

Graft Copolymerization of Ethyl acrylate onto Sodium salt of Partially Carboxymethylated Sodium Alginate: Optimal Reaction Variables and Characterization

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ABSTRACT

Graft copolymerization of ethyl acrylate (EA) onto Sodium salt of Partially Carboxymethylated Sodium alginate (Na-PCMSA, $\overline{DS} = 0.605$) was carried out using ceric ammonium nitrate (CAN) as a redox initiator. The optimal reaction conditions were evaluated by varying various reaction parameters and the influence of synthesis variables was studied. The experimental results were analyzed in terms of the proposed kinetic scheme and were found to be in very good agreement with it. The influence of carboxymethyl groups introduced into the sodium alginate molecules with regard to its behaviour towards ceric induced grafting with EA was also investigated. The percent grafting of EA onto Na-PCMSA ($\overline{DS} = 0.605$) was determined as a function of compositions of mixed solvents comprising of methanol : water, ethanol : water, n-propanol : water, n-butanol : water and carbon tetrachloride : water systems. All the products were characterized by the help of FTIR, SEM and TGA techniques. The synthesized novel graft copolymer, Na-PCMSA-g-PEA, may find its potential application as a metal adsorbent.

Keywords: Sodium salt of partially carboxymethylated sodium alginate, Graft copolymerization, Ethyl acrylate, Optimal reaction conditions, Characterization

Introduction

Graft copolymerization of vinyl monomers onto naturally occurring polymers has gained importance in modifying the physical and chemical properties of polymers. Among chemical methods, redox-initiated grafting is advantageous because in the presence of redox system,

grafting can be carried out under milder conditions with minimum side reactions. In our laboratory, by the process of grafting, physical and chemical properties of synthetic monomer are superimposed onto the properties of different natural polymers using redox system[1-5].

Alginate, an industrially important marine polysaccharide, is obtained by extracting from brown algae. It is composed of (1-4)-linked β -D-mannuronic acid and α -L-guluronic acid blocks[6]. Literature survey reveals that there are many reports on grafting of various vinyl monomers onto sodium alginate using different initiating systems[7-13]. However, the reports on modification of sodium salt of partially carboxymethylated sodium alginate(Na-PCMSA) via grafting are scantily available[14, 15]. In the present work, we attempted to modify Na-PCMSA by free radical graft copolymerization of ethyl acrylate and evaluated the optimal reaction conditions for affording maximum percentage of grafting. This has been done not only to develop specialty polymeric materials but also to elucidate the grafting mechanism. The novel Na-PCMSA-g-poly(hydroxamic acid) ion exchange resin may be prepared by treating the optimally synthesized graft copolymer [Na-PCMSA-g-PEA (%G = 340.45)] of the present work with hydroxylamine hydrochloride which may find its potential application as adsorbent material to remove the dyes and heavy metal ions from the industrial effluents and other waste water.

Experimental

Materials and Methods

Sodium alginate (SA) was kindly supplied by LobaChemie Pvt. Ltd., Mumbai. The methods of preparation and purification of Na-PCMSA were followed as described earlier[14]. The degree of substitution of Na-PCMSA was measured by following the Acid-Wash method [16] and it was found to be 0.605. EA (Fluka, Switzerland) was washed with 2% sodium hydroxide solution to remove the stabilizer. After treating it with alkali solution, it was washed repeatedly with distilled water till it was freed from alkali and finally dried over anhydrous sodium sulphate and then distilled at atmospheric pressure and the middle fraction was used. CAN of reagent grade and analar grade nitric acid (both Qualigens Fine Chemicals, Mumbai, India Ltd.) were used as received. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water

was used for the preparation of all the solutions as well as for polymerization reactions.

Graft copolymerization

(i) Graft Copolymer of Na-PCMSA (Na-PCMSA-g-PEA)

A 500 mL three-necked flask equipped with mechanical stirrer, a reflux condenser and a gas inlet system was immersed in a constant temperature bath for grafting reactions. In a typical reaction, varying amount (0.5 – 3.0g) of Na-PCMSA ($\overline{DS} = 0.605$) was dissolved in low conductivity water (100 mL) with constant stirring and bubbling a slow stream of nitrogen gas for 1h at the desired temperature (15° –55°C). Freshly prepared 10 mL solution of CAN (10.0×10^{-3} M to 80.0×10^{-3} M) in nitric acid (Nil – 1.0 M) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction solution and freshly distilled ethyl acrylate (EA) monomer (0.051 M to 0.506 M) was added. The grafting reactions were carried out for varying time intervals (0.5 to 10 h). After completion of the reaction, the mixture was immediately poured into excess of methanol to coagulate the polymer. The crude copolymer product was filtered, repeatedly washed with nitric acid as well as 90% methanol and finally washed with pure methanol. The crude copolymer thus obtained was dried under vacuum at 40°C. The homopolymerpoly(ethyl acrylate) (PEA) was separated from the crude graft copolymer by extraction with acetone for 48h. After complete removal of the homopolymer, the pure graft copolymer was dried at 40°C under vacuum to a constant weight.

