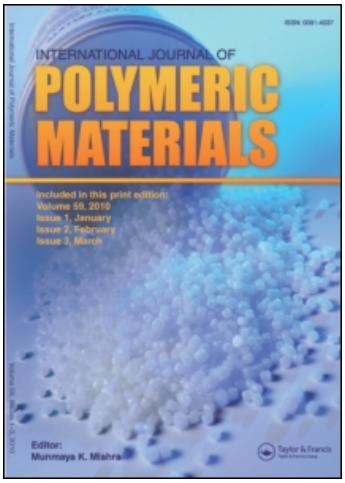

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Optimization of Reaction Parameter to Prepare 2-HEMA-g-NaPCMS Using CAN as an Initiator

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Sodium Salt of partially carboxymethylated starch -g-poly(hydroxyethyl methacrylate) (Na-PCMS-g-PHEMA) copolymers containing 40–50% PHEMA were prepared with ceric ammonium nitrate initiation. All the experiments were run with Na-PCMS($DS = 1.10$). Graft copolymers were characterized with respect to % PHEMA, % total conversion, %grafting, %grafting efficiency and confirmation of grafting was done by Infrared Spectral Analysis. Variables investigated in the graft copolymerization reaction were nitric acid concentration, reaction time, reaction temperature, and ceric ion concentration. The results are discussed with illustrations.

Keywords: Carboxymethylated starch; Poly(hydroxyethyl methacrylate); Ceric ion initiation

1. INTRODUCTION

Ceric ion has been used extensively as redox initiator for grafting of vinyl monomers onto natural as well as synthetic polymers [1–6]. A number of research articles have been published in the field of grafting using Ce(IV) as a redox initiator [7–12] Na-PCMS is perhaps less studied industrial carbohydrate as far as the modification is concerned. It is frequently called Sodium Starch Glycolate. It is produced

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by a number of authors with varying degrees of substitution [13–20]. We are interested to graft 2-HEMA onto Na-PCMS($DS = 1.10$) using Ceric Ammonium Nitrate (CAN) a novel initiator. In the present study starch is etherified so as to graft copolymerise with 2-HEMA. An important advantage of graft copolymerization may be the fact that Na-PCMS and PHEMA are supposed to be held together by chemical bonding rather than existing merely as a physical mixture. The two dissimilar polymers therefore may tend to be more intimately associated, and separation of the two polymer phases may be less likely to occur. Graft copolymers of Na-PCMS with water soluble vinyl monomers have been successfully synthesized and recently [21, 22] used for the controlled action of bioactive agents.

We have made a study of the synthesis and characterization of Na-PCMS graft copolymer with 2-HEMA into water with CAN initiation. Graft copolymers containing about 40–50% PHEMA can be easily prepared with minimal formation of ungrafted homopolymer of 2-HEMA. We have examined some of the more important variables in the graft copolymerization reaction and their effects on graft copolymer structure. Infrared Spectral analysis helps in confirming the structure of graft copolymer thus produced.

2. EXPERIMENTAL

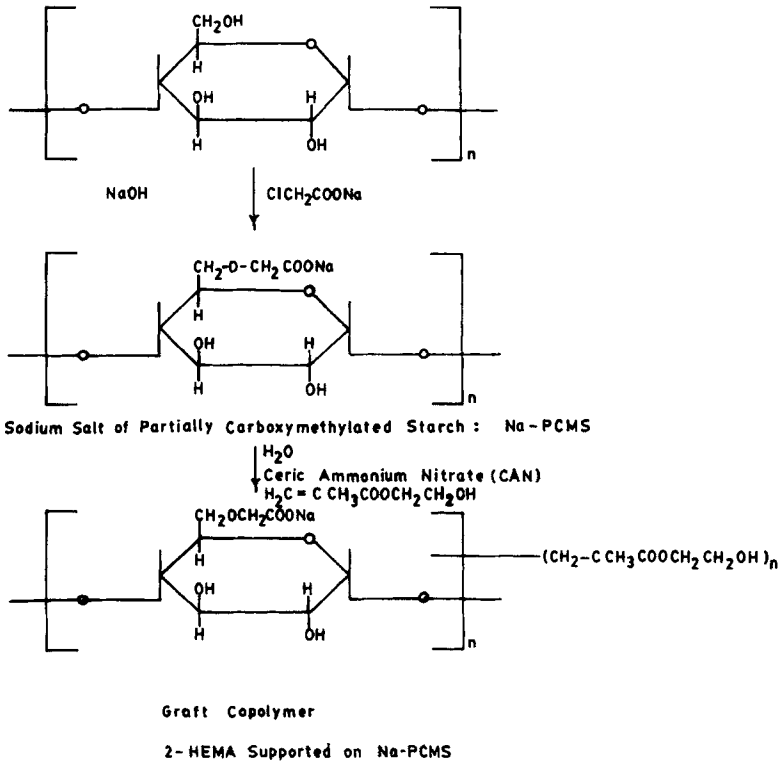
Starch(L. R) from Qualigem fine chemicals, Mumbai, 2-HEMA distilled, CAN(A. R) were used. All other reagents and solvents were of lab grade. Twice distilled water was used for the preparation of solutions as well as in graft copolymerization reactions.

