Graft Copolymerization of Acrylamide–Methylacrylate Comonomers onto Cellulose Using Ceric Ammonium Nitrate

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ABSTRACT: The graft copolymerization of acrylamide–methylacrylate comonomers was carried out using ceric ammonium nitrate as initiator in the presence of nitric acid at 25 ± 1°C. The effects of feed molarity, feed composition, reaction time, and temperature on graft yield (%*G*) and other grafting parameters were investigated. The determination of rate of ceric (IV) ions disappearance as a function of feed molarity and reaction time was useful in the determination of the rate of ceric (IV) ions consumption during graft copolymerization. The graft yield (%*G*) in the presence of acrylamide increases because of the synergistic effect of acrylamide comonomer. The composition of the grafted chains (F_{AAm}) varies on varying the feed composition and reaction temperature but is almost constant during feed molarity variation. The Mayo and Lewis method was used to determine the reactivity ratios of acrylamide (r_1) and methylacrylate (r_2), which are 0.65 and 1.07, respectively. The product of reactivity ratio (r_1 r_2) is less then unity; hence, an alternate arrangement of comonomer blocks in the grafted copolymer chain is proposed. The rate of graft copolymerization of comonomers onto cellulose is second power to the concentration of comonomers and square root to the concentration of ceric ammonium nitrate. Suitable reaction steps for graft copolymerization of comonomers onto cellulose are proposed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2631–2642, 2002

Key words: graft copolymerizaton; cellulose; ceric ammonium nitrate; acrylamide; methylacrylate

INTRODUCTION

Graft copolymerization of vinyl monomers onto natural and synthetic polymers has advantages of adding properties of the monomer used for graft copolymerization. A considerable number of studies on graft copolymerization of single monomers onto cellulose using different methods of initiation has been reported.[1–5] But graft copolymerization of binary mixtures of vinyl monomers has special importance in comparison to simple grafting of individual monomers. This technique of grafting of monomer mixtures has the advantage of creating grafted chains with tailor-made properties for specific applications. The synergistic effect of the comonomer in grafting mixtures plays an important role in controlling the composition and graft yield onto cellulose. Very few reports are available about grafting of vinyl monomers from their mixtures onto cellulose.[6] The graft yield of acrylonitrile–methylmethacrylate comonomer mixtures decreases on increasing the acrylonitrile content in the feed.[6] The grafting of acrylic acid and styrene monomer mixtures onto polypropylene has been reported, and the composition of grafted chains was estimated by an infrared (IR) technique.[7] The composition of grafted chains has shown dependence on irradiation dose, feed composition, and the solvent used for graft copolymerization.[8] The graft copolymerization of vinyl monomers onto cellulose has been carried out using photosensitizers,[9,10] magnetic field,[11] radiation,[12] and redox initiators.[13] However, with these techniques, the extent of ungrafted homopolymer has been high in comparison with that from ceric (IV) ions-initiated grafting[14,15] in which homopolymerization of vinyl monomers has been minimal. The ceric (IV) ions readily form radicals at the cellulose backbone through a single electron transfer process.[16] However, the efficiency of ceric (IV) ions for grafting depends on the pH of medium.[17] Although grafting of acrylamide onto cellulose has been reported individually, the grafting of acrylamide in the presence of methylacrylate comonomer has not been reported so far in the literature. Therefore, we investigated the grafting of acrylamide using methylacrylate as comonomers onto cellulose in the presence of ceric (IV) ions in an acidic medium. In addition, we evaluated the effects of feed molarity and feed composition on graft yield and composition of grafted chains.

EXPERIMENTAL

Chemicals

Acrylamide (Loba Chemie, Mumbai, India) was purified by recrystallization from benzene and dried in a

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vacuum desiccator. Methylacrylate (E. Merck, India) was vacuum distilled and stored at <5°C. Ceric ammonium nitrate (CAN) and nitric acid were reagent grade chemicals and used without further purification. Cellulose powder (Mn = 4.1 $\times 10^5$ g mol^{-1}) was obtained from Loba Chemie, Mumbai, India and was washed with methanol and deionized water. This purified cellulose was treated for 24 h with sodium hydroxide at a concentration of 0.1 mol dm^{-3} and then dried under reduced pressure at room temperature on phosphorus pentaoxide.

Graft copolymerization

The graft copolymerization was carried out by adding 1.0 g of purified cellulose ($M_n = 4.1 \times 10^5$ g mol^{-1}) to 100 mL of a solution of 6.0×10^{-2} mol dm^{-3} nitric acid in a three-necked, round-bottom flask that was fitted with an electrically operated stirrer and kept in a thermostat maintained at 25 ± 0.1°C. A calculated amount of CAN was added to obtain a concentration of 7.5×10^{-3} mol dm^{-3} in the reaction mixture, and the solution was purged with nitrogen gas for 15 min to remove oxygen from the solution. To initiate grafting, calculated amounts of comonomers (1.278 g of acrylamide and 1.032 g of methylacrylate) were added to the reaction flask, and a constant supply of nitrogen in the reaction mixture was maintained until graft copolymerization was accomplished. The reaction was stopped by adding a 5.0% solution of hydroquinone (w/v) to the reaction mixture, and the graft product was obtained by pouring the reaction mixture into an excess of methanol. Finally, the product was separated by filtration and washed repeatedly with hot and cold water to remove unreacted acrylamide and methylacrylate monomers. During this washing, some ungrafted polyacrylamide was also removed. The purified grafted product was finally dried in vacuum desiccator.

Ceric (IV) ions consumption

To estimate the ceric (IV) ions used in graft copolymerization, an aliquot of 5.0 mL of reaction mixture was taken out and poured into excess ferrous ammonium sulfate solution. The ceric (IV) ions consumed in graft copolymerization were estimated by back titrating the excess ferrous ammonium sulfate with ceric sulfate in the presence of *o*-phenanthroline as indicator.

