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RESEARCH ARTICLE

GRAFT COPOLYMERIZATION OF METHACRYLIC ACID ON TO POTATO STARCH INITIATED BY CERIC AMMONIUM NITRATE

***Dr. Vidyagauri Lele and Kusum Baser**

Department of Chemistry, N.G. Acharya and D.K. Marathe College, Chembur, Mumbai-400 071, India

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ABSTRACT

The grafting of methacrylic acid on to granular potato starch in an aqueous medium initiated by ceric ammonium nitrate (CAN) has been studied. The effect of initiator concentration, monomer concentration, polymerization time and temperature, material to liquor ratio and presence of solvent have been studied in terms of percentage grafting (%PG) and grafting efficiency (%GE). The %GE was found to decrease with increase in monomer concentration, but the reverse trend was obtained on increasing the polymerization time, temperature and concentration of initiator. Acid hydrolysis and infrared (IR) spectroscopy were used for the confirmation of graft copolymer formation.

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INTRODUCTION

Starch is a renewable resource, cost effective biopolymer. Chemically modified starches with improved properties are gaining increasing importance (Abo-Shosha *et al.*, 1992; Bayazeed *et al.*, 1989 and Hebeish *et al.*, 1992) in industry not only because they are low cost but mainly because the polysaccharide portion of the product is bio-degradable causing the finished product to lose its integrity and be reduced to particles small enough to be of minimal damage to the environment. Chemical modification of starch is generally effected by grafting vinyl monomers onto it. Methacrylic acid (MAA) has been graft polymerized onto starch using various initiator systems, such as potassium per sulphate (Khalil *et al.*, 1993; Lai *et al.*, 2006), ammonium peroxydisulphate, manganese (IV)-acid system,chromic acid, (Pathania *et al.*, 2012) ammonium persulphate (Sun *et al.*, 2003) etc. However few attempts have been made to graft –polymerize MAA using tetravalent cerium as initiator (Athawale *et al.*, 1997). The present study therefore, reports the graft copolymerization of MAA onto starch using Ce^{+4} as initiator. The optimum conditions for grafting are established with respect to initiator concentration, monomer concentration, polymerization time and temperature, material to liquor ratio and solvent.

MATERIALS AND METHODS

Insoluble Potato starch supplied by Thomas Bakerchemicals., Mumbai, India was first dried at 110^0C for 10 hours to remove absorbed moisture and then was stored over anhydrous $CaCl_2$. Methacrylic acid was used as supplied and stored in refrigerator. Ceric ammonium nitrate (CAN) (J. T. Baker Chemical Co., NJ, USA), was dried in over at 110^0C in oven for 6 hours and then stored over $CaCl_2$ in desiccator. It was used as 0.1 mol/L solution prepared in molar nitric acid (AR grade, s. d. Fine Chemicals, India).

Graft Copolymerization

The reaction was carried out by taking the mixture of 2 g of dried starch with 70 mL of water and stirring to make uniform slurry in presence of air at 400 rpm. It was then treated with predetermined quantity of CAN for 10 min to facilitate free radical formation on it, it was followed by addition of monomer and then the total volume was made to 100 mL with distilled water. After certain time, the reaction mixture was immediately filtered through preweighed Whatman filter paper no. 40. The residue was made free of homopolymer by repeatedly washing with water. After extraction of homopolymer the residue was dried in Vacuum-oven at 110^0C for 24 hours. Control reactions were carried out with 2g of starch under identical experimental conditions except the addition of monomer in each set of reaction.

****Corresponding author: Dr. VidyagauriLele***
Department of Chemistry, N.G. Acharya and D.K. Marathe College, Chembur, Mumbai-400 071, India

