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K. M. Joshi[a]; V. K. Sinha[a]; C. P. Patel[a]; H. C. Trivedi[a]
[a] Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

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CERIC-INDUCED GRAFTING OF ACRYLONITRILE ONTO SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED STARCH

K.M. Joshi, V.K. Sinha, C.P. Patel and H.C. Trivedi*

Department of Chemistry,
Sardar Patel University,
Vallabh Vidyanagar - 388 120,
Gujarat State/India.

ABSTRACT

Sodium salt of partially carboxymethylated starch (Na-PCMS, $\overline{DS}$=0.317) was graft copolymerized with acrylonitrile (AN) using ceric ammonium nitrate (CAN) as an initiator. The optimized reaction conditions affording the maximum percentage of grafting are determined by varying the concentrations of nitric acid, initiator and monomer together with temperature and time. The results are discussed.

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* Correspondence author

INTRODUCTION

In an attempt to modify water soluble polymers, we have successfully grafted different vinyl monomers onto the sodium salt of partially carboxymethylated amylose (Na-PCMA) [1-5] as well as onto sodium alginate [6-11] using chemical as well as radiation methods and studied the biodegradable behaviour of sodium alginate-graft-acrylonitrile by studying its interactions with different microorganisms [12].

In our previous papers, we reported graft copolymerization of AN onto sodium salt of partially carboxymethylated starch (Na-PCMS) by irradiation [13] as well as using Ce^{+4} - amine system as redox initiator [14] and determined the water retention values of saponified Na-PCMS-g-PAN samples of different degrees of substitution [15]. In the present work, grafting of AN onto Na-PCMS ($\overline{DS}$=0.317) is investigated in the presence of Ce^{+4} and the reaction conditions for graft copolymerization are optimized.

EXPERIMENTAL

Materials

Starch used for the preparation of Na-PCMS was extracted from potatoes with usual procedure [16]. Acrylonitrile (AN) was distilled at an atmospheric pressure through a fractionating column and centre cut was used in the copolymerization reactions. Ceric ammonium nitrate, CAN (analar grade, Glaxo Laboratories), was used. Fresh solutions of the initiator were used by dissolving the required amount of CAN in HNO_3. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through freshly prepared alkaline pyrogallol solution. The conductivity water was used for the preparation of solutions as well as in polymerization reactions.

Preparation of Na-PCMS and Measurement of $\overline{DS}$

Sodium salt of partially carboxymethylated starch (Na-PCMS) was prepared from starch following the method of Abdel-Akher et al [17]. The sample of Na-PCMS was purified by usual precipitation method. The acid form of Na-PCMS (i.e. HPCMS) was obtained by passing its solution through a regenerated cation exchanger (Amberlite IR-120) resin. The average degree of substitution ($\overline{DS}$) was determined from the normality of HPCMS solution by pH-metry and the dry weight of HPCMS by evaporating a known volume of HPCMS solution [18]. The Control Dynamics Digital pH-meter (C.D. Instrumentation, Banglore) was used for carrying out pH-measurements. The $\overline{DS}$ of Na-PCMS was found to be 0.317.

Graft Copolymerization

The grafting reactions were carried out under a nitrogen atmosphere in a 250 mL three necked flask equipped with a reflux condenser, a stirrer and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, 2.0 g (dry basis) of Na-PCMS ($\overline{DS}$=0.317) was dissolved in conductivity water (50 mL) with constant stirring and bubbling a slow stream of nitrogen, for 30 min at the desired temperature (15-50°C). The freshly prepared 10 mL solution of CAN (0.1 to 0.3 M) in nitric acid (0.05 to .0 M) was added and stirred for 20 min. Nitrogen was continuously passed through this solution and freshly distilled acrylonitrile monomer (0.468 M to 1.635 M) was added. The grafting reactions were carried out for varying time intervals (30 min to 24 hr). After completion of the reaction, the mixture was immediately filtered and the crude copolymer product was washed with nitric acid solution and water. The crude copolymer thus obtained was dried under vacuum at 40°C. The crude copolymer was freed from ungrafted PAN by extraction with dimethylformamide (DMF) for 48 h. After complete removal of homopolymer, the residue was dried at 40°C under vacuum until constant weight was obtained.