Extraction of ungrafted homopolymers

During graft copolymerization of acrylamide and methylacrylate onto cellulose, small amounts of ungrafted polyacrylamide and polymethylacrylate were also formed, which were coprecipitated on pouring the reaction mixture into the methanol. These ungrafted homopolymers were not removed during washing with water, so it was necessary to remove the ungrafted polyacrylamide and polymethylacrylate from the crude. To ensure complete removal of these ungrafted homopolymers, the grafted crude was Soxhlet extracted for 40 h with water and acetone. The extracted homopolymers were obtained by precipitating in methanol and were dried to constant weight for estimating other grafting parameters.

Extraction of ungrafted copolymers

The ungrafted copolymers were obtained by extracting the grafted crude with dimethylformamide (DMF) in a Soxhlet apparatus and precipitating in water. The molecular weights of the extracted copolymers were determined by gel permeation chromatography (GPC).

Extraction of ungrafted cellulose

The grafting of acrylamide and methylacrylate onto cellulose is expressed as apparent graft yield (%G) and as true graft yield (%G_T) by determining weight percent of grafted comonomers with respect to the amount of cellulose taken initially in the reaction mixture for grafting and with respect to the amount of cellulose on which grafting of comonomers has actually taken place after graft copolymerization, respectively. Hence, separation of cellulose was necessary to determine the true grafting (%G_T) and percent cellulose conversion (%C_c), characteristic parameters of graft polymerization. Therefore, after extracting the ungrafted homopolymers and copolymers from the crude, the ungrafted cellulose was extracted by keeping the cellulose sample in a cuoxam solution[18] containing 1.2% $NaHSO_3$ and stirring vigorously. At the end of 6 h, the residue was filtered, washed with dilute acetic acid and deionized water, and vacuum dried to a constant weight at 50°C.

Extraction of grafted copolymers

The grafted copolymers were obtained by hydrolyzing the cellulose extracted samples in 72% sulfuric acid[19] at 30°C. At the end of 4 h, the reaction mixture was diluted with water to an acid concentration of 4% and refluxed for 6 h. The copolymers were obtained by precipitating the filtrate in a water–methanol mixture (80:20). The composition of the grafted copolymers was determined by elemental analysis with a Perkin-Elmer 240 C Elemental Analyzer. The molecular weights of the copolymers were determined by GPC.

Characteristic grafting parameters

Percent graft yield (%G): Weight percent of grafted polymer with respect to initial weight of cellulose.
Percent true grafting (%G_T): Weight percent of grafted polymer with respect to actual weight of the cellulose on which grafting has taken place.
Percent homopolymer (%C_{hp}):Weight percent of monomer converted into ungrafted homopolymer.
Percent conversion (%C_g): Weight percent of the monomer converted into grafted polymer.
Percent cellulose conversion (%C_c): Weight percent of the initial cellulose that is grafted.
Percent efficiency (%G_E): Weight percent of total polymer that is grafted onto the cellulose.
Grafted frequency (G_F): Number of grafted polymer chains (N_{gp}) per chain of the cellulose.

Characterization

IR analysis

The IR spectra of grafted copolymers, recorded with a Perkin-Elmer-1600 FTIR (Fourier transform infrared) spectrophotometer, were used to determine the composition of grafted copolymers using percent transmittance (% T) at 1668 and 1750 cm^{-1} for the carbonyl group (>C═O) in acrylamide and methylacrylate, respectively. The optical density ratio (ODR), determined by using following relationship, was used to analyze the mole fractions of acrylamide (F_{AAm}) and methylacrylate (F_{MA}) in the grafted copolymers using the calibration curve of ODR versus the composition of known copolymers:

$$\text{ODR} = \frac{\log (\text{Baseline \% T}_{1750}/\text{MA \% T}_{1750})}{\log (\text{Baseline \% T}_{1668}/\text{AAm \% T}_{1668})} \quad (1)$$

Elemental analysis

Elemental analysis was used to prepare standard copolymers samples and to determine the composition of grafted copolymer chains onto the cellulose by estimating nitrogen contents with a Heraeus Carlo Ebra 1108 elemental analyzer.

Molecular weight measurements

The molecular weights of polyacrylamide[20] and polymethylacrylate were determined by a viscometric method using following equations:

$$[\eta]_{27^\circ c} = 6.8 \times 10^{-4}\ \text{cm}^3\ \text{g}^{-1}\ \bar{M}_V^{0.66} \quad \text{(for PAAm in 1 M } NaNO_3) \quad (2)$$

$$[\eta]_{20^\circ c} = 3.5 \times 10^{-4}\ \text{cm}^3\ \text{g}^{-1}\ \bar{M}_V^{0.81} \quad \text{(for PMA in butanone)} \quad (3)$$

The molecular weights of the grafted and ungrafted copolymers were determined with a gel permeation chromatograph (PL-GPC-120-UK) equipped with three PL-aqua gel columns in series (PL-aqua gel 40 10 μm, PL-aqua gel 50 10 μm, PL- aqua gel 60 10 μm) and an ultraviolet (UV) detector (λ_{max} = 208 nm). A 200-μL copolymer solution of 0.1 mg/mL was loaded and eluted with DMF at a flow rate of 1.0 mL/min at 25°C. The universal calibration curve was recorded with a polymethylmethacrylate calibration kit.