(ii) Graft Copolymer of SA (SA-g-PEA)

In order to understand the influence of introduction of the carboxymethyl groups (in SA molecule) on the grafting yields, we have also carried out the grafting of EA onto SA using the established optimal reaction conditions in the case of grafting of EA onto Na-PCMSA ($\overline{DS} = 0.605$). The experimental procedure for the synthesis of the graft copolymer, SA-g-PEA, is the same as discussed above.

(iii) Effect of Reaction Medium on Grafting

In order to study the effect of the reaction medium on grafting we have carried out the graft copolymerization reactions, as per the procedure described above, in different water/solvent (75 : 25, 50 : 50, 25 : 75 and 00 :100) mixtures using the evaluated optimized reaction conditions in the case of grafting of EA onto Na-PCMSA ($\overline{DS}=0.605$). The solvents used

include methanol, ethanol, n-propanol, n-butanol and carbon tetrachloride.

Isolation of Grafted Chains

The graft copolymer of Na-PCMSA ($\overline{DS} = 605$) containing PEA was hydrolyzed by refluxing for 12 h in 1N HCl as suggested by Brockway and Seaberg[17]. After all the Na-PCMSA went into the solution, a resinous mass was obtained which was characterized with IR spectroscopy.

FTIR Spectra

The IR Spectra of Na-PCMSA ($\overline{DS} = 0.605$), Na-PCMSA-g-PEA and PEA were taken in KBR pellets using Nicolet Impact 400D Fourier Transform Infra Red Spectrophotometer.

Thermogravimetric Analysis (TGA)

The thermal behaviour of Na-PCMSA ($\overline{DS} = 0.605$), Na-PCMSA-g-PEA (%G = 340.45) and PEA has been examined in an inert atmosphere at a heating rate of 10°C/min with the help of Mettler Toledo make (model TGA 851^e) thermo gravimetric analyzer.

Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make was used to obtain the micrographs of Na-PCMSA ($\overline{DS} = 0.605$) and Na-PCMSA-g-PEA (%G = 340.45).

Grafting Yields and Kinetic Parameters

The percentage of grafting, grafting efficiency, percentage homopolymer and rates of polymerization (R_p), graft copolymerization (R_g) and homopolymerization (R_h) were evaluated by the help of the following expressions[1]:

$$(i) \text{ Percentage Grafting (\%G)} = \frac{\text{Wt. of Polymer grafted}}{\text{Wt. of homopolymer}} \times 10^2 \quad (1)$$

$$(ii) \text{ Percentage Grafting Efficiency (\%GE)} = \frac{\text{Wt. of Polymer grafted}}{\text{Wt. of Polymer grafted} + \text{Wt. of Homopolymer}} \times 10^2 \quad (2)$$

$$(iii) \text{ \% Homopolymer (\%Hp)} = 100 - \%GE \quad (3)$$

$$(iv) R_p \text{ (mol.L}^{-1} \cdot \text{s}^{-1}) = \frac{\text{Wt. of Polymer Grafted} + \text{Wt. of Homopolymer}}{\text{Mol. wt. of monomer} \times \text{Reaction time (sec)} \times \text{Vol. of the reaction mix. (mL)}} \times 10^3 \quad (4)$$

$$(v) R_g \text{ (mol.L}^{-1} \cdot \text{s}^{-1}) = \frac{\text{Wt. of Polymer Grafted}}{\text{Mol. wt. of monomer} \times \text{Reaction time (sec)} \times \text{Vol. of the reaction mix. (mL)}} \times 10^3 \quad (5)$$

$$(vi) R_h \text{ (mol.L}^{-1}\text{.s}^{-1}\text{)} = \frac{\text{Wt. of Homopolymer}}{\text{Mol.wt. of monomer} \times \text{Reaction time (sec)} \times \text{Vol. of the reaction mix. (mL)}} \times 10^3 \quad (6)$$

RESULTS AND DISCUSSION

Determination of optimum reaction conditions

In order to understand the reaction mechanism of grafting of EA onto Na-PCMSA, the influence of synthetic variables such as concentrations of initiator (CAN), nitric acid, monomer (EA) as well as reaction time, temperature and amount of substrate were studied and the reaction conditions for optimum grafting have been evaluated.

Effect of Backbone Concentration

The influence of varying amount of Na-PCMSA on %G as well as %GE has been studied by varying the amount of Na-PCMSA from 0.5 to 3.0 g and the results are shown in Figure 1(a). As it can be seen from the figure that the grafting yields increased initially with an increasing the amount of Na-PCMSA up to 1.5 g and thereafter decreased with further increase in the amount of Na-PCMSA. Thus, the observed increase in the grafting yields with the increasing amount of Na-PCMSA may be due to the fact that the number of Na-PCMSA macroradicals available for grafting increase with increase in the amount of Na-PCMSA. The reduction in the grafting yields beyond optimum value could be attributed to the increase in the viscosity of the reaction medium which restricts the movements of macroradicals, thereby decreasing the grafting yield values. Similar results are also reported in the literature[3, 18-20].