2.1. Graft Copolymerization

Na-PCMS was prepared according to method described by Abdel Akher *et al.* [16]. All the grafting reactions were conducted under a nitrogen blanket in a 250 ml 3 neck flask equipped with stirrer, addition funnel and a gas inlet system. The whole assembly is immersed in a constant temperature bath.

In a typical graft copolymerization reaction, Na-PCMS (4 gm) was stirred in bidistilled water(55 ml) and sparged with a slow stream

of nitrogen for one hour at 25 to 40°C. A freshly prepared solution (10 ml) of 0.2 to 0.4 M CAN in 0.1 to 0.5 M HNO_3 was added and stirred for 20 min. Distilled 2-HEMA monomer(10 ml) was added. The grafting reactions were carried out for varying time intervals(1 to 4.5 hrs). After completion of the reaction, the mixture was immediately filtered and the crude copolymer product was washed with HNO_3 solution and bidistilled water. The crude copolymer thus obtained was dried in vacuum at 50°C. The crude copolymer was freed from ungrafted PHEMA by extraction with dimethyl formamide(DMF) for 24 hours. After complete removal of homopolymer the residue was dried in vacuum at 50°C till constant weight was obtained. The reaction scheme is shown in Scheme 1.



SCHEME 1 Represents the reaction scheme: To synthesize graft copolymer.

The %total conversion(%Ct), %grafting(%G), %grafting efficiency(%GE) and %add-on were evaluated by the following expressions: [23, 24].

1. %total conversion(%Ct)

$$= \frac{\text{weight of polymer grafted} + \text{weight of homopolymer}}{\text{weight of monomer charged}} \times 100$$

2. $$\%\text{grafting}(\%G) = \frac{\text{weight of polymer grafted}}{\text{Initial weight of substrate}} \times 100$$

3. %grafting efficiency(%GE)

$$= \frac{\text{weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of homopolymer}} \times 100$$

4. %add on = %weight of PHEMA in 100 g of Na-PCMS.

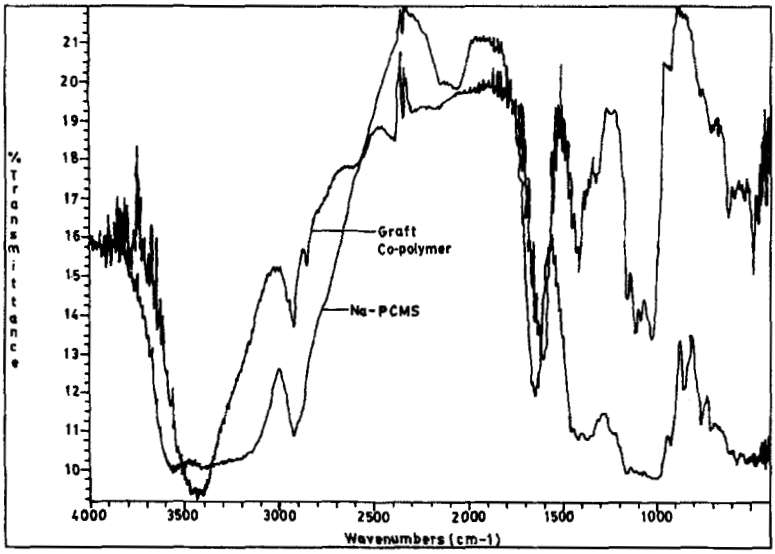


FIGURE 1 IR spectrum of Na-PCMS and graft copolymer.

2.2. Characterization

Infrared Spectral analysis helps in confirming the formation of graft copolymers. The spectra of Na-PCMS-g-PHEMA samples were taken in KBr palets using a FTIR, inkjet nicolet 400D spectrophotometer. Figure 1 represented the IR spectra of Na-PCMS-g-PHEMA. It has been observed that the graft copolymer showed an absorption band of Na-PCMS as well as an additional band at 1740 cm^{-1}, characteristic band of PHEMA. This band is not present in the IR spectrum of Na-PCMS. It gives a proof for the grafting of acrylate monomer.

3. RESULTS AND DISCUSSION

3.1. Effect of Reaction Time

The results for effect of reaction time are shown in Table I. It shows that a constant value of about 54% in 3–4 hrs and total conversion is about 126%. The percentage grafting proceeds at a faster rate upto 4 hrs followed by a slower rate of increase in percentage grafting beyond 4 hr. The decrease in %G with time could be attributed to decrease in concentration of both the initiator and the monomer, as well as reduction in the number of active sites on the Na-PCMS backbone accessible for grafting as the reaction proceeds. %GE decreases rapidly in the beginning perhaps because the 2-HEMA molecules can't reach the radical sites easily and homopolymer formation is favoured. With increase in reaction time the amount of

TABLE I Grafting yields for the graft copolymerization of 2-HEMA on Na-PCMS at various times

Sr. No.	*Time (hr)*	*%Total conversion (%Ct)*	*%Grafting (%G)*	*%Grafting efficiency (%GE)*	*%Add on*
1	1	92.08	161.95	78.56	39.48
2	1.5	110.71	195.30	78.79	48.42
3	2	122.53	215.32	78.49	52.38
4	2.5	126.36	219.10	78.49	53.02
5	3	127.57	220.14	78.49	53.20
6	3.5	131.95	225.25	79.00	54.03
7	4	134.14	226.57	79.21	54.25
8	4.5	137.02	231.16	78.49	54.96

graft copolymer formation increase even though %GE still decrease because the homopolymer is being formed. It is observed that %G rises with a rapid initial rate and reaches to a value of 215% in 4 hrs. Beyond this time it remains constant.