Thermal analysis

The thermal stability of the cellulose and grafted cellulose was determined by recording thermogravimetric (TG) and differential TG (DTG) thermograms with a Perkin-Elmer 7.0 System at a constant heating rate of 10°C/min under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The individual grafting of acrylamide onto cellulose was substantially low in comparison to the graft yield obtained with mixtures of acrylamide and methylacrylate comonomers in the solution. This result clearly indicates that the presence of methylacrylate has a synergistic effect on the acrylamide monomer for grafting onto cellulose.[21] The grafted chains obtained after hydrolyzing the grafted cellulose were purely copolymers of acrylamide and methylacrylate monomers, which clearly indicates that the grafting of monomers onto cellulose from their mixtures is highly influenced by their interactions in solution. Hence, grafted chains of acrylamide and methylacrylate on cellulose were missing during graft polymerization of acrylamide and methylacrylate comonomers from their mixtures onto cellulose in the presence of CAN as initiator. The free radical formation tendency of ceric (IV) ions onto the cellulose backbone by hydrogen ion abstraction[16] facilitates the participation of comonomers exclusively in graft copolymerization rather than the formation of homopolymers and ungrafted copolymers in the reaction mixture. At low concentration of nitric acid, the efficiency of ceric (IV) ions in the formation of active sites on the cellulose backbone was low because of the formation of a less active species of ceric (IV) ions in the reaction mixture; hence, the concentration of nitric acid was considerably more than the concentration of CAN. The IR spectra of polyacrylamide- and polymethylacrylate-grafted cellulose have additional bands at 1676 and 1783 cm^{-1}, corresponding to the carbamide group of acrylamide and the ester carbonyl group of the methylacrylate (Figure 1, spectrum B), respectively, which were not present in ungrafted cellulose (Figure 1, spectrum A). The absorption bands of copolymers on cellulose have shown variation on comparing absorp-

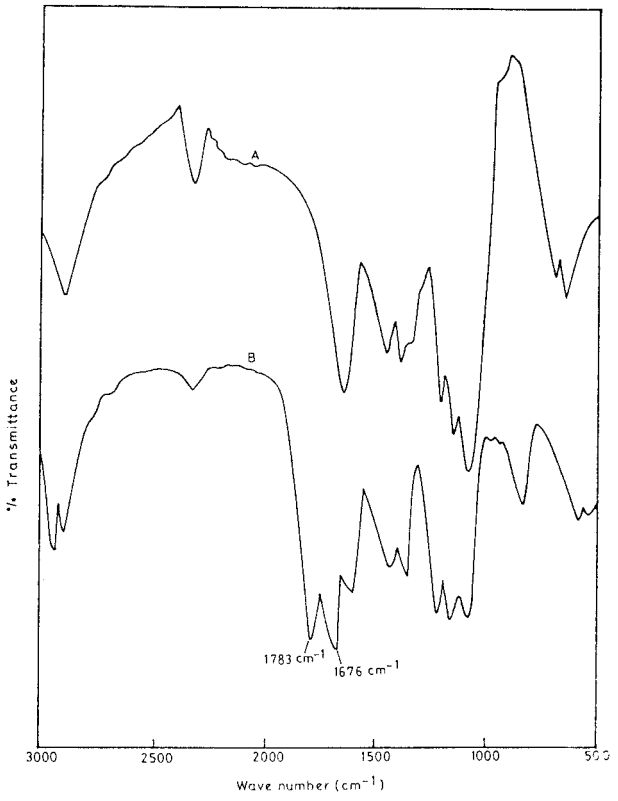


Figure 1 FTIR spectra of (A) cellulose and (B) poly(acrylamide-co-methylacrylate) copolymer grafted cellulose.

tion bands of ungrafted copolymers (1668 and 1750 cm^{-1}). Thermogravimetric analysis (TGA) results show high thermal stability for polyacrylamide- and polyacrylamide–methylacrylate copolymer-grafted cellulose in comparison with pure and polymethylacrylate-grafted cellulose (Figure 2). These results clearly indicate that graft copolymerization of a mixture of acrylamide and methylacrylate comonomers is useful to improve the thermal stability of the cellulose in comparison to polymethylacrylate-grafted cellulose. To gain further insight into the mechanism of grafting of comonomers onto cellulose, graft copolymerization was carried out at different feed molarities, feed compositions, and reaction times, and grafting parameters were evaluated to substantiate the effect of these experimental variations.

Effect of feed molarity

To investigate the effect of acrylamide and methylacrylate comonomer concentration on graft yield (% 9) and other grafting parameters, graft copolymerization was carried out while varying the feed molarity from 5.0×10^{-2} to 50.0×10^{-2} mol dm^{-3} at a fixed feed composition ($f_{AAm} = 0.6$) and at constant concentrations of CAN ($7.5.0 \times 10^{-3}$ mol dm^{-3}) and nitric acid (6.0×10^{-2} mol dm^{-3}) at 25°C. The percent graft yield (%G) and grafting parameters are shown in Figure 3a and Table I. The graft yield (%G) increased almost linearly on increasing the feed molarity up to 30.0×10^{-2} mol dm^{-3}, but this increase deviated from linearity on further increase in feed molarity beyond 30.0×10^{-2} mol dm^{-3} (Figure 3a). The increasing trends in true grafting (%G_T), percent graft conversion (%C_g), and efficiency of grafting (%G_E) clearly indicate that on increasing the feed molarity up to 30.0×10^{-2} mol dm^{-3}, the comonomers were consumed in the formation and growth of the grafted chains onto the cellulose (Table Ia). This result is also apparent from the increasing trend in cellulose conversion (%C_c) on increasing the feed molarity. At high feed molarity ($>30.0 \times 10^{-2}$ mol dm^{-3}), the viscosity of the medium increased, which retarded the rate of diffusion of monomeric units from the solution phase to the active sites at the cellulose. Therefore, the grafting parameters show a decreasing trend on increasing the feed molarity beyond 30.0×10^{-2} mol dm^{-3}. At high feed molarity, the swelling effect of the solvent on cellulose also decreased; hence, grafting of copolymer chains was confined to the cellulose surface rather than to the matrix of the cellulose. This phenomenon resulted in a decrease in the number of grafting chains (N_{gp}) and frequency of grafting (G_F) at high feed molarity ($>30.0 \times 10^{-2}$ mol dm^{-3}; Table Ib). This decreasing trend in graft copolymerization resulted in a substantial increase in the rate of formation of ungrafted homopolymers (%C_{hp}) and copolymers (%C_{cp}; Table Ia). The

