Synthesis and Characterization of Butyl Acrylate Graft Sodium Salt of Partially Carboxymethylated Starch

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ABSTRACT: Graft copolymers were synthesized by graft copolymerization of butyl acrylate (BA) onto sodium salt of partially carboxymethylated starch (Na-PCMS). Ceric ammonium nitrate (CAN), a redox initiator, was used for initiation of graft copolymerization reaction. All the experiments were run with Na-PCMS having degree of substitution, DS = 0.35. The grafting reaction was characterized by parameters such as % total conversion (%Ct), % grafting (%G), % grafting efficiency (%GE), and % add-on. Graft copolymers were characterized by infrared spectral analysis and scanning electron microscopy. Variables affecting graft copolymerization reaction such as nitric acid concentration, reaction time, reaction temperature, and ceric ion concentration were investigated. The results revealed that $0.3M$ CAN as initiator, $0.3M$ HNO_3, with reaction time 4–4.5 h at 25–30°C were found as suitable parameters for maximum yield of graft copolymerization reaction. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3334–3340, 2006

Key words: graft copolymers; carboxymethylated starch; polybutyl acrylate; ceric ammonium nitrate
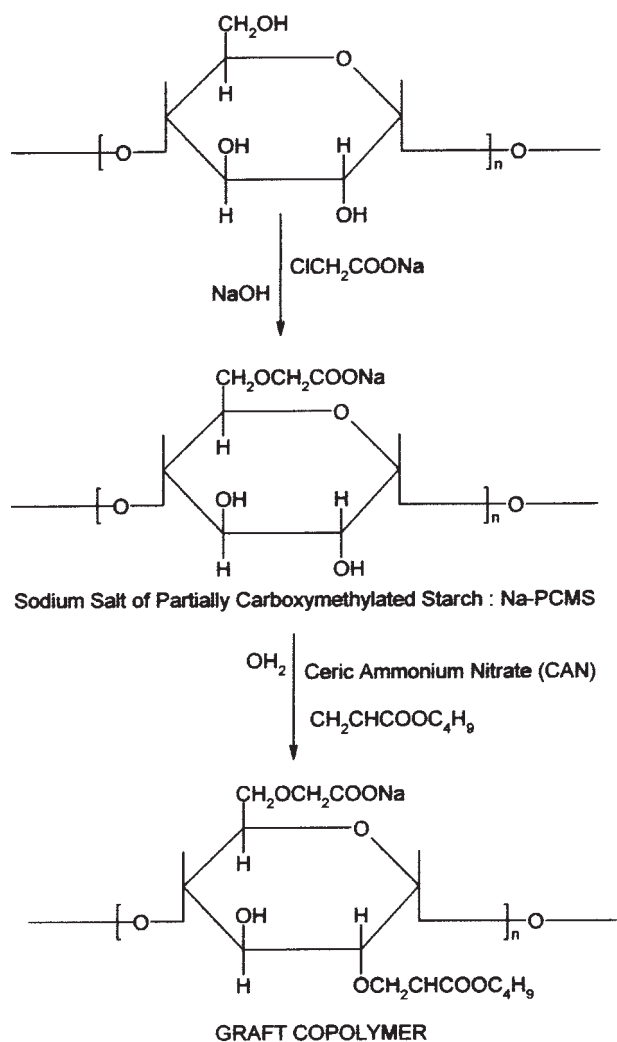
INTRODUCTION

Among the methods of alteration of structure and properties of polymeric materials, graft polymerization technique has received considerable attention from either scientists or technologists all over the world, specially regarding those systems in which the substrate is a biopolymer such as starch[1] or modified starch.[2] Polysaccharide graft copolymers have been prepared to add new properties to the natural polymers such as fiber,[2] cellulose,[3–7] guar gum,[8] chitosan,[9] starch,[10,11] etc., with a minimum loss of native properties. Since last three decades, grafting of various monomers onto starch has been the most frequently attempted method to impart desirable properties to the polysaccharide without sacrificing its biodegradable nature.[12–14]

The exclusive literature review reveals that various acrylic monomers viz., methyl, ethyl, and butyl acrylates as well as methyl methacrylate and ethyl methacrylate are grafted onto starch using ceric ammonium nitrate as an indicator and influence of reaction time on various reaction parameters like percentage grafting efficiency and percentage grafting is reported.[15–19] These graft copolymers are widely used as matrices for drug delivery systems.[20–21]

