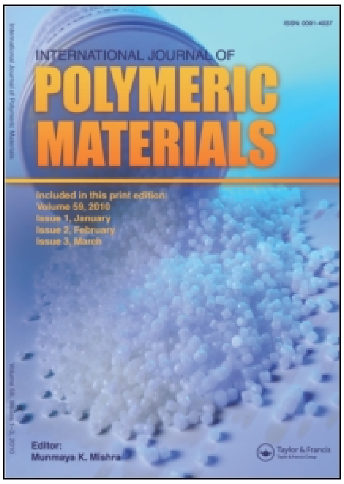

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# Optimization of reaction parameters to prepare HPMA- g -Na-PCMS using can as an initiator

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# OPTIMIZATION OF REACTION PARAMETERS TO PREPARE HPMA-*g*-Na-PCMS USING CAN AS AN INITIATOR

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*Sodium salts of partially carboxymethylated starch-g-poly(hydroxypropyl methacrylate)(Na-PCMS-g-PHPMA) copolymer containing 35–45% PHPMA were prepared using ceric ammonium nitrate (CAN) as an initiator. All the experiments were run with Na-PCMS (DS-1.10). Graft copolymers were characterized with respect to % PHPMA, % 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 illustration.*

**Keywords:** carboxymethylated starch, poly(hydroxypropyl methacrylate), graft copolymer, synthesis, cerium ions

## 1. INTRODUCTION

Graft copolymerization of vinyl monomers on synthetic and natural polymers has been studied extensively using a variety of methods to indicate the formation of graft copolymer chain. Due to ease of application, ceric ion initiated graft copolymerization of vinyl monomers on

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We are grateful for contributions of Dr. H. K. Patel, Principal, and Shri. K. M. Patel, Head, I.C. Department of the college for providing necessary laboratory facilities.

Address correspondence to Vijay Kumar Sinha, Department of Industrial Chemistry, V. P. and R. P. T. P. Science College, Sardar Patel University, Vallabh Vidyanagar-388 120 Gujarat, India. E-mail: paresh781@yahoo.com various substrates has gained considerable importance and is one of the most widely used methods of initiating the grafting reaction [1].

Graft copolymers of the hydroxylic methacrylates HEMA and HPMA onto amylopectine were prepared with a view to substitute pure synthetic polymer [2]. Hydroxylic methacrylate is grafted on Na-PCMS using CAN as an initiator. The variables investigated were nitric acid concentration, reaction time, reaction temperature, and ceric ion concentration [3]. Ceric ion is extensively used as a redox initiator to prepare graft copolymers of natural and modified polysaccharides with vinyl monomers [4–10].

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 by a number of methods with varying degrees of substitution [11–15].

The object of this work is to graft HPMA onto Na-PCMS ($DS = 1.10$) using ceric ammonium nitrate (CAN) a novel initiator. The sodium salt of carboxymethyl starch was prepared by standard slurry process. Later it was graft copolymerized with HPMA. Graft copolymers containing about 35–45% PHPMA can be easily prepared with minimum formation of ungrafted homopolymer of HPMA. 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

### 2.1. Materials

Starch (L.R.) from Qualigen Fine Chemicals, Mumbai, India, HPMA distilled, and CAN (A.R.) were used. All other reagents and solvents were of Lab Grade. Double distilled water was used for the preparation of solutions as well as in graft copolymerization reactions.

### 2.2. Graft Copolymerization

The graft copolymerization reaction was carried out according to the method described elsewhere [3].

### 2.3. Characterization

The % total conversion (%Ct), %grafting (%G), % grafting efficiency (%GE) and % add on were calculated by the following expressions.

1. % Total conversion (%Ct)

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

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

3. % Grafting efficiency (%GE)

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

4. % add on = % weight of PHPMA in 100 gm of Na-PCMS.

## 2.4. Infrared Spectral Analysis

The spectra of Na-PCMS-*g*-HPMA samples were taken in KBr pellets using a FTIR, inkjet nicolet 400D spectrophotometer. Infrared spectral analysis helps in confirming the formation of graft copolymer. Figure 1 represented the IR spectra of Na-PCMS-*g*-HPMA. It has been observed that the graft copolymer showed absorption band of Na-PCMS as well as additional band at 1740 $\text{cm}^{-1}$, characteristic band of PHPMA. This band is not present in the IR spectrum of Na-PCMS. This gives a proof of grafting a hydroxylic methacrylate (i.e., HPMA monomer).