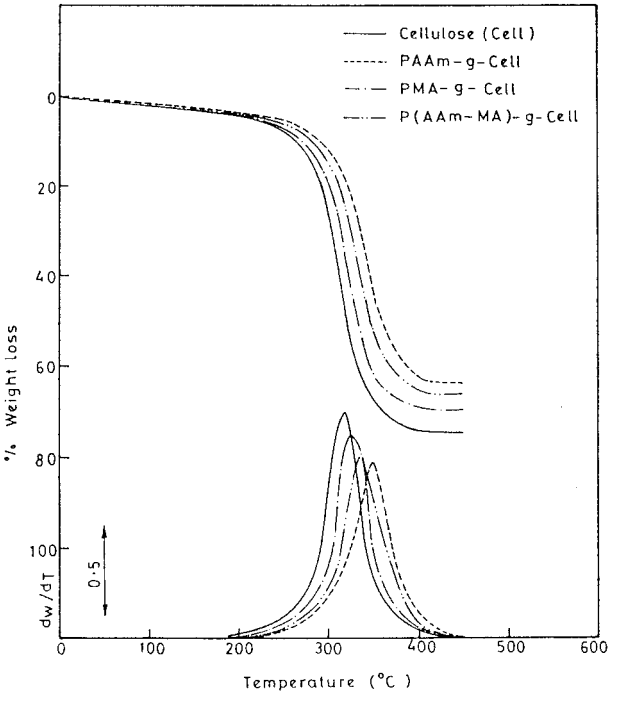
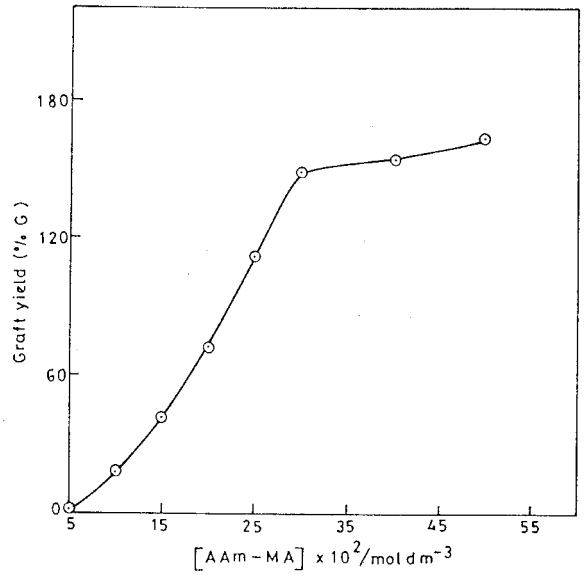
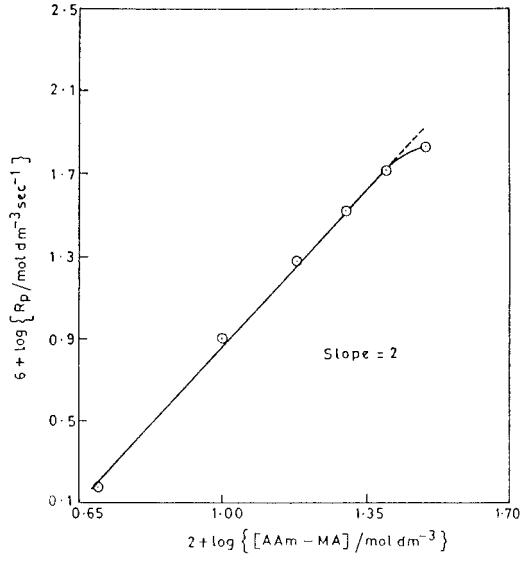


Figure 2 TGA and DTGA curves of cellulose and grafted cellulose.



(a)



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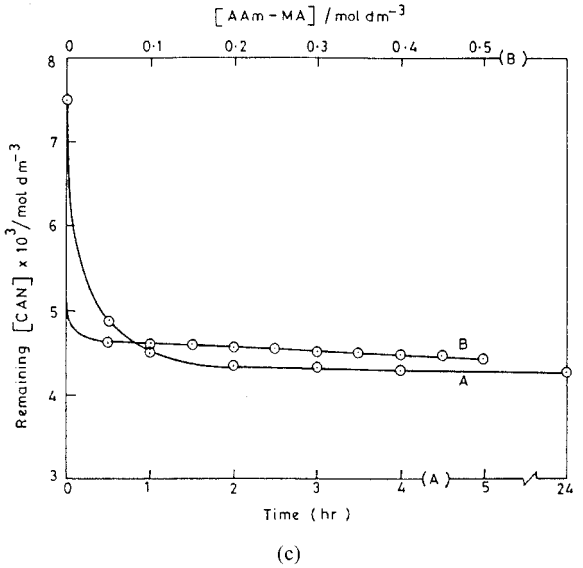


(c)

number (N_{cp}) and molecular weights of the ungrafted copolymers [M_w (Cp)] also increased on increasing the feed molarity beyond 30.0×10^{-2} mol dm^{-3} (Table Ib). The dispersity ($\bar{M}_w/\bar{M}_n$) in molecular weight of grafted copolymers was minimal (1.62) at a feed molarity of 15.0×10^{-2} mol dm^{-3}, but was significant above and below 15.0×10^{-2} mol dm^{-3} feed molarity (Table Ib). The composition of the grafted copolymers (F_{AAm}) during feed molarity variation was constant, which indicates that the monomer–monomer interactions were almost constant during feed molarity variations. The rate of graft copolymerization (R_P) of comonomers was estimated at different feed molarity and used to estimate order of graft copolymerization by drawing a plot between log R_P versus [AAm-MA], which shows a second order with respect to the concentration of comonomers (Figure 3b).