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However, it was found that there is not much work reported about the utilization of starch derivatives in grafting application. Therefore, in the present work, an attempt has been made to graft butyl acrylate onto chemically modified starch (carboxymethylated starch, CMS). CMS is one of the most important derivatives of starch in which certain OH groups are substituted by ether group $—O—CH_2—COOH$. The term CMS is commercially applied for the water soluble starch ether, which is actually the sodium salt of carboxymethyl starch. It is frequently called the sodium starch glycolate.[22] Synthesis of CMS has been reported in the literature by many scientists.[23–26] The carboxymethyl starch (CMS) finds wide applications in sizing fabrics,[27] as polyelectrolyte in suspensions of hydrophilic materials, as hemostatic agent in surgical,[28] fire retardant,[29] and as crack resistant in coating of kaolin.[30]

Our aim was to synthesize graft copolymer of polysaccharides to obtain materials that profit from the particular properties of both natural and synthetic macromolecules. Thus, in this work, we have synthesized graft copolymer of butyl acrylate and sodium salt of partially carboxymethylated starch using ceric ammonium nitrate (CAN) redox initiation method.[31] Ceric ion oxidation will generate radical sites on the carbohydrate backbone where grafting will occur. We have chosen butyl acrylate (BA) as a comonomer because of its known biocompatibility and nontoxic behavior,[32] together with ease of polymerization.

Scheme 1 Butyl acrylate supported onto sodium salt of partially carboxymethylated starch.

The objective of present work was to synthesize, characterize, and optimize the reaction parameters for the graft copolymerization between butyl acrylate and carboxymethylated starch. Graft copolymers were essentially characterized by infrared spectral analysis and scanning electron microscopic analysis. Till date, butyl acrylate has not been studied for grafting onto carboxymethyl starch. So it is intended to add the information on grafting of butyl acrylate onto carboxymethyl starch.

EXPERIMENTAL

Materials and methods

Starch for Na-PCMS was supplied by M/s National Chemicals, Vadodara, India. Butyl acrylate monomer was supplied by M/s Gujarat State Fertilizer Company (polymer unit), Vadodara, India. Ceric ammonium nitrate (CAN) and all other reagents were of the A.R. grade.

Synthesis of Na-PCMS

Na-PCMS was prepared as per our previously reported method.[33] A three-necked flask (250 mL) was equipped with stirrer, a gas inlet tube, and water condenser was placed in a constant temperature bath consisting of an electric bulb connected to a Rheostat, which helps in maintaining the desired temperature range by responding to the change in temperature fluctuation. Mixture of starch (5 g) in 150 mL isopropyl alcohol was stirred vigorously under nitrogen blanket for 15 min. After this, 20 mL of 30% (w/v) aqueous sodium hydroxide was added drop wise during next 15 min at room temperature. Stirring was continued for 1 h to activate starch. Then, 6 g sodium monochloroacetate was added slowly at 50°C. The temperature was kept constant for 5 h with continuous stirring. After completion of carboxymethylation, the reaction mixture was filtered through sintered glass G-2 funnel. The product was suspended in 300 mL of methanol and neutralized with acetic acid, filtered, and washed with methanol and dried at 60°C.

Optimization of reaction parameters to prepare BA-*g*-Na-PCMS

All the grafting reactions were conducted under nitrogen blanket. A three-necked flask equipped with stirrer, addition funnel, and a gas inlet system, immersed in a constant temperature bath was used as reaction kettle. In a typical graft copolymerization reaction, Na-PCMS (4 g) was stirred in double-distilled water (55 mL) and purged with a slow stream of nitrogen for 1 h at room temperature. A freshly prepared solution (10 mL) of 0.2 to 0.4M CAN in 0.1 to 0.5M HNO$_3$ was added and stirred for 20 min. Inhibitor-free butyl acrylate monomer (10 mL) was then added drop wise through addition funnel. The grafting reaction was carried out for varying time intervals (1–4.5 h) and at varying temperature (25–40°C). After completion of graft copolymerization reaction, the mixture was filtered and the
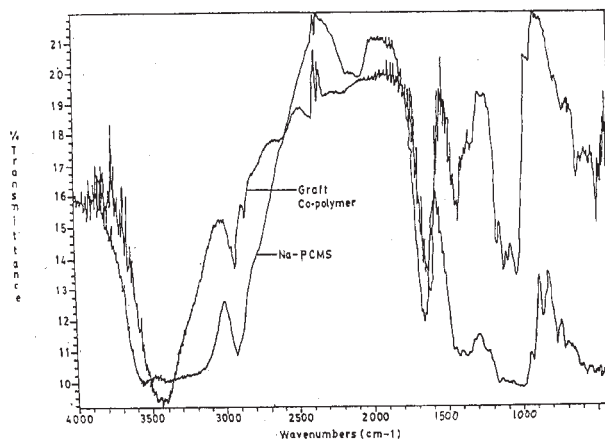