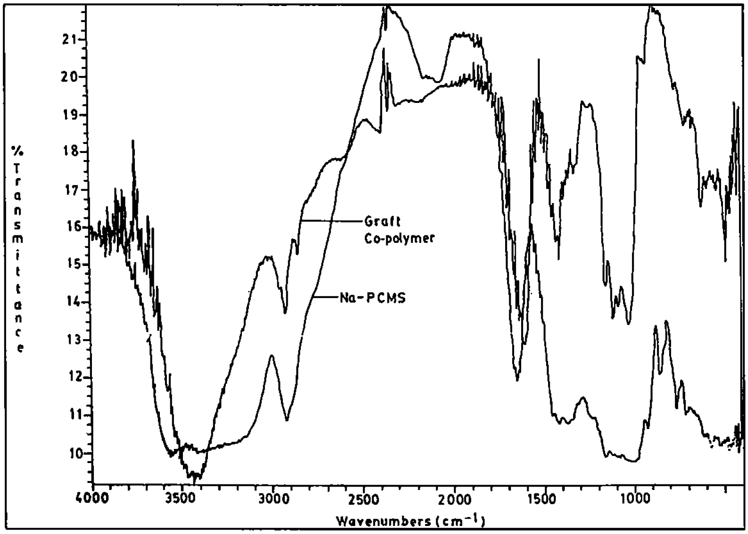

**FIGURE 1** IR spectrum of Na-PCMS and graft copolymer.

# 3. RESULTS AND DISCUSSION

## 3.1. Effect of Reaction Time

The graft copolymerization reaction is carried out for various time intervals. The results are shown in Table 1. It shows that a constant value of 45% add-on in 3.5–4.5 hrs and total conversion is about 118%. The % grafting proceeds at a faster rate up to 4.5 hrs followed by a slower rate of increased % grafting. Beyond 4.5 hrs the decrease in %G with time could be attributed to decreasing concentration of both the initiator and monomer, as well as reduction in number of active sites on Na-PCMS backbone accessible for grafting as the reaction proceeds. %GE remains constant upto 3 hrs because the HPMA molecules cannot reach the radical sites easily and homopolymer formation is favored and it decreases after 4.5 hr. It is observed that %G rises with a rapid initial rate and reaches a value of 208% in 4.5 hrs.

## 3.2. Effect of Reaction Temperature

The graft copolymerization reaction is carried out in the range of 25°C–45°C keeping the other parameters constant. The results are shown in Table 2. It can be concluded form the table that %Ct as well as %GE increase with increase in temperature from 25°C to 35°C but decrease with further increase in temperature. The initial rise in temperature causes dissociation of initiator at high rate and enhanced initiation of Na-PCMS as well as diffusion and mobility of monomer from the aqueous phase to backbone resulting in considerable improvement in the graft yield. Further rise in temperature beyond 35°C leads to decrease of %Ct and %G i.e. from 115.35% to 96.42% and

**TABLE 1** Grafting Yields for the Graft Copolymerization of HPMA onto Na-PCMS at Various Times

| Sr. no. | Time (hr.) | % Total conversion (%Ct) | % Grafting (%G) | % Grafting efficiency (% GE) | % Add on |
|---|---|---|---|---|---|
| 1 | 1 | 82.87 | 145.76 | 70.71 | 36.65 |
| 2 | 1.5 | 99.64 | 175.77 | 70.82 | 42.92 |
| 3 | 2 | 110.28 | 193.79 | 70.82 | 42.81 |
| 4 | 2.5 | 113.73 | 197.19 | 70.82 | 44.37 |
| 5 | 3 | 114.82 | 198.13 | 70.82 | 44.37 |
| 6 | 3.5 | 118.76 | 202.73 | 71.15 | 44.63 |
| 7 | 4 | 120.73 | 203.92 | 71.35 | 45.17 |
| 8 | 4.5 | 123.32 | 208.05 | 71.55 | 45.28 |
| 9 | 5 | 125.37 | 212.25 | 70.65 | 45.63 |