The effect of feed molarity variation has also been investigated on rate of ceric (IV) ions disappearance, as shown in Figure 3c. The results clearly indicate that on varying the feed molarity, the rate of ceric (IV) ions disappearance did not change. This result provides evidence that ceric (IV) ions were not directly involved in the formation of active radicals onto the monomers, which would have resulted in a significant variation in the rate of ceric (IV) ions consumption on varying the feed molarity.

Effect of feed composition

To evaluate the effect of monomer–monomer interactions on graft yield and composition of grafted copolymer chains, the graft copolymerization of acrylamide–methylacrylate comonomers was carried out at different mole fractions of the acrylamide (f_{AAm}) in the feed at constant feed molarity (30.0×10^{-2} mol dm^{-3}) of comonomers and at constant concentrations of the CAN (7.5×10^{-3} mol dm^{-3}) and nitric acid (6.0×10^{-2} mol dm^{-3}). The extent of graft yield (%G) using individual monomers was also determined to compare the effect of comonomer on grafting parameters. The data are shown in Figure 4a and Table II. The graft yield (%G) as a function of mole fraction of acrylamide (f_{AAm}), shown in Figure 4a, clearly indicates an increasing effect of mole fraction of acrylamide (f_{AAm})

Figure 3 (a) Graft yield (%G) as a function of feed molarity: [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [cellulose] = 1.0 g, time = 60 min, temperature = 25°C. (b) Log–log plot of R_p versus [AAm-MA]: [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-3} mol dm^{-3}, f_{AAm} = 0.6, [cellulose] = 1.0 g, time = 60 min, temperature = 25°C. (c) Ceric (IV) ions consumption as a function of reaction time (A) and feed molarity (B): f_{AAm} = 0.6, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, temperature = 25°C, [AAm-MA] = 30.0×10^{-2} mol dm^{-3} (A).

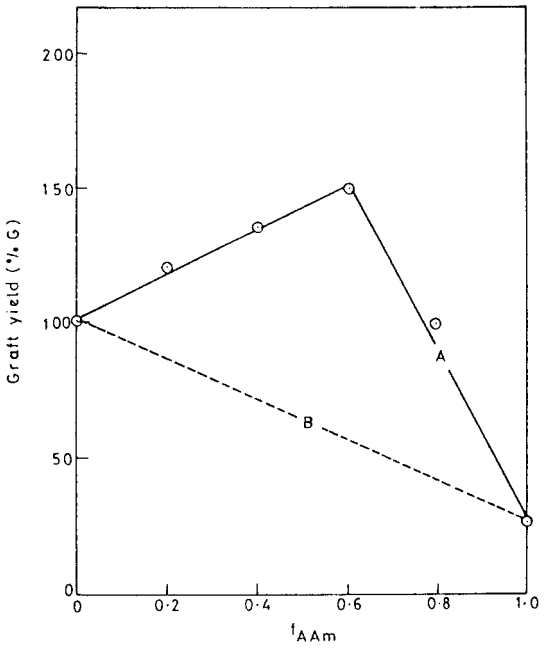
TABLE I
Effect of Comonomer Concentration on Grafting Parameters at 25°C[a,b]

a	[AAm-MA] × 10^2 mol dm^{-3}	% G_T	% C_T	% C_g	% C_{cp}	% C_c	% G_E
	5.0	235	13.40	10.38	1.87	31.00	28.43
	10.0	246	26.00	22.98	1.68	34.00	88.50
	15.0	253	40.29	35.98	2.33	40.00	89.24
	20.0	258	51.94	46.94	2.20	48.00	91.86
	25.0	307	63.26	58.18	2.43	52.00	92.56
	30.0	344	69.26	64.50	2.42	56.00	93.12
	40.0	330	70.00	50.00	8.19	59.00	71.62
	50.0	319	71.00	42.59	12.17	63.00	60.07

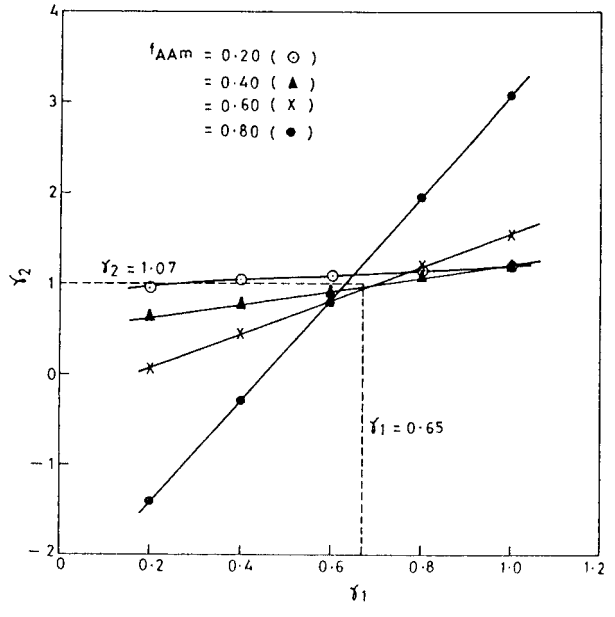
b	[AAm-MA] × 10^2 mol dm^{-3}	G_F	$N_{gp} \times 10^6$	$N_{cp} \times 10^6$	$\bar{M}_w \times 10^{-3}$ (G_p)	$\bar{M}_w/\bar{M}_n$ (G_p)	$\bar{M}_w \times 10^{-3}$ (C_p)
	5.0	0.40	0.18	0.18	387	1.95	73
	10.0	0.82	0.68	0.29	428	1.64	81
	15.0	1.24	1.33	0.44	502	1.62	99
	20.0	1.73	2.03	0.47	614	1.73	139
	25.0	2.13	2.69	0.48	772	1.86	188
	30.0	2.48	3.38	0.49	845	1.92	228
	40.0	2.50	3.58	2.63	925	2.15	260
	50.0	2.63	3.90	4.78	991	2.36	261

