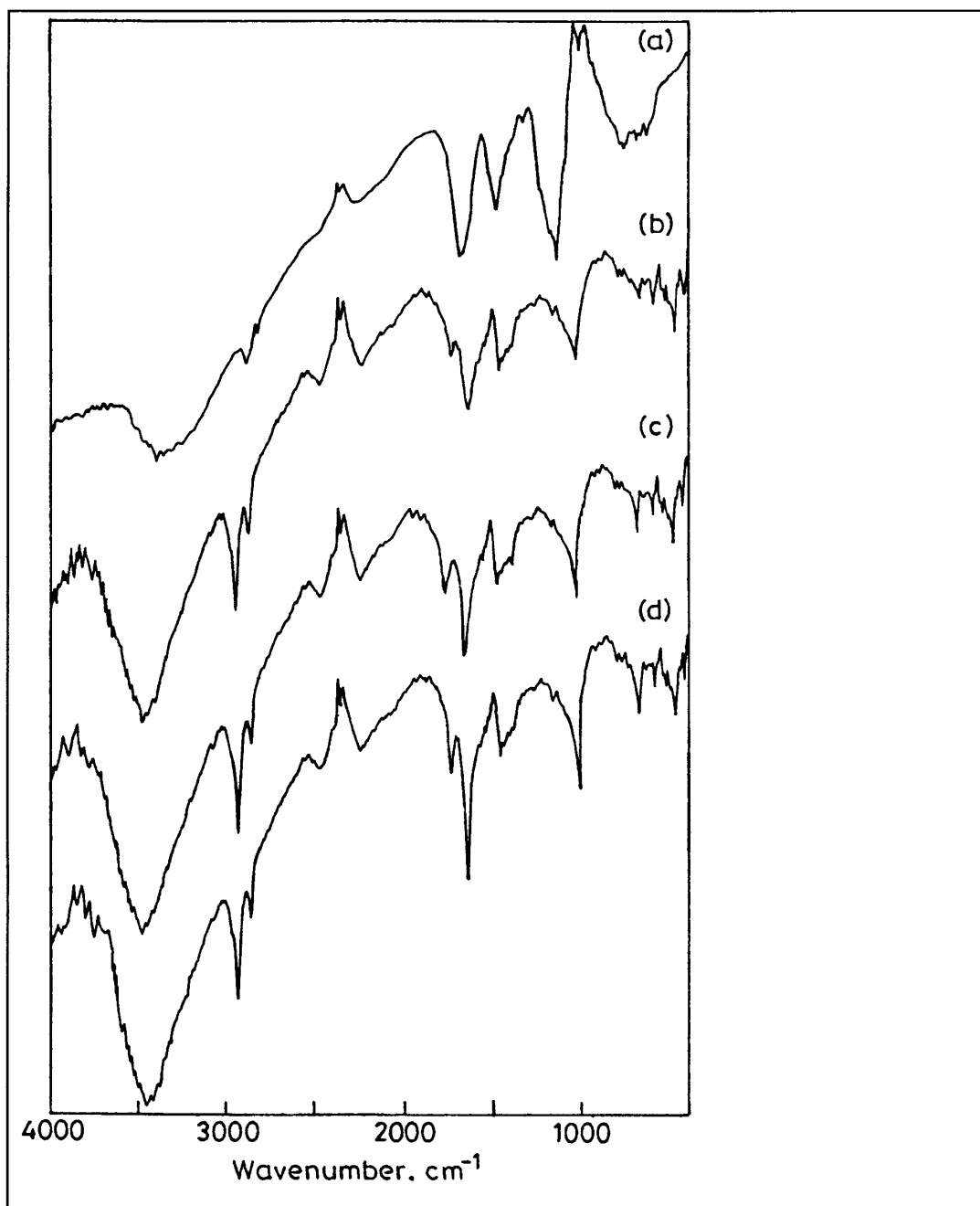


Figure 1. FTIR Spectra of PSY (a) PSY-g-PAM copolymers (b) AM= 0.07 moles, (c) AM=0.14 mole, (d) AM =0.21 mole

Conclusions

Grafting of PSY with AM has been done successfully by using CAN/HNO₃ redox initiator system. The acrylamide concentrations were kept less than 2.0M and CAN concentration less than 0.1M to prevent homopolymerisation. FTIR has been used to confirm the grafting of AM on to PSY. The percent grafting increases, with increase in concentration of AM (from 0.07 to 0.21 mole) and CAN. An increase in AM concentration at fixed CAN concentration increased the intrinsic viscosity of the samples whereas the increase in CAN concentration at fixed monomer concentration caused a decrease in intrinsic viscosity.

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