**TABLE 2** Grafting Yields for the Graft Copolymerization of HPMA onto Na-PCMS at Various Temperatures

| Sr. No. | Temp. °C | % Total conversion (%Ct) | % Grafting (%G) | % Grafting efficiency (% GE) | % Add on |
|---|---|---|---|---|---|
| 1 | 25 | 106.74 | 190.45 | 71.64 | 45.23 |
| 2 | 30 | 110.27 | 193.82 | 70.65 | 46.21 |
| 3 | 35 | 115.35 | 198.46 | 72.84 | 47.38 |
| 4 | 40 | 96.42 | 155.40 | 66.98 | 38.79 |
| 5 | 45 | 82.65 | 125.80 | 62.45 | 28.84 |

198.46% to 155.40% respectively. Further it is observed that %GE decreases from 72.84% to 66.98% with the increase in temperature beyond 35°C which may be explained by the fact that the solubility of monomer in the aqueous phase increases and the acceleration of 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 promoter even if it is present in small amount. It may change the concentration of active species of Ceric ion and may affect the formation of complex between ceric ion and monomer. It is observed from Table 3 that there exists an optimum nitric acid concentration (0.35 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 macro radicals is less possible due to decrease in concentration. So from the table it can be said that at higher acid concentration the

**TABLE 3** Grafting Yields for the Graft Copolymerization of HPMA onto Na-PCMS at Various Nitric Acid Concentrations

| Sr. no. | Nitric acid conc. (mole/lit.) | % Total conversion (%Ct) | % Grafting (%G) | % Grafting efficiency (% GE) | % Add on |
|---|---|---|---|---|---|
| 1 | 0.1 | 87.32 | 159.25 | 74.31 | 39.80 |
| 2 | 0.15 | 88.30 | 161.38 | 73.69 | 39.45 |
| 3 | 0.2 | 89.91 | 162.69 | 72.74 | 40.67 |
| 4 | 0.25 | 95.73 | 167.85 | 71.53 | 44.80 |
| 5 | 0.3 | 110.27 | 193.79 | 70.64 | 47.05 |
| 6 | 0.35 | 115.65 | 198.46 | 66.77 | 47.35 |
| 7 | 0.4 | 93.59 | 105.45 | 68.49 | 39.86 |

**TABLE 4** Grafting Yields for the Graft Copolymerization of HPMA onto Na-PCMS at Various Ceric Ammonium Nitrate Concentrations

| Sr. no. | CAN conc. (mole/lit.) | % Total conversion (%Ct) | % Grafting (%G) | % Grafting efficiency (% GE) | % Add on |
|---|---|---|---|---|---|
| 1 | 0.20 | 57.96 | 102.36 | 71.02 | 34.92 |
| 2 | 0.25 | 95.13 | 171.45 | 72.21 | 42.62 |
| 3 | 0.30 | 110.27 | 193.79 | 70.64 | 44.14 |
| 4 | 0.35 | 115.65 | 198.46 | 66.77 | 47.35 |
| 5 | 0.40 | 102.71 | 147.91 | 60.75 | 36.63 |

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 4. It is observed that formation of homopolymer is Considerably less at low initiator concentration while there is a significant yield of HPMA-*g*-Na-PCMS at various CAN concentration. The values of %G and %Ct increase rapidly in the beginning. At 0.35 M initiator concentration %G of 198% and %Ct 115% is obtained. Furthermore there is a decrease in %GE with rise in initiator concentration. The fast dissociation of ceric ammonium nitrate may account for its higher %GE in the initial stages, since less ceric ion could be available for initiation.

## 4. CONCLUSION

We have examined some of the important variables in the ceric ammonium nitrate initiated graft copolymerization of HPMA onto Na-PCMS and have determined their effects on %total conversion, %grafting, %grafting efficiency and % add on. Typically, 0.35 M CAN, 0.35 M nitric acid, 4.5–5 hr reaction time and 30–35°C reaction temperature are found best suited for the maximum yield of the graft copolymerization reaction. The products obtained are characterized by FTIR analysis which shows typical absorption band of HPMA at 1740 $\mathrm{cm}^{-1}$ confirming the structure of the graft copolymer.

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