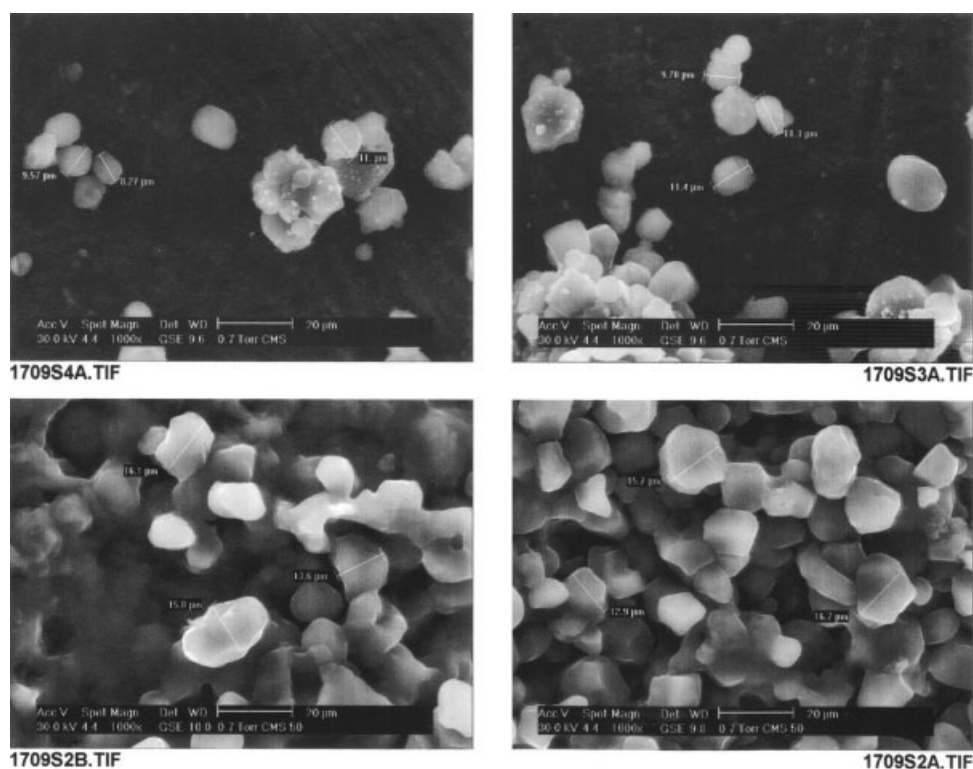**Figure 1** IR spectra of Na-PCMS and BA-*g*-Na-PCMS.

Figure 2 1709S3A and 1709S4A are the images of Na-PCMS (on the top) 1709S2A and 1709S2B are the images of BA-*g*-Na-PCMS (at the bottom).

crude product was washed with HNO_3 followed by distilled water. The crude copolymer thus obtained was dried under vacuum at 50°C. The crude copolymer was purified by extraction with dimethyl formamide (DMF). For this crude copolymer was stirred in DMF for 24 h. DMF dissolved homopolymer—poly(butyl acrylate) (PBA) from crude copolymer. After complete removal of homopolymer (PBA), the copolymer was dried under vacuum at 50°C. The weight obtained after PBA removal indicates the weight of actual graft copolymer. The weight of PBA incorporated in grafting (% add on) is then obtained by subtracting the weight of PCMS (4 g) from the weight of graft copolymer. The reaction scheme is shown in Scheme 1.