Effect of Initiator Concentration

Figure 1(b) represents the influence of the initiator (CAN) concentration on the grafting yields. It becomes evident from this figure that with increasing ceric-ion concentration, the values of the grafting yields are found to be increased and reached the maximum values of % G and % GE to be 263.84% and 94.57% respectively at $[\text{Ce}^{+4}] = 0.04 \text{ mol /L}$. Thus, the observed increase in the grafting yields within the CAN concentration range of 0.01-0.04 mol/L may be explained on the basis of the fact that in this concentration range of the initiator the formation of sufficient number of ceric ions in the reaction mixture at a 0.10 mol/L concentration of nitric acid takes place which are ultimately consumed in the formation of active sites on the Na-PCMSA backbone to facilitate graft copolymerization of EA onto it. The observed decreasing

trend in the grafting yields beyond the optimum concentration of the initiator may be attributed to the steric hindrance created by the growing grafted chains at the Na-PCMSA surface. Similar results are also reported in the literature[1, 8, 14, 21, 22].

Effect of Nitric acid Concentration

The effect of nitric acid concentration on the grafting yields is shown in Figure 1(c). The maximum values of the grafting yields (%G = 261.54% and %GE = 96.68%) have been achieved at the optimum concentration of nitric acid (0.4 mol/L) beyond which both the values are found to be decreased. Even in the absence of nitric acid the value of %G is found to be higher which may be due to the possibility that, in an aqueous medium Na-PCMSA ionizes fully to a greater extent which facilitates the diffusion of monomer as well as initiator leading to a higher value of grafting (131.64%)[1-3]. Below the optimum concentration, the concentration of the ceric ion will be higher and therefore it may accelerate the termination of growing polymeric grafting chains resulting in the decrease in the grafting yields[2, 19] .

Effect of Monomer Concentration

The graft copolymerization has been recorded at different concentrations of EA ranging from 0.051 to 0.506 mol/L keeping other variables constant and the results are shown in Figure 1(d). It can be seen from this figure that initially %G increases with increasing concentration and reaches a maximum value of 228.15% at [EA] = 0.304 mol/L. The enhancement of grafting by increasing monomer concentration could be ascribed to the greater availability of monomer molecules in the close proximity to the Na-PCMSA macroradicals. However, the observed decrease in %G and %GE, beyond the optimum monomer concentration is attributed to the formation of homopolymer by the combination and disproportionation reactions of the PEA macroradicals. Further, formation of more homopolymer results in an increase in the viscosity of the reaction medium thereby restricting the mobility of the growing polymeric chains to the active sites and hence a decrease in grafting is observed[21, 23, 24].

Effect of Reaction Time

Figure 1(e) represents the effect of reaction time on the grafting yields. It becomes evident from this figure that %G increases up to a maximum of 218.05% within 5h beyond

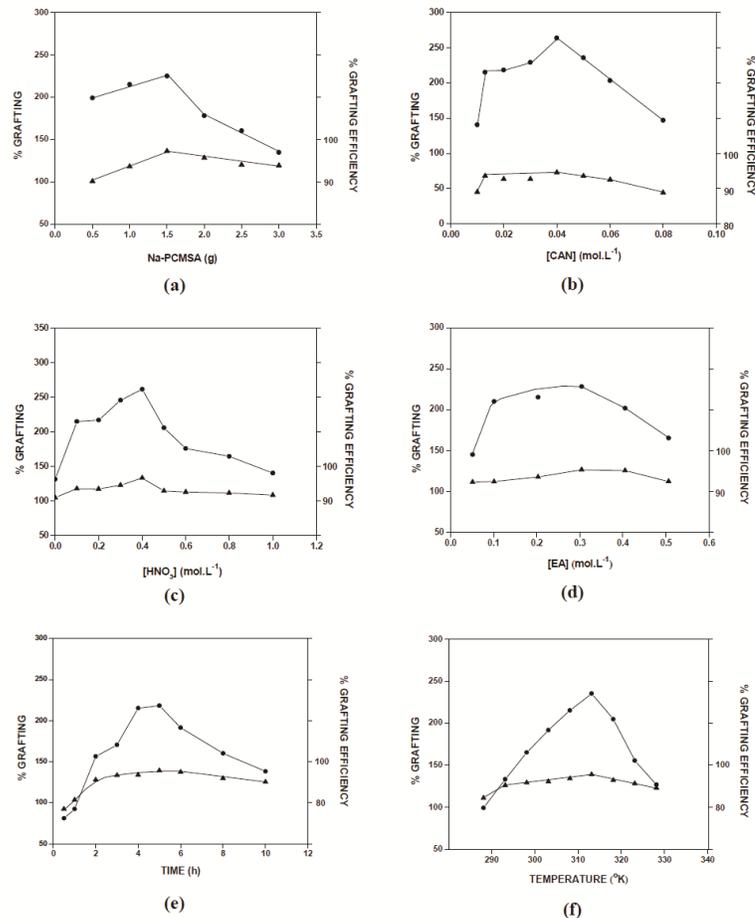


Figure1: Influence of (a) amount of sodium salt of partially carboxymethylated sodium alginate; (b) ceric ammonium nitrate (CAN) concentration; (c) nitric acid concentration; (d) ethyl acrylate (EA) concentration; (e) reaction time and (f) reaction temperature on: (●) - %G; or (▲) - %GE.

which it decreases. The observed increase in %G with the increase in reaction time could be attributed to the increase in the number of grafting sites on the Na-PCMSA backbone and the addition of monomer molecules to the growing grafted chains. However, the decrement in %G and %GE beyond 5h can be rationalized on account of depletion of monomer and initiator concentration with the progress of the reaction. Similar time dependency of grafting yields is also reported in the literature[8, 14, 25].