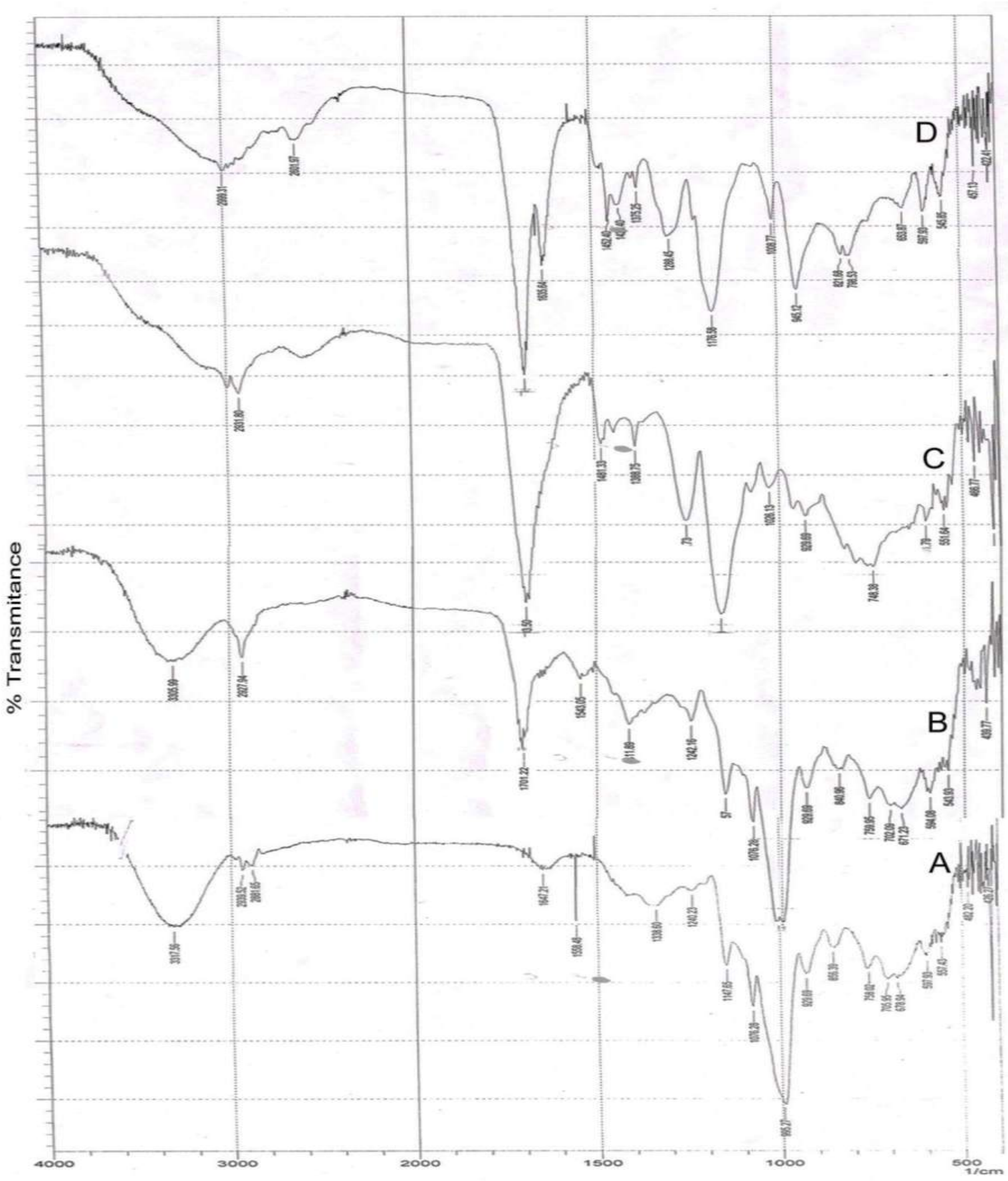

Fig.1. FTIR spectraof (A) Starch (B) S-g-(MAA) (C) Acid hydrolyzed S-g-(MAA) (D) Poly(MAA)

Infrared spectroscopy

Infrared (IR) spectra of pure starch, starch graft copolymer, hydrolyzed starch graft copolymer and poly (MAA) were recorded on Shimadzu FTIR- single beam spectrophotometer in the range of 4000-400cm^{-1}using ATR method.

Acid hydrolysis

In order to separate the grafted polymer from starch backbone, the s-g-poly (MAA) copolymer were subjected to acid hydrolysis. Graft copolymer was refluxed in 1N hydrochloric Acid for 1 hour. Residue was washed with dimethyl formamide in order to ensure complete removal of starch hydrolysis products.IR spectra of dried product was found to be identical with poly(MAA), which unambiguously indicated the formation of s-g- (MAA).

RESULTS AND DISCUSSION

Physical appearance

Starch-g-MAA was white or slightly yellowish-white powder.

Confirmation of graft copolymer formation

Gravimetric estimation

The graft copolymerization was followed gravimetrically. The increase in the weight of the residue for each copolymerization compared with the control reaction, confirms the occurrence of grafting. The control reaction was carried out with 2g of starch using 0.006mol/L CAN at 30°C for 180min.