Grafting parameters like percent total conversion (%Ct), percent grafting (%G), percent grafting efficiency (%GE), and percent add on were evaluated by the following expressions:

1. Percent total conversion (%Ct): It shows the total increase in weight % of substrate (PCMS) before and after the grafting process. The formula for calculation is:

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

TABLE I
Grafting Yields for Graft Copolymerization of BA onto Na-PCMS:
Effect of Reaction Time

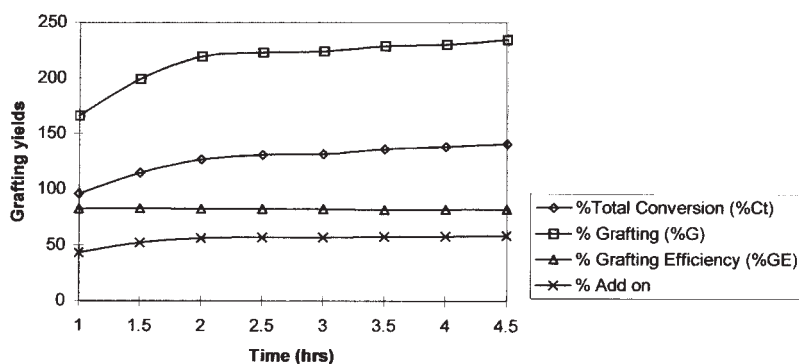| Time (h)	Percentage total conversion (%Ct)	Percentage grafting (%G)	Percentage grafting efficiency (%GE)	Percentage add-on (%add-on)
1	96.08	165.95	82.56	43.48
1.5	114.71	199.30	82.79	52.42
2	126.53	219.32	82.49	56.38
2.5	130.66	223.10	82.49	57.02
3	131.57	224.14	82.49	57.20
3.5	135.95	229.25	82.00	58.03
4	138.14	230.57	82.21	58.25
4.5	141.02	235.16	82.49	58.96

Figure 3 Effect of reaction time on grafting yields.

2. Percent grafting (%G): It shows the weight percent of polymer (PBA) actually grafted on the substrate (PCMS). The formula for calculation is:

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

3. Percent grafting efficiency (%GE): It is the efficiency in percentage of a polymer (PBA) to graft on the substrate (PCMS) under given set of conditions. The formula for calculation is:

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

4. Percent add on (%add on) = percent weight of PBA in 100 g of Na-PCMS.

RESULTS AND DISCUSSION

Evidence of grafting

1. The physical mixture obtained by dispersing BA-*g*-Na-PCMS (2.0 g) in DMF containing PBA (1.0 g) was stirred for 24 h at room temperature. After filtration, the residue was extracted with DMF for 48 h, when all the PBA was quantitatively removed leaving behind 1.978 g BA-Na-PCMS. This result shows that the homopolymer is quantitatively removed from the physical mixture by extraction.

2. The simplest method to prove the formation of the graft copolymer is based on the differences in solubility between the graft copolymer and the ungrafted homopolymer. BA-*g*-Na-PCMS is soluble in water and PBA is soluble in benzene. When the reaction product was Soxhlet-extracted with benzene and water alternatively for 48 h, an insoluble solid remained. A physical mixture of BA-*g*-Na-PCMS and PBA was treated in the same way and was found to dissolve completely.

3. Infrared spectral analysis was used to confirm the graft copolymerization reaction. The IR spectra of Na-PCMS and BA-*g*-Na-PCMS were recorded using KBr pellets on FTIR, Inkjet Nicolet 400D spectrophotometer. Figure 1 shows comparative IR spectra of Na-PCMS and BA-*g*-Na-PCMS. A key band is obtained at 1640 cm^{-1}, attributed to a carboxylic ester carbonyl group of PBA. No such band is present in the spectrum of Na-PCMS (Fig. 1). Thus, the presence of an addi-
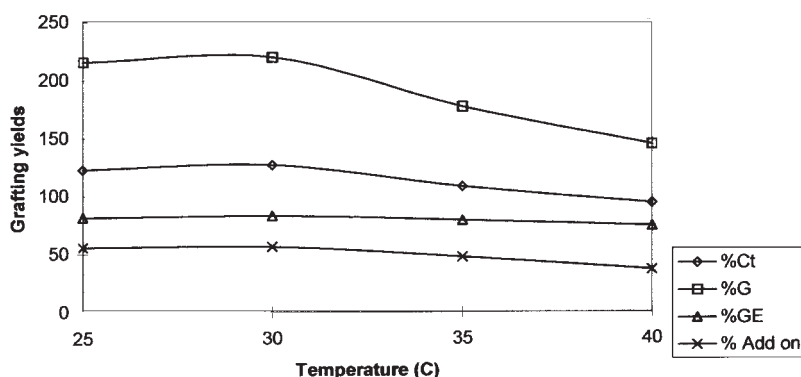

Figure 4 Effect of reaction temperature on grafting yields.