Effect of Reaction Temperature

In the present work, the graft copolymerization reaction was studied by varying the reaction temperature from 15°C to 55°C keeping other variables constant. The results

regarding the influence of temperature on the grafting yields are depicted in Figure 1(f). It becomes evident from this figure that %G increases with the rise of temperature from 15°C to 40°C beyond which it decreases with further increase in temperature. The behaviour of variation of %G with temperature, in the temperature range of 15°C to 40°C, can be ascribed to the fact that with the initial rise in temperature, as the kinetic energy of the molecules increases, more and more radicals get drifted at a faster rate to the Na-PCMSA backbone, resulting in the increasing in %G. However, after reaching the optimum temperature, with further increase in temperature, a considerable amount of homopolymer is formed, which results in an increase in the viscosity of the reaction medium and it provides a hindrance for the radicals to move forward to the active sites of Na-PCMSA backbone resulting in the decrease in the grafting yields. In addition, at higher temperature, the substantial increase in the rate of chain transfer and chain termination reactions between grafted chains and monomer molecules also would lead to the observed decrease in %G as well as %GE. Similar results are also reported in the literature[7, 10, 14, 26-28]. Thus, from the above discussion the optimal reaction conditions evaluated in the case of graft copolymerization of EA on to Na-PCMSA ($\overline{DS} = 605$) are: Na-PCMSA ($\overline{DS} = 0.605$) = 1.5 g (dry basis); [CAN] = 0.04 mol.L⁻¹; [HNO₃] = 0.40 mol.L⁻¹; [EA] = 0.304 mol.L⁻¹; Time = 5 h; Temperature = 40°C and Total Volume = 150 mL. At the optimum grafting reaction conditions, the maximum values of the grafting yields achieved are %G = 340.45, %GE = 92.56 and %H_p = 7.44.

Evaluation of Energy of Activation

The natural log of % grafting (ln %G) versus 1/T was plotted for the initial portion of the curve i.e. 15°C to 35°C [cf. Figure 1(f)] as shown in Figure 2 and these values are found to fall on a straight line with good correlation coefficient value. The least square value of the overall

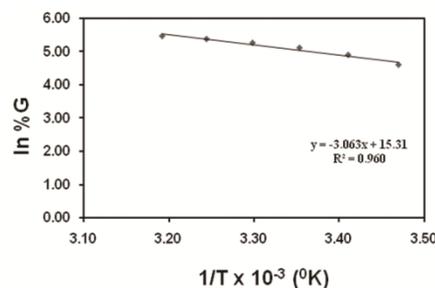
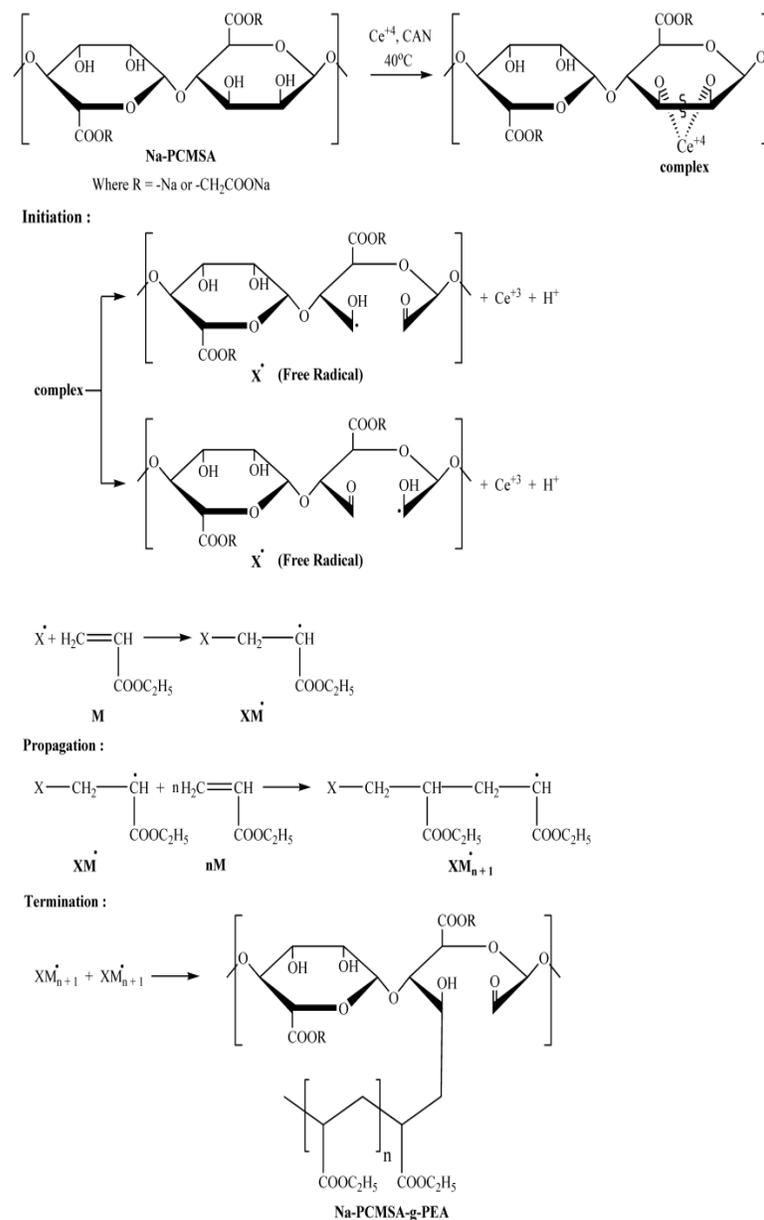


Figure 2: Plot of ln %G versus T⁻¹.

activation energy of grafting (E_g) was calculated and was found to be 25.46 kJ/mol. Similar results are also reported in the literature[1, 2, 14, 29].