3.2. Effect of Reaction Temperature

The grafting is carried out at different temperature 25°C to 40°C, keeping the other parameters constant. The results are shown in Table II. It is seen from the table that %Ct as well as %G increase with increase in temperature from 25 – 30°C but decreased with further rise in temperature. From this results, rise in temperature cause dissociation of initiator at high rate enhanced ionization of Na-PCMS as well as diffusion and mobility of monomer from the aqueous phase to the backbone, resulting in considerable improvement in the graft yield. Further, rise in temperature leads to decrease of %Ct and %G. Further, it is observed that %GE decreases with the increase in temperature which may be explained by the fact that solubility of monomer in the aqueous phase increases and the acceleration of the termination reaction leads to formation of more homopolymer.

3.3. Effect of Nitric Acid Concentration

In ceric ion initiated grafting reaction mineral acid is found to act as a catalyst even if it present in small amount. It may change the concentration of active species of Ce(IV) and may affect the formation of complex between Ce(IV) and monomer. It is observed from the Table III that there exist and optimum nitric acid concentration

TABLE II Grafting yields for the graft copolymerization of 2-HEMA on Na-PCMS at various temperatures

Sr. No.	*Temp* (°C)	*%Total conversion* (*%Ct*)	*%Grafting* (*%G*)	*%Grafting efficiency* (*%GE*)	*%Add on*
1	25	118.65	211.45	79.59	51.69
2	30	122.52	215.32	78.49	52.21
3	35	103.63	172.66	74.42	43.09
4	40	89.00	139.77	69.38	32.04

TABLE III Grafting yields for the graft copolymerization of 2-HEMA on Na-PCMS at various nitric acid concentrations

Sr. No.	*Nitric acid conc^n (mole/lit)*	*%Total conversion (%Ct)*	*%Grafting (%G)*	*%Grafting efficiency (%GE)*	*%Add on*
1	0.1	97.02	176.94	81.46	44.22
2	0.2	99.90	180.76	80.82	45.18
3	0.3	122.52	215.32	78.49	52.38
4	0.4	103.98	117.16	76.10	44.28

(0.3 M) which affords maximum grafting. Beyond this concentration of nitric acid %add on and %G decreases. This is due to the fact that as [H+] increases, the recombination and disproportionation of the graft macroradicals is less possible due to decrease in concentration. So from the table it can be said that at higher acid concentration the coagulation of colloidal homopolymer in solution increases during grafting and there is decrease in %G and %GE.

3.4. Effect of Initiator Concentration

The grafting parameters are presented in Table IV. It is observed that formation of homopolymer is considerable less at low initiator concentration while there is a significant yield of 2-HEMA onto Na-PCMS at various CAN concentration. The values of %G and %Ct increases rapidly in the beginning. At 0.3 M initiator concentration a %G of 215% and %Ct 122.54% is obtained. Furthermore, there is a decrease in %GE with rise in initiator concentration. The fast dissociation of CAN may account for its higher %GE in the initial stages, since less Ce(IV) could be available for initiation.

TABLE IV Grafting yields for the graft copolymerization of 2-HEMA on Na-PCMS at various Ceric Ammonium Nitrate (CAN) concentrations

Sr. No.	*CAN conc^n (mole/lit)*	*%Total conversion (%Ct)*	*%Grafting efficiency (%G)*	*%Grafting (%GE)*	*%Add on*
1	0.20	64.41	113.73	78.89	38.80
2	0.25	105.70	189.99	80.24	47.35
3	0.30	122.52	215.32	78.49	52.38
4	0.30	114.12	188.37	73.72	46.99
5	0.40	108.74	164.34	67.50	40.71

4. CONCLUSION

We have studied some of the more important variables in the ceric ammonium nitrate initiated graft copolymerization of 2-HEMA onto Na-PCMS and have determined their effects on %total conversion, %grafting, %grafting efficiency and %add on. Na-PCMS (DS = 1.10) and twice distilled water is prime requirement for the reaction to occur. Typically, 0.3 M CAN, 0.3 M Nitric Acid, 4–4.5 hr reaction time and 25–30°C reaction temperature is found best suitable for the maximum yield of the graft copolymerization reaction. The products obtained are characterized essentially by Fourier Transform Infrared spectral analysis which helps in confirming the real structures of graft copolymer. Products obtained may find application in the field of biomedical polymers specifically utilization for the sustained release of bioactive agents.

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