[a] [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [cellulose] = 1.0 g, time = 60 min.

on graft yield (%*G*). This increasing effect of acrylamide comonomer on graft yield (%*G*) was evident up to 0.6 mol fraction of acrylamide (f_{AAm}) in the feed and sharply decreased on further increase of acrylamide mole fraction (f_{AAm}) beyond 0.6 mol fraction. Similar trends were observed with true grafting (%G_T), percent graft conversion (%*C*g), and efficiency of grafting (G_E), as shown in Table IIa. At high mole fraction of acrylamide ($f_{AAm} > 0.6$ mol), the frequency of grafting (G_F) and number of grafted chains (N_g) also increased (Table IIb). The decreasing trend in cellulose conversion (%C_c) beyond 0.6 mol fraction of acrylamide (Table IIa) clearly indicates that acrylamide has a low affinity of grafting onto cellulose; hence, the magnitude of grafting parameters decreased with a reaction mixture with a high mole fraction of acrylamide ($f_{AAm} > 0.6$ mol). At high mole fraction of acrylamide ($f_{AAm} > 0.6$ mol), the acrylamide–acrylamide interactions became stronger than the acrylamide–methylacrylate interactions; hence, grafted chains were formed with a higher mole fraction of acrylamide ($F_{AAm} = 0.74$) than of methylacrylate ($F_{MA} = 0.26$) (Table IIc). The grafted chains were of pure acrylamide when the mole fraction of the acrylamide (f_{AAm}) in the feed reached unity (Table IIa). The ungrafted homopolymers (%C_{hp}) and copolymers (%C_{cp}) continued to increase beyond 0.6 mol fraction of acrylamide, but overall conversion (%C_T) showed a decreasing trend at high mole fraction of acrylamide ($f_{AAm} > 0.6$ mol; Table IIa). The molecular weight of grafted copolymers (M_w of Gp) increased on increasing the mole fraction of the acrylamide from 0.2 to 0.6, but on further increases in the mole fraction of acrylamide beyond 0.6, the M_w of Gp showed a decreasing trend (Table IIb). The compositional analysis of the grafted chains by elemental and IR studies indicates the synergistic effect of the acrylamide on methylacrylate. The presence of acrylamide increased the mole fraction of methylacrylate into the grafted copolymer chains, as is clear from the data shown in Table IIc. The compositional data were used to determine the reactivity ratios of acrylamide (r_1) and methylacrylate (r_2) by the Mayo and Lewis Method,[22] as shown in Figure 4b. The values of reactivity ratios of acrylamide (r_1) and methylacrylate (r_2), 0.65 and 1.07, respectively, clearly indicate that acrylamide has low reactivity in comparison to methylacrylate. The average sequence lengths of acrylamide ($\bar{m}M_1$) and methylacrylate ($\bar{m}M_2$), calculated as a function of feed composition, increased on increasing the mole fraction in the feed (Table IIc). The run number (*R*) increased up to 0.6 mol fraction of acrylamide (f_{AAm}), but on further increase of the mole fraction of acrylamide (f_{AAm}) beyond 0.8, the run number (*R*) decreased because of the high average sequence lengths of acrylamide block ($\bar{m}M_1$) in the grafted copolymer chains. On increasing the mole fraction of the acrylamide (f_{AAm}), the probability ($P_{AAm\text{-}AAm}$) of addition of acrylamide monomer to the growing chains ended as the acrylamide monomer increased, as clearly indicated by the values shown in Table IIc. The product of the reactivity ratios r_1 and r_2 is less than unity; hence, sequence lengths of acrylamide ($\bar{m}M_1$) and methylacrylate ($\bar{m}M_2$) in the grafted copolymer chains have been assumed to be arranged in the following alternating fashion:



(a)



(b)

Figure 4 (a) Percent graft yield (%*G*) as a function of feed composition (f_{AAm}): [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, time = 60 min, temperature = 25°C. (b) Mayo and Lewis plot for reactivity ratios: [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, time = 60 min, temperature = 25°C.

$$\text{-(AAm)}_{\bar{m}M_1}\text{-(MA)}_{\bar{m}M_2}\text{-(AAm)}_{\bar{m}M_1}\text{-(MA)}_{\bar{m}M_2}\text{-}$$

The values of sequence lengths mM_1 and mM_2 depend on feed composition (f_{AAm}) or the factors that affect the monomer–monomer interactions in the feed.