TABLE II
Grafting Yields for Graft Copolymerization of BA onto Na-PCMS:
Effect of Reaction Temperature

Temperature (°C)	Percentage total conversion (%Ct)	Percentage grafting (%G)	Percentage grafting efficiency (%GE)	Percentage add-on (%add-on)
25	122.65	215.45	81.59	55.69
30	126.52	219.32	82.49	56.21
35	107.63	176.66	78.42	47.09
40	93.00	143.77	73.38	36.04

tional band at 1640 cm^{-1} in the graft copolymer gives evidence for grafting which is a characteristic >C=O band of butyl acrylate. This band is not present in the IR spectrum of Na-PCMS.

4. Surface morphology of the graft copolymer prepared was evaluated with the help of scanning electron micrograph. Scanning electron microscope of make Philips XL 30 ESEM TMP + EDAX was used to get the surface morphological analysis. SEM micrograph of pure Na-PCMS and graft copolymers were taken. Images shown on top in Figure 2 (1709S3A and 1709S4A) are of pure Na-PCMS while image shown at bottom in Figure 2 (1709S2A and 1709S2B) are of graft copolymer. Comparison of scanning electron micrographs of grafted Na-PCMS and ungrafted Na-PCMS indicates that the surface morphology of Na-PCMS before grafting has small granular structure but shows increased granular size topography after treatment (as indicated by difference in particle size). Thus, comparison of these figures reveals that grafting has taken place.

Effect of reaction time

The results for effect of reaction time on graft copolymerization reaction are shown in Table I and Figure 3. It shows that the percent grafting proceeds at a faster rate up to 2.5 h followed by a slower rate of increase in percent grafting beyond 2.5 h. This is due to decrease in concentration of 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. The negligible variation of %GE values was observed with time and the value remains around 82%. It is observed that %G rises with a rapid initial rate and reaches to a value of 235.16% in 4.5 h. Beyond this time, it remains constant.

Effect of reaction temperature

The grafting is carried out at different temperature from 25 to 40°C keeping the other parameters constant (Fig. 4). 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 to 30°C, but decreased with further rise in temperature (30–40°C). Results show that initially the rise in temperature caused dissociation of initiator at high rate which in turn enhance the 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. %GE also decreases with the increase in temperature, which may be explained by the fact that solubility of monomer in the aqueous phase increases and acceleration of the termination reaction leads to formation of more homopolymer.

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 quantity (0.1 to 0.4M HNO$_3$). Addition of nitric acid to
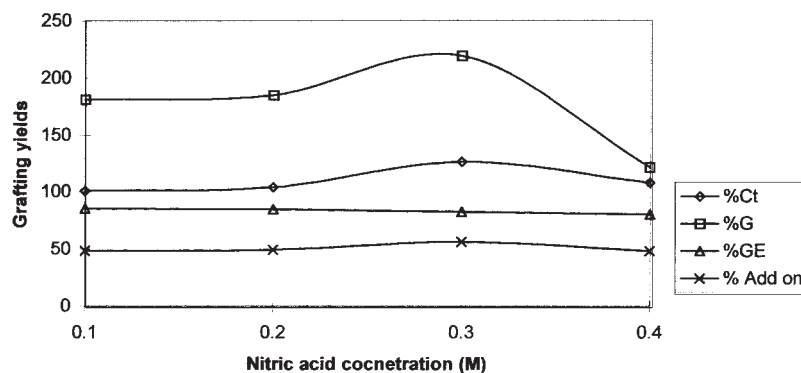

Figure 5 Effect of nitric acid concentration on grafting yields.