The percentage of total conversion (% C_t), percentage grafting (% G) and percentage grafting efficiency (% GE) were evaluated by the following expressions :

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

$$\%\ G = \frac{\text{Weight of polymer grafted}}{\text{Initial weight of substrate}} \times 100$$

$$\%\ GE = \frac{\text{Weight of polymer grafted}}{\text{Weight of polymer grafted} + \text{Weight of homopolymer}} \times 100$$

IR Spectra

IR spectra of Na-PCMS, Na-PCMS-g-PAN and PAN samples were taken in KBr pellet form using a Perkin-Elmer Model 983 spectrophotometer.

RESULTS AND DISCUSSION

In order to optimize the conditions for grafting, the concentrations of initiator, nitric acid and monomer together with temperature and time were varied.

Effect of Reaction time

Figure 1 shows the effect of reaction time on the percentage grafting. It is clear from this figure that grafting proceeds at a faster rate upto 4 hr followed by a slower rate of increase in percentage grafting upto 24 h. The decrease in rate of grafting with time could be attributed to decrease in concentration of both the initiator and the monomer as well as a reduction in the number of sites on the Na-PCMS backbone accessible for grafting as the reaction proceeds. The grafting efficiency (Figure 2) decreases rather rapidly in the beginning perhaps because the monomer molecules cannot reach the radical site easily and homopolymer formation is favoured. With the increase in reaction time the amount of graft copolymer formation increases, even though the percent grafting effiency still decreases because the homopolymer is still being formed. The percentage of total conversion (Figure 3) increases linearly for the first 4 h and then attains a

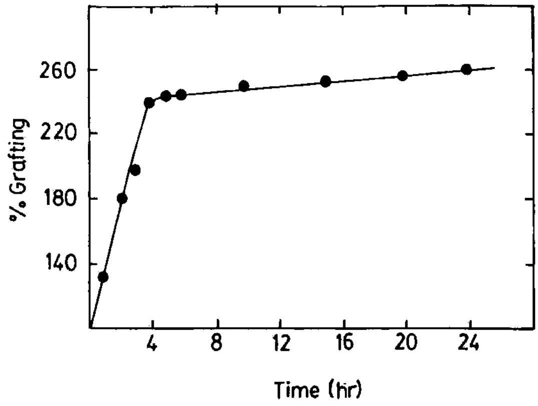

Figure 1 : Influence of reaction time on percentage grafting Na-PCMS ($\overline{DS}$ = 0.317) = 2.0 g (dry basis), [HNO_3] = 0.3 N, [AN] = 1.169 mol/L, [CAN] = 0.20 M, Temperature=30°C, H_2O=50 mL, Total Volume=65 mL.

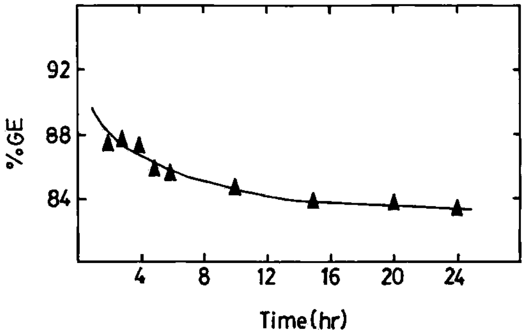

Figure 2 : Influence of reaction time on percentage grafting efficiency.