Kinetics and Mechanism

The mechanism of free radical graft copolymerization of EA onto Na-PCMSA ($\overline{DS} = 605$) is expected to proceed according to the scheme, which has been proposed earlier by us[8]. Scheme 1 represents the mechanistic pathway for the synthesis of Na-PCMSA-g-PEA. The



Scheme 1: Mechanistic pathway for the synthesis of Na-PCMSA-g-PEA.

present experimental results, as tabulated in Tables 1 and 2, have been treated in light of the proposed kinetic scheme and accordingly the plot of R_g versus $[CAN]^{0.5}$ should be linear at lower $[CAN]$. Such type of typical plot obtained in the present case is shown in Figure 3 which is found to be linear at lower $[CAN]$, indicating that termination takes place by recombination of double radicals as per Eqn. 12 of the kinetic scheme proposed earlier[8]. However, the plot deviates from linearity at higher initiator concentration further indicating that the termination takes place by single radical, as per Eqn. 15 of the kinetic scheme proposed earlier[8] leading to the decrease in the rate of graft copolymerization. The effect of the monomer (EA) concentration as well as the initiator (CAN) concentration on the overall rate of polymerization (R_p) as expected on the basis of the relationship derived earlier^[8] is also exemplified in Figure 4. As evident, the plots of R_p versus $[M]^2$ and R_p versus $1/[Ce]^{+4}$ are found to be linear in the present case, supporting the proposed kinetic scheme[8].

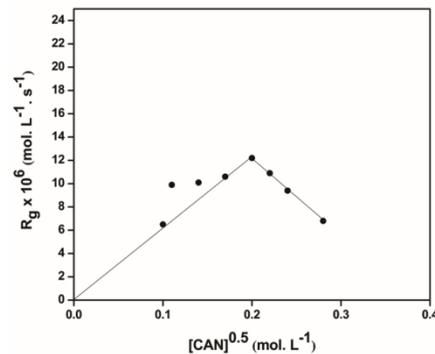


Figure 3: Plot of (●) - $R_g \times 10^6$ versus $[CAN]^{0.5}$

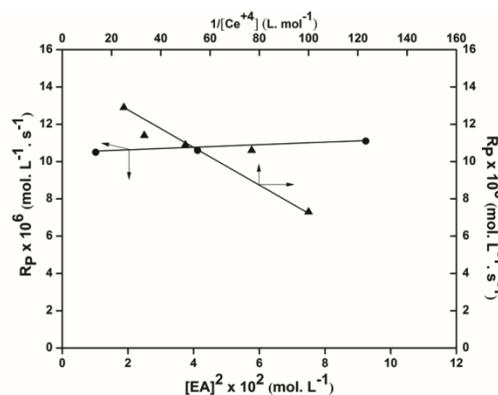


Figure 4: Plot of (●) - $R_p \times 10^6$ versus $[M]^2$ & (▲) - $R_p \times 10^6$ versus $1/[Ce]^{+4}$

Table 1: Rates of polymerization (R_p) and graft copolymerization (R_g) for grafting of EA onto Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA, $\overline{DS} = 0.605$) at various initiator concentrations^a.

[CAN] x 10 ³ (mol/L)	$R_p \times 10^6$ (mol.L ⁻¹ .s ⁻¹)	$R_g \times 10^6$ (mol L ⁻¹ .s ⁻¹)
10.0	7.3	6.5
13.0	10.6	9.9
20.0	10.9	10.1
30.0	11.4	10.6
40.0	12.9	12.2
50.0	11.6	10.9
60.0	10.2	9.4
80.0	7.7	6.8

^aReaction conditions: Na-PCMSA = 1.0 g (dry basis); [CAN] = Varied as shown; [HNO₃] = 0.10 mol/L; [EA] = 0.203 mol/L; Time = 4h; Temperature = 35°C and Total Volume = 150 mL

Effect of Reaction Medium

The grafting of EA onto Na-PCMSA ($\overline{DS} = 0.605$) using CAN as an initiator was also studied in water/solvent mixtures. The solvents used include methanol, ethanol, n-propanol, n-butanol and carbon tetrachloride. The results obtained are summarized in Table 3. Water soluble organic solvents might affect the swelling properties of Na-PCMSA. Any change in Na-PCMSA swellability would be reflected on the behaviour of Na-PCMSA towards grafting since diffusion of monomer and initiator, availability of functional groups (sites of grafting), propagation and termination of the graft etc. would depend to a considerable extent on the

Table 2: Rate of polymerization (R_p) for grafting of EA onto Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA, $\overline{DS} = 0.605$) at various monomer concentrations^a.