Effect of ceric (IV) ions concentration

The grafting parameters of acrylamide–methylacrylate comonomers have also been evaluated at different concentrations of CAN ranging from 1.5 to 12.0×10^{-3} mol dm^{-3} at constant feed molarity (30.0×10^{-2} mol dm^{-3}), feed composition (f_{AAm} = 0.6), and concentration of nitric acid (6.0×10^{-2} mol dm^{-3}). The grafting parameters as a function of CAN concentration are shown in Table III and Figure 5a.On increasing the CAN concentration from 1.5×10^{-3} mol dm^{-3} to 7.5×10^{-3} mol dm^{-3}, the graft yield (%*G*) and other grafting parameters showed an increasing trend (Figure 5a and Table III). On further increasing the concentration of CAN beyond 7.5×10^{-3} mol dm^{-3}, the grafting parameters showed a decreasing trend (Figure 5a). The initial increases in graft yield (%*G*), true grafting (%G_T), and graft conversion (%C_g) have been attributed to the formation of active ceric (IV) ions from CAN in the presence of sufficient amount of nitric acid (6.0×10^{-2} mol dm^{-3}). The ceric (IV) ions so produced created sufficient active sites on the cellulose backbone to initiate graft copolymerization of comonomers. The increasing trends in cellulose conversion (%C_c) and frequency of grafting (G_F) up to 7.5×10^{-3} mol dm^{-3} concentration of CAN strongly support the explanation that ceric (IV) ions were consumed in the formation of active sites on the cellulose backbone. With the further increase in CAN concentration beyond 7.5×10^{-3} mol dm^{-3}, the graft yield (%*G*) and graft conversion (%C_g) showed a decreasing trend. A similar effect was observed on number of grafted chains (N_{gp}) and frequency of grafting (G_F), as shown in Table IIIb. The increasing trend in cellulose conversion (%C_c) at the high concentration of CAN (>7.5×10^{-3} mol dm^{-3}) has been attributed to the oxidative degradation of cellulose[23,24] by excess ceric (IV) ions in the reaction mixture, which is also clear from the decreasing trend in frequency of grafting (G_F) and number of grafted chains (N_{gp}; Table IIIb). This decreasing trend in grafting parameters at higher concentration of CAN (>7.5×10^{-3} mol dm^{-3}) is due to insufficient amount of nitric acid (6.0×10^{-2} mol dm^{-3}) to generate reactive ceric (IV) ions from CAN to produce active sites onto the cellulose backbone. In absence of sufficient amount of nitric acid, the ceric (IV) ions are hydrolyzed and therefore not capable of creating active sites on the cellulose backbone (Table IIIa). The decreasing trend in graft yield (%*G*) and other grafting parameters is also due to the steric hindrance created by the grafted chains on the cellulose backbone; hence, the efficiency of ceric (IV) ions to create active centers on the cellulose backbone was decreased. The effect of CAN on the rate of graft copolymerization (R_P) was evaluated and used to calculate the order of graft copolymerization reaction with respect to

TABLE II
Effect of Feed Composition (f_{AAm}) on Grafting Parameters at 25°C[a,b,c]

a	f_{AAm}	% G_T	% C_T	% C_g	% C_{cp}	% C_c	% G_E
	0.00	316	41.86	38.75	3.10	48.00	92.59
	0.20	323	51.80	48.19	1.08	52.00	93.02
	0.40	335	60.41	56.25	1.58	54.00	93.10
	0.60	344	69.26	64.50	2.42	56.00	93.12
	0.80	316	51.35	45.04	2.88	48.00	87.71
	1.00	293	21.59	12.20	9.38	32.00	56.52

b	f_{AAm}	G_F	$N_{gp} \times 10^6$	$N_{cp} \times 10^6$	$\bar{M}_w \times 10^{-3}$ (G_p)	$\bar{M}_w/\bar{M}_n$ (G_p)	$\bar{M}_w \times 10^{-3}$ (Cp)
	0.00	1.49	2.56	0.82	874	2.24	231
	0.20	2.29	2.89	0.35	772	1.86	178
	0.40	2.41	3.17	0.36	803	1.89	229
	0.60	2.48	3.38	0.49	885	1.92	228
	0.80	2.36	2.77	0.66	706	1.96	177
	1.00	2.33	1.04	1.64	503	2.12	261

c	f_{AAm}	% Cellulose in graft	% Branches in graft	F_{AAm}	% N	$\bar{m}$ M_1	$\bar{m}$ M_2	R	$P_{(AAm,AAm)}$
	0.00	32	68	0.00	—	—	—	—	0.00
	0.20	30	70	0.18	2.91	1.14	5.90	28.40	0.14
	0.40	29	71	0.37	6.47	1.38	2.82	47.62	0.30
	0.60	27	73	0.55	9.79	1.80	1.87	54.49	0.49
	0.80	32	68	0.74	13.50	2.83	1.38	47.50	0.72
	1.00	55	45	1.00	19.61	—	—	—	1.00

[a,b,c] [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.50×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, time = 60 min, temperature = 25°C, [cellulose] = 1.0 g; $\bar{m}M_1$ and $\bar{m}M_2$ are the average sequence lengths of AAm and MA monomers in the grafted copolymer chains (G_p), respectively.

the concentration of CAN. The slope of log–log plot of R_P versus [CAN] is 0.5, which indicates square root dependence on the concentration of CAN (Figure 5b).

Effect of reaction time

To analyze the effect of reaction time on grafting parameters, the graft copolymerization was carried out at dif-

TABLE III
Effect of [CAN] on Grafting Parameters at 25°C[a,b]

a	[CAN] $\times 10^3$ mol dm^{-3}	% G_T	% C_T	% C_g	% C_{cp}	% C_c	% G_E
	1.5	292	31.84	28.39	1.03	42.0	89.04
	3.0	328	44.16	40.25	1.38	45.0	91.17
	4.5	346	51.50	47.61	1.90	47.0	91.66
	6.0	340	60.00	55.84	1.94	52.0	92.80
	7.5	344	69.26	64.5	2.42	56.0	93.12
	9.0	338	66.66	61.29	2.51	55.0	92.15
	10.5	333	63.05	57.37	2.46	53.5	91.03
	12.0	326	60.72	54.34	2.46	53.0	90.00

b	[CAN] $\times 10^3$ mol dm^{-3}	G_F	$N_{gp} \times 10^6$	$N_{cp} \times 10^6$	$M_w \times 10^{-3}$ (Gp)	M_w/M_n (Gp)	$M_w \times 10^{-3}$ (Cp)
	1.5	1.32	1.35	0.16	1210	2.52	405
	3.0	1.83	2.00	0.23	1023	2.20	341
	4.5	2.10	2.41	0.32	810	1.78	256
	6.0	2.28	2.88	0.34	831	1.86	251
	7.5	2.48	3.38	0.49	845	1.92	228
	9.0	2.41	3.24	0.51	935	2.15	268
	10.5	2.36	3.08	0.52	984	2.30	267
	12.0	2.32	3.00	0.54	1033	2.46	264

[a,b] [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol. dm^{-3}, f_{AAm} = 0.6, [cellulose] = 1.0 g, time = 60 min.