TABLE III
Grafting Yields for Graft Copolymerization of BA onto Na-PCMS:
Effect of Nitric Acid Concentration

Nitric acid concentration (mol/L)	Percentage total conversion (%Ct)	Percentage grafting (%G)	Percentage grafting efficiency (%GE)	Percentage add-on (%add-on)
0.1	101.02	180.94	85.46	48.52
0.2	103.90	184.76	84.82	49.18
0.3	126.52	219.32	82.49	56.38
0.4	107.98	121.16	80.10	48.28

CAN-initiated graft copolymerization (Fig. 5) may influence the reaction by two factors.

1. It may change the concentration of active species of Ce(IV) and
2. It may affect the formation of complex between Ce(IV) and monomer.

It is observed from the Table III that there exists an optimum nitric acid concentration (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 macroradical is less possible due to decrease in concentration. Also at higher acid concentration, the coagulation of colloidal homopolymer in solution increases during grafting and there is decrease in %G and %GE.

Effect of initiator concentration

The grafting parameters are presented in Table IV. It was observed that formation of homopolymer is less at low initiator concentration. The values of %G and %Ct increases rapidly in beginning. At 0.3*M* initiator concentration, a %G of 215% and %Ct 122.54% is obtained. A similar trend was observed with CAN concentration and %add-on. Further increase in concentration has adverse effect and decrease %G, %GE, and %add-on (Fig. 6).

Increase in the %G and %Ct at low initiator concentration (0.2–0.3 mol/L) may be due to the fact that the range of concentration activation along the backbone takes place immediately, followed by graft copolymerization of monomer onto backbone. High concentration of initiator may cause reduction in grafting due to an increase in the number of backbone radicals terminated prior to butyl acrylate additions. Furthermore, homopolymerization will be more at higher initiator concentration which competes with the grafting reaction for monomer availability. This leads to a decrease in the graft yield.

It is also observed from the Table IV that 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. It was suggested that higher the Ce(IV) concentration, greater will be the termination of growing grafted chains, resulting in reduction of %G as well as % GE. It is reasonable to expect a similar termination with increase in the initiator concentration, the consequence of which leads to a steady decrease in grafting efficiency.

CONCLUSIONS

Na-PCMS can be grafted successfully by using CAN as the redox initiator. Effect of various reaction parameters on %G, %GE, %Ct, and %add-on was evaluated. It was observed that reaction parameters significantly affect grafting characteristics of resulting copolymer. The maximum yield of graft copolymer was obtained at 0.3*M* CAN, 0.3*M* HNO$_3$, 4–4.5 h reaction time, and 25–30°C temperatures. The graft copolymer was

TABLE IV
Grafting Yields for Graft copolymerization of BA onto Na-PCMS: Effect of Ceric
Ammonium Nitrate (CAN) Concentration

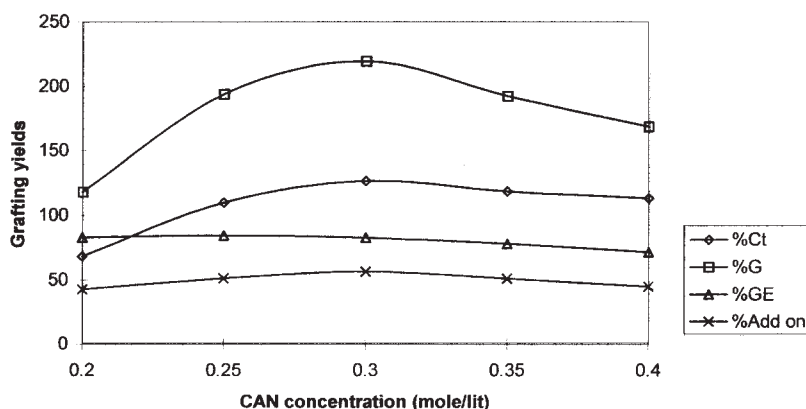| CAN concentration (mol/L)	Percentage total conversion (%Ct)	Percentage grafting (%G)	Percentage grafting efficiency (%GE)	Percentage add-on (%add-on)
0.20	68.41	117.73	82.89	42.80
0.25	109.70	193.99	84.24	51.35
0.30	126.52	219.32	82.49	56.38
0.35	118.12	192.37	77.72	50.99
0.40	112.74	168.34	71.50	44.71

Figure 6   Effect of CAN concentration on grafting yields.

characterized by solubility, IR spectrum, and SEM analysis.

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