[EA] (mol/L)	$R_p \times 10^6$ (mol.L ⁻¹ .s ⁻¹)
0.051	7.3
0.101	10.5
0.203	10.6
0.304	11.1
0.405	9.9
0.506	8.3

^aReaction conditions :Na-PCMSA = 1.0 g(dry basis); [CAN] = 0.013 mol/L; [HNO₃] = 0.10 mol/L; [EA] = Varied as shown; Time = 4h; Temperature = 35°C and Total Volume = 150 mL

swelling properties of Na-PCMSA.

Table 3: Influence of reaction medium on grafting of ethyl acrylate (EA) onto Sodium salt of partially Carboxymethylated sodium alginate (Na-PCMSA, $\overline{DS} = 0.605$)^a.

Solvent	Water/Solvent Ratio(V/V)	%Grafting(%G)	%Grafting Efficiency(%GE)
Methanol	100:00	340.45	92.56
	75:25	296.34	92.07
	50:50	282.15	90.07
	25:75	271.41	87.80
	00:100	252.27	82.70
Ethanol	100:00	340.45	92.56
	75:25	290.40	91.50
	50:50	273.02	88.10
	25:75	265.61	86.77
	00:100	250.93	80.12
n-propanol	100:00	340.45	92.56
	75:25	246.09	88.63
	50:50	236.03	84.52
	25:75	227.33	83.10
	00:100	216.69	80.23
n-butanol	100:00	340.45	92.56
	75:25	230.02	83.32
	50:50	220.71	82.00
	25:75	212.88	78.39
	00:100	200.17	72.08
Carbon tetrachloride	100:00	340.45	92.56
	75:25	69.55	63.87
	50:50	64.54	60.72
	25:75	59.43	60.18
	00:100	53.61	57.43

^aReaction Conditions: Na-PCMSA = 1.5g (dry basis); [CAN] = 0.04 mol.L⁻¹; [HNO₃] = 0.40 mol.L⁻¹; [EA] = 0.304 mol.L⁻¹; Time = 5 h; Temperature = 40°C and Total Volume = 150 mL

It becomes evident from the results of Table 3 that regardless of the water/solvent mixture employed, a substantial amount of grafting is obtained. A regular decrease in %G is observed with increasing the solvent ratio in the water/solvent mixture. This could be interpreted in terms of the adverse effect of the solvent on the swelling properties of Na-PCMSA in water by the fact that as the amount of organic solvent increases, the swelling of Na-PCMSA decreases which reduces the ionization of –CH₂COONa groups along the sodium alginate molecules, as a

result of which the attraction of Ce^{+4} to the sodium alginate molecule will be reduced, leading to the formation of lower amount of grafts.

It can be further seen from the results of Table 3 that the reaction medium plays an important role in graft copolymerization reaction. The magnitude of grafting differs significantly with the type and ratio of solvent used in the mixture. It is interesting to note that in the present case, the graft yield follows the order:

methanol > ethanol > n-propanol > n-butanol > carbon tetrachloride

when solvent constitutes either 25%, 50%, 75% or 100% in the water/solvent mixtures.

The lower alcohols are very soluble in water, and the solubility diminishes as molecular weight increases. Each alcohol consists of a carbon chain (always non polar) and a OH group (which is polar). Therefore, the solubility of alcohols in water is to be expected, since the oxygen atom of the hydroxyl group in the alcohols can form hydrogen bonds with the water .

In the lower alcohols, the hydroxyl group constitutes a large part of the molecule, whereas the hydrocarbon character increases with the molecular weight of the alcohol and hence the solubility in water decreases[30]. However, in the case of carbon tetrachloride, the intermolecular forces between carbon and chloride are strong and hence it is not soluble in water. Therefore, a decreasing trend in % grafting is observed from methanol to carbon tetrachloride irrespective of the value of the water/solvent ratio. It is important to note further from the results of Table 3 that among all the water/solvent mixtures used, water/methanol at a ratio of 75/25 constitutes the most favourable medium for graft copolymerization of EA onto Na-PCMSA ($\overline{DS} = 0.605$) using CAN as an initiator giving rise to highest value of %G = 296.34. This can be attributed to the small molecule of methanol and also to its high polarity, which is not only capable of swelling the trunk polymer but also has the additional advantage of being miscible with the monomer (EA), thereby simplifying the access and diffusion to the grafting sites in the Na-PCMSA. Similar results are also reported in the literature[31, 32].

Effect of Substrate Structure

As shown in Table 4 the introduction of carboxymethyl groups in the SA molecule enhances the behaviour of SA towards grafting of EA. As a result of which the values of % G and

%GE.

Table 4: Results of grafting yields (%G, %GE and %H_p) obtained in the case of grafting of EA onto Sodium alginate (SA) (under optimum reaction conditions derived for Na-PCMSA) and Na-PCMSA ($\overline{DS} = 0.605$)^a.