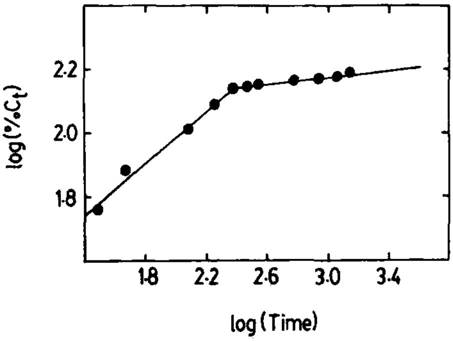

Figure 3 : Plot of log(% C_t) versus reaction time.

constant value. Thus it can be concluded that a period of 4 h is the optimum duration for grafting of AN onto Na-PCMS. In 4 h duration maximum amount of graft copolymer is formed and the amount of homopolymer formed is minimum. Beyond this time the grafting parameters increase slowly until 24 h is reached.

Effect of Temperature

Figure 4 shows the influence of temperature on %C_t or % G or % GE. It can be seen from this figure that %C_t or % G or % GE increases with rise in temperature from 15°C to 30°C but decreases with further rise in temperature to 50°C. The dependence of the percentage grafting on temperature can be ascribed to the swelling of Na-PCMS and an enhancement of the rate of diffusion of monomer. With any further increase in temperature the graft copolymerization occurs with poor selectivity, and various hydrogen abstraction and chain

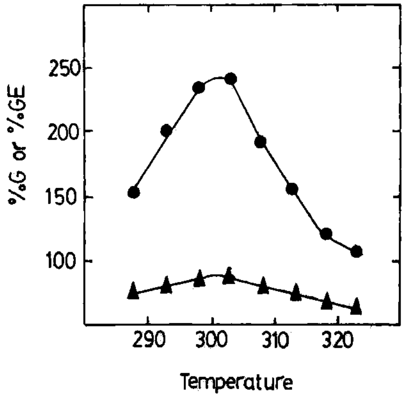

Figure 4 : Effect of temperature on % G(●), % GE (▲) Na-PCMS ($\overline{DS}$ = 0.317) = 2.0 g (dry basis), [HNO_3] = 0.3 N, [AN] = 1.169 mol/L, [CAN] = 0.20 M, Time = 4 h, H_2O = 50 mL, Total Volume = 65 mL.

transfer reactions might be accelerated and thus lead to a decrease in % G as well as % C_t. The decrease in % GE at higher temperature (Figure 4) may be attributed to the solubility of monomer in the aqueous phase and also to the acceleration of the termination reactions which leads to the formation of more homopolymer. Similar results have been reported in the literature [1, 19-22].

Effect of Acid Concentration

The concentration of nitric acid was varied in the range 0.05-1.00 M, keeping the concentrations of all other reagents fixed. The effect of acid concentration on the percentage grafting is shown in Figure 5. It is seen that

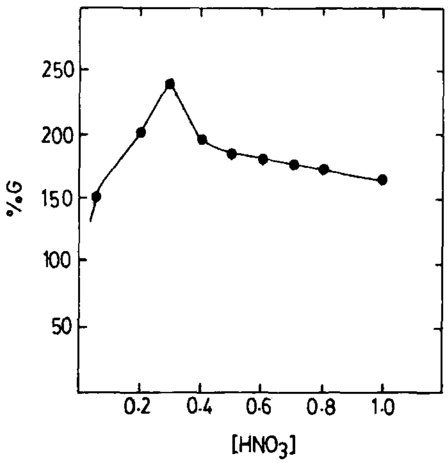

Figure 5 : Influence of nitric acid concentration on percentage grafting

Na-PCMS ($\overline{DS}$ = 0.317) = 2.0 g (dry basis), [AN] = 1.169 mol/L, [CAN] = 0.20 M, Time = 4 h, Temperature=30^{o}C, H_2O=50 mL, Total Volume=65 mL.

there exists an optimum concentration of nitric acid (0.30N) which affords maximum grafting. Beyond this concentration, the percentage of grafting decreases. The initial increase in grafting with increased acid concentration may be due to a decrease in the termination rate of the growing polymer chain or an increase in the initiation rate. However, at higher acid concentrations, the decrease in the percentage of grafting could be attributed to a corresponding reduction in ceric-Na-PCMS complex formation as well as an increase in polymer termination rates. Rao et al [23] have made similar observations.