IR Spectroscopy

The FTIR spectra of potato starch, starch-g-(MAA), acid hydrolyzed starch-g-(MAA) and poly (MAA) are depicted in figure 1. Fig. 1A and 1D show IR spectra of pure starch and Poly (MAA) respectively. Characteristic peaks for starch (Fig 1A) are the C-O stretching vibrations at 1170-1020cm^{-1}, 2939cm^{-1} indicate C-H vibration for CH_2 group, while the broad 3600-3000cm^{-1} region stems from O-H stretching vibrations. There is one more peak at 1640-1650cm^{-1} that is characteristics for starch. Pal. Mal. And Sing (2005) believe that this peak originate from the first overtone –OH bonding, and Lee, Kweon, Koh and Lim (2004) believe that this peak originate from the stretching C-O-C vibrations. The characteristic peaks for poly (methacrylic acid) (Fig1D) are 2931cm^{-1}, originate from stretching C-H vibration, peak on 1710cm^{-1}originate from C=O vibrations of carboxyl group, peak on 1253cm^{-1} originate from C-O vibration and peak on 1165cm^{-1} originate from C-O stretching vibrations. Fig (C) superimposed on Fig (D) shows all characteristic peaks of Poly (MAA).

Fig. 1B depicts the FTIR spectrum of S-g-(MAA) with percentage of grafting of 39.55%.In this spectrum all characteristic peaks of starch and poly (MAA) are present. The most important peaks between 3600-3000cm^{-1}and 1170-1020cm^{-1}originate from starch. Peak at 1710cm^{-1}originate from poly (MAA) and confirm the grafting of MAA on starch.

Grafting parameters

The grafting parameters namely the percentage grafting efficiency (%GE) and percentage grafting (%G) were based on gravimetric estimation and were calculated as follows (Athawale and 1998):

$$\%GE = 100\,(W_2 - W_1)\,/W_3$$
$$\%G = 100\,(W_2 - W_1)\,/W_1$$

Where W_1 W_2 and W_3 are the weights of pure starch, graft copolymer and monomer respectively.

Effect of initiator concentration

Table 1 shows the effect of concentration of CAN on the %GE and %G. The %GE and %G initially increases steadily with the increase in CAN from 0.001 to .006mol/l, however these grafting parameters later on decrease gradually with further rise in concentration of CAN.

Table 1. Effect of initiator concentration on the grafting of MAA on insoluble potato starch

CAN(mol/L)	%G	%GE
0.001	13.87	13.84
0.002	15.47	15.43
0,004	18.80	18.75
0.006	27.40	27.33
0.008	24.45	24.38
0.010	23.10	23.04

[Reaction conditions: Starch=2g,[MAA] 0.233 mol/L in each case the volume was made to 100 mL of distilled water ;30°C for 180 min.]

Table 1 shows the effect of concentration of CAN on the %GE and %G. The %GE and %G initially increases steadily with the increase in CAN from 0.001 to .006mol/l, however these grafting parameters later on decrease gradually with further rise in concentration of CAN.

The initial rise in %G and %GE may be attributed to the formation of increasing number of free radicals on the starch backbone at which the monomer molecules can be grafted at. The decline in %GE and %G at higher concentration of CAN (>0.006mol/L) may be rationalized as follows:

(i) Non-availability of sites on starch molecules at which CAN can react to generate more free radicals;
(ii) The initiation of homopolymerization by unutilized CAN.

In the case of grafting initiated by a chemical initiator, the extent of grafting increases with the increase of initiator concentration up to a certain limit, beyond which grafting no longer increases (Nicolic *et al*., 2012).

Effect of monomer concentration

Table 2 shows the effect of concentration of MAA on the %GE and % G. With increase in [MAA] from 0.118 to 1.132 mol/L % GE shows a gradual decrease from 27.36 to 8.11 %, in contrast %G rises from 14.35 to 39.55. As [MAA] increases, most of the monomer is consumed in homopolymer formation rather than grafting on to starch. This is evident from the fact that the viscosity of the reaction medium, in which homopolymer is soluble, increases with rise in [MAA]. Furthermore the large deposits of homopolymer reduce the accessibility of starch macro radicals to the monomer molecule. In short both the higher rate of homo polymerization and the lower accessibility of starch macro radicals, play key roles in lowering of the %GE at higher concentration of monomer. Indeed in order to obtain maximum %GE, 0.118 mol/L is a suitable concentration of [MAA] for grafting on to starch.

Table 2. Effect of monomer concentration on the grafting of MAA on to insoluble potato starch

MAA(mol/L)	%G	%GE
0.118	14.35	27.36
0.233	27.40	27.33
0.470	29.80	14.71
0.705	32.85	10.83
1.132	39.55	8.11

[Reaction conditions:Starch=2g,[CAN] 0.006 mol/L in each case in 100 of distilled water ; 30° for 180 min.]