Structure	Grafting Yields		
	%G	%GE	% H _p
SA	210.30	91.32	8.68
Na-PCMSA	340.45	92.56	7.44

^aOptimum Reaction Conditions: SA/Na-PCMSA = 1.5 g (dry basis); [CAN] = 0.04 mol.L⁻¹; [HNO₃] = 0.40 mol.L⁻¹; [EA] = 0.304 mol.L⁻¹; Time = 5 h; Temperature = 40°C and Total Volume = 150 mL are found to be higher in the case of grafting of EA onto Na-PCMSA ($\overline{DS} = 0.605$) compared to SA.

This could be attributed to the combined influence of the following factors. First, the carboxymethyl groups increase the swellability of SA, thereby facilitating the diffusion of monomer (EA) and initiator (CAN), second the introduction of carboxymethyl groups along the SA chains introduces the negative charges which attract ceric ions to the SA molecules leading to the formation of more active sites on the SA backbone, available for the monomer (EA), thus increasing the reactivity of SA. Similar results are also reported in the case of grafting of 4-vinylpyridine onto modified cellulosic fibers[33] and photo-grafting of methyl methacrylate onto sodium salt of partially carboxymethylated guar gum[34].

Characterization

FTIR Spectra

Figures 5(a), 5(b), and 5(c) represent the IR spectra of Na-PCMSA ($\overline{DS} = 0.605$), Na-PCMSA-g-PEA and PEA respectively. It is very interesting to note from Figure 5(a) that the absorption peak at $\sim 1745 \text{ cm}^{-1}$ is a strong one and is assigned to C=O stretching, suggesting the presence of $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-$ moiety in the Na-PCMSA. The presence of $-\text{COO}$ moiety present in Na-PCMSA is also evident from the absorption bands appeared at $\sim 1620 \text{ cm}^{-1}$ and $\sim 1420 \text{ cm}^{-1}$. The IR spectrum of the graft copolymer, Na-PCMSA-g-PEA [Figure 5(b)] showed

absorption bands of Na-PCMSA as well as an additional strong absorption band at $\sim 1734 \text{ cm}^{-1}$ assigned to C=O stretching of ester group ($-\text{COOCH}_3$), characteristic of the methacrylates. The IR

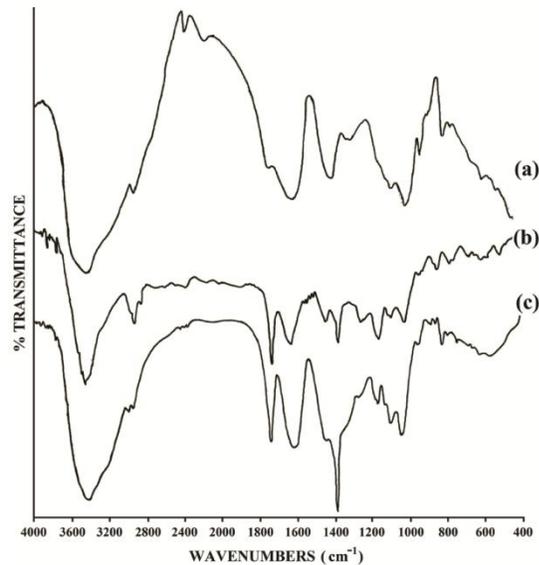


Figure 5: FTIR spectra of (a) Na-PCMSA; (b) Na-PCMGG-g-PEA and (d) PEA

spectrum of PEA [Figure 5(c)] indicates the presence of C=O stretching at $\sim 1736 \text{ cm}^{-1}$. This may be attributed to the fact that hydrolysis of the graft copolymer, Na-PCMSA-g-PEA, gives back ethyl acrylates. Thus, the results of Figures 5(a) to 5(c) provide a substantial evidence of grafting of EA onto Na-PCMSA ($\overline{DS} = 0.605$).

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a simple and accurate method for studying the decomposition pattern and the thermal stability of the polymers. Figure 6 shows the

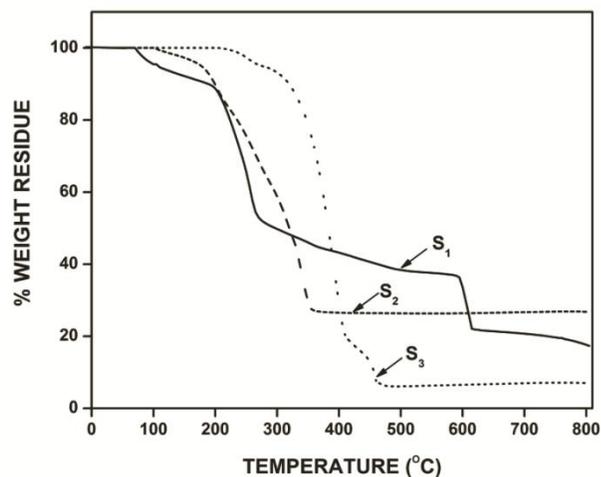


Figure 6: TG thermograms for Na-PCMSA (S_1); Na-PCMGG-g-PEA (S_2) and PEA (S_3) at $10^\circ\text{C}/\text{min}$

primary thermograms for Na-PCMSA (S_1), Na-PCMSA-g-PEA (S_2) and PEA (S_3) samples. It becomes evident from the thermogram of Na-PCMSA [Figure 6 (S_1)] that the decomposition process in N_2 for Na-PCMSA occurs in two stages. However, the initial slight weight loss (7.80%) in the temperature range 35°C - 150°C is merely due to evaporation of absorbed moisture. The rapid decomposition occurs in the first stage (150°C - 340°C) with the onset of the decomposition temperature (IDT) at 150°C , resulting in the major weight loss of 45.40% (Table 5). This first step exhibits maximum rate of weight loss at 240°C . In the temperature range 340°C - 530°C the sample degrades very slowly and loses 8.97% of its original weight.