Effect of Initiator Concentration

Figure 6 shows the dependence of percentage of grafting on the initiator concentration. The percentage of grafting increases with an increase in the intitiaor concentration but reaches a maximum value of 239.25% at 0.20 M CAN. Increasing the initiator concentration further resulted in a decrease of the percentage of grafting. A relatively high concentration of the initiator may cause a reduction of grafting due to an increase in the number of Na-PCMS radicals terminated prior to AN addition. Furthermore, homopolymer formation at higher initiator concentrations which compete with the grafting reaction for available monomer could lead to a decrease in the percentage of grafting. Several authors have reported similar trends for the ceric ion graft copolymerization of cellulosic substrates [24-26].

Effect of Monomer Concentration

The effect of monomer concentrations on the percentage of grafting as well as on the grafting efficiency is shown in Figure 7. It is evident from this figure that as the monomer concentration increases from 0.468 M to 1.169 M, the values of % G as well as % GE increases and then decreases. The lower concentrations of monomer favour graft copolymerization but with higher monomer concentrations the primary radicals attack the monomer instead of reacting with the backbone polymer, thereby producing the homopolymer and less percentage of grafting. It can also be noted that once

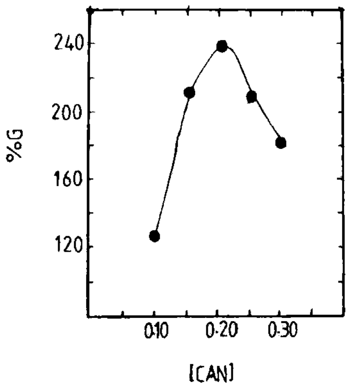

Figure 6 : Influence of ceric ammonium nitrate (CAN) concentration on percentage grafting.
Na-PCMS ($\overline{DS}$ = 0.317) = 2.0 g (dry basis), $[HNO_3]$ = 0.3 N, [AN] = 1.169 mol/L, Time = 4 h, Temperature=30°C, H_2O=50 mL, Total Volume=65 mL.

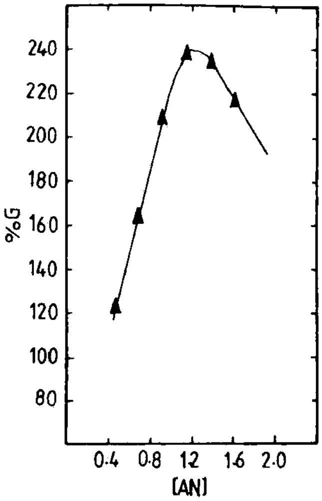

Figure 7 : Influence of monomer (AN) concentration on percentage of grafting.
Na-PCMS ($\overline{DS}$ = 0.317) = 2.0 g (dry basis), $[HNO_3]$ = 0.3 N, [CAN] = 0.20 M, Time = 4 h, Temperature = 30°C, H_2O = 50 mL, Total Volume = 65 mL.

the graft copolymer radical has formed, the excess monomer will shield the graft copolymer which may inhibit the rate of graft copolymerization. In addition to this the excess of monomer will be available for initiator radicals to initiate the homopolymerization reaction and thereby decrease the grafting efficiency (Figure 7).

Evidence of Grafting

The formation of graft copolymer was confirmed by IR spectroscopy. The IR spectra of Na-PCMS, PAN and Na-PCMS-g-PAN were taken in the range of 1000-4000cm^{-1}. It was observed that the graftcopolymer showed absorption bands of Na-PCMS and an additional band at 2250cm^{-1} which has been attributed to the C≡N stretching mode, characteristic of the spectra of PAN. Thus, the presence of the additional band at 2250cm^{-1} in the graft copolymer indicates that the grafting has taken place.

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