However, the increase in %G is merely due to a decrease in the ratio of starch to monomer with increase in monomer concentration.

Effect of polymerization temperature

As the present study was confined to granular starch, the temperature was not allowed to exceed the gelatinization temperature. The result obtained for the graft copolymerization at temperature between 30 and 50°C are tabulated in Table 3. Table 3, shows the effect of polymerization temperature on the %GE and %G. It is observed that higher the temperature, the higher the %GE and %G. This favorable effect of temperature on grafting could be ascribed to (1) increase in the mobility of monomer molecules and their collision with starch macro radicals, and (2) increased propagation of starch grafts.

Table 3. Effect of polymerization Temperature on the grafting of MAA on to insoluble potato starch

Temperature (°C)	%G	%GE
30	24.80	24.73
35	26.50	26.43
40	27.45	27.38
45	28.05	27.98
50	28.50	28.42

[Reaction conditions: Starch=2g, [CAN] 0.006mol/L, [MAA]0.233mol/L in each casein 100 of distilled water; for180min.]

Effect of polymerization Time

Table4 shows the effect of polymerization time on %G and %GE.It is seen that the grafting shows an initial fast rate which slows down with time and then level off. As the time proceeds more and more monomer gets reacted to form the growing grafted chains. Leveling of grafting is perhaps a direct consequence of the depletion in monomer concentration and less availability of monomer for further grafting.

Table 4. Effect of polymerization Time on the grafting of MAA on to insoluble potato starch

Time(min)	%G	%GE
60	17.00	16.95
120	21.85	21.79
180	24.80	24.74
240	24.95	24.88
300	25.05	24.98

[Reaction conditions: Starch=2g, [CAN] 0.006 mol/L, [MAA]0.233mol/Lin each casein 100 ml of distilled water; 30°C.]

Effect of polymerization material to liquor ratio

Table 5 exhibits the dependence of %G and GE on the material to liquor ratio, the material to liquor ratio was changed by decreasing the quantity of water in the reaction mixture. It is evident that the decrease in the quantity of liquor favors the rate of grafting (Athawale *et al.*, 1998). As the quantity of liquor is reduced, the kinetic probability of collision between monomer molecules and starch macro radicles increases resulting in a rise in %GE and %G. The maximum %GE was obtained at material to liquor ratio of 1:10.Further decrease in the quantity of liquor led to a decline in % GE, Probably because of the restricted movement of the monomer molecules in a relatively small volume of the reaction mixture of 40 ml. In other words a material –to-liquor ratio of 1:10 is most suitable.

Table 5. Effect of polymerization material to liquor ratio on the grafting of MAA on to insoluble potato starch

Material to liquor ratio	%G	%GE
1:25	27.40	27.33
1:20	28.95	28.87
1:15	31.85	31.77
1:10	35.10	35.01
1:5	34.50	34.41

[Reaction conditions:Starch=2g,[CAN]0.006 mol/L [MAA] 0.233mol/Lin each case in 100 ml of distilled water;30 for 180min.]

Effect of solvent

Table6 shows the effect of various solvent on grafting of MA on granular potato starch.%G and %GE follows the order methanol> ethanol> propanol.

Table 6. Effect of solvent on the grafting of MAA on to insoluble potato starch

solvent	%G	%GE
Methanol	25.75	25.68
Ethanol	22.70	22.64
Propanol	14.00	13.96

[Reaction conditions:Starch=2g[CAN]0.006 mol/L[MAA] 0.233mol/L in each case in100 ml of distilled water; 30°C for 180min.]

With increase in molecular weight of alcohol, %G and %GE decreases from methanol to propanol. This can be attributed to the size of the hydrocarbon groups of alcohols and their dielectric constant of alcohols. When size of the hydrocarbon group increases, the hydroxyl group accounts for progressively lesser molecular weight of alcohol as a result the miscibility of the alcohol with water decreases. Also with increase in size of hydroxyl group, there is a corresponding decrease in dielectric constant from methanol to propanol.

Values of dielectric constant are tabulated below

Solvent	Dielectric constant
Water	81
Methanol	32.7
Ethanol	24.5
Propanol	20.18

So the high polarity of water must be playing a role in the grafting of hydrophilic, polar monomer such as MAA on to starch. As the dielectric constant of the medium of reaction decreases from pure water to Water-Propanol system through other two mediums namely water-methanol and water-ethanol, the grafting reaction is less favored. This is exhibited through decrease in %G and %GE with change in medium.

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