Table 5 : Percent weight loss of Na-PCMSA ($\overline{DS} = 0.605$), Na-PCMSA-g-PEA (% G = 340.45) and PEA in different temperature ranges.

Sample	Temperature range ($^\circ\text{C}$)	T_{\max} ($^\circ\text{C}$)	Weight loss (%)	Temperature Characteristics				IPDT ($^\circ\text{C}$)
				T_i (IDT) ($^\circ\text{C}$)	T_f (FDT) ($^\circ\text{C}$)	T_{10} ($^\circ\text{C}$)	T_{50} ($^\circ\text{C}$)	
S_1	35-150	—	7.80	150	680	190	295	432
	150-340	240	45.40					
	340-530	—	8.97					
	530-680	595	16.81					
	680-750	—	1.31					
S_2	35-120	—	1.14	120	420	200	320	275
	120-420	320	72.41					
	420-500	—	0.11					
S_3	35-160	—	0.00	160	520	320	385	340
	160-520	380	93.85					
	520-600	—	—					

Where S_1 = Na-PCMSA; S_2 = Na-PCMSA-g-PEA; S_3 = PEA

The second step of decomposition commences from 530°C and completes at 680°C involving about 16.81% weight loss with a maximum weight loss at 595°C .

The graft copolymer, Na-PCMSA-g-PEA, shows only one stage decomposition pattern [Figure 6(S_2)]. The sample begins to decompose at 120°C and loses its weight gradually up to

420°C involving about 72.41% weight loss with a maximum weight loss at 320°C. In the case of PEA [Figure 6(S₃)] also the overall degradation occurs involves only single steps. The degradation occurs in the temperature range 160-520°C involving about 93.85% weight loss with a maximum rate of weight loss at 380°C. The values of temperature characteristics and integral procedure decomposition temperature as well as the percentage weight loss in different temperature ranges for Na-PCMSA (\overline{DS} = 0.605), Na-PCMSA-g-PEA(% G = 340.45) and PEA are tabulated in Table 5. The thermal stability of Na-PCMSA has been found to be decreased upon grafting of EA onto it.

Scanning Electron Microscopy (SEM)

Figures 7(a) and 7(b) represent the scanning electron micrographs of Na-PCMSA and Na-PCMSA-g-PEA respectively. The comparison of the micrographs led to reveal that the distinct morphological differences are discernible in their surface topology indicating that the grafting has taken place.

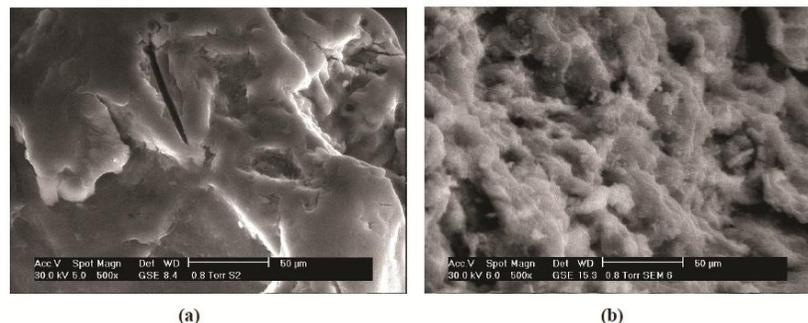


Figure 7: Scanning Electron Micrographs of (a) Na-PCMSA (500X) and (b) Na-PCMSA-g-PEA(500X).

Conclusions

In summary, we have reported first time the evaluation of the optimum reaction conditions for ceric-induced graft copolymerization of EA onto Na-PCMSA (\overline{DS} = 0.605) by varying various reaction conditions. The influence of the reaction conditions on grafting yields has been discussed. Under the optimized reaction conditions the maximum percentage of grafting yields achieved are % G = 340.45 and % GE = 92.56. The experimental results have been analyzed in terms of the earlier proposed kinetic scheme and are found to be in good

agreement with it. The overall activation energy of grafting (E_g) has been found to be 25.46 kJ/mol. The grafting of ethyl acrylate (EA) onto Na-PCMSA ($\overline{DS} = 0.605$) has also been studied in different water/solvent mixtures. From the results it has been observed that the magnitude of grafting differs significantly with the type and ratio of solvent used in the mixture. Of the water/solvent mixtures used, water/methanol at a ratio of 75:25 is found to constitute the most favourable medium for graft copolymerization of EA onto Na-PCMSA ($\overline{DS} = 0.605$) giving rise to highest value of percentage of grafting. The influence of the carboxymethyl group introduced to the SA molecule on its behaviour toward ceric-induced grafting with EA has also been investigated. FTIR, TGA and SEM techniques have been successfully used to characterize all the products. The optimally synthesized graft copolymer, Na-PCMSA-g-PEA, of the present work may find its potential application as a novel metal adsorbent after its treatment with hydroxylamine hydrochloride. Further work in this direction is in progress.

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