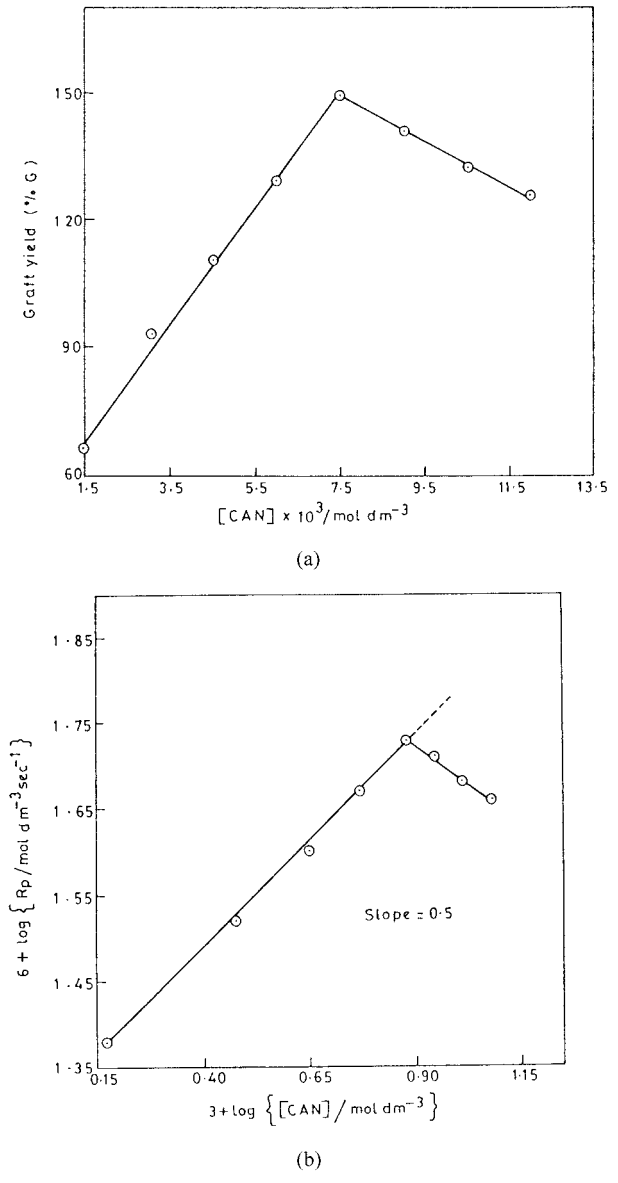


Figure 5 (a) Percent graft yield (%*G*) as a function of [CAN]: [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, time = 60 min, temperature =25°C. (b) Log–log plot of R_p versus [CAN]: [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, time = 60 min, temperature = 25°C.

ferent time intervals at constant concentrations of comonomers (30.0×10^{-2} mol dm^{-3}), CAN (7.5×10^{-3} mol dm^{-3}), and nitric acid (6.0×10^{-2} mol dm^{-3}) and at constant composition of the feed (f_{AAm} = 0.6). The graft yield (%*G*), determined from cellulose samples collected at different intervals of reaction time, indicates a substantial increasing trend up to 8 h and a leveling off after 8 h when the graft yield becomes almost constant (Table IVa and Figure 6). Similar trends are exhibited by true grafting (%G_T), percent graft conversion (%C_g), efficiency of grafting (% G_E), and frequency of grafted chains (G_F) onto cellulose (Tables IVa and IVb). The increasing trend in cellulose conversion (%C_c), on increasing reaction time has clearly indicated that the extent of grafting has increased because of the formation of new grafted chains on active sites on the cellulose backbone that were previously lying unutilized. This explanation is also clear from the increasing trend in the frequency of grafting (G_F) and the number of grafted chains (N_{gp}) seen on increasing the reaction time of graft copolymerization. The plateau in the graft yield curve (Figure 6) after 8 h has been attributed to the decrease in activity of the comonomers in the feed after 8 h; hence, the rate of diffusion of the comonomers has also decreased from solution phase to cellulose backbone where growth of polymer chains was in progress. The steric hindrance offered by the grafted chains onto the cellulose has also contributed significantly to retarding the rate of grafting after 8 h of graft copolymerization. These investigations have clearly indicated that a constant rate of graft copolymerization may be achieved by maintaining a constant supply of comonomers in the reactor. The steric hindrance of grafted copolymer chains may be reduced by using solvent with sufficient swelling effect on cellulose that a constant rate of diffusion of comonomers in the cellulose matrix could be maintained. The effect of reaction time was also estimated on ceric (IV) ions disappearance, as shown Figure 3a. The extent of ceric (IV) ions disappearance was maximum up to 1 h of the reaction time and after 1 h, the ceric (IV) ions consumption became almost zero as indicated by the constant concentration of the remaining ceric (IV) ions in the solution (Figure 3a). This result indicates that all active sites on the cellulose backbone were formed during the initial first hour of graft copolymerization and that after 1 h, the ceric (IV) ions participation in formation of active sites on the cellulose was negligible. This phenomenon has been attributed to retardation in rate of diffusion of ceric (IV) ions from the solution phase to cellulose[19] due to the hindrance offered by the grafted chains onto the cellulose backbone. The increasing trend in molecular weights ($\bar{M}_w$) of the grafted copolymer chains (G_p) and ungrafted copolymer chains (C_P) has been attributed to continued growth of growing chains by the addition of the monomeric units (Table IVb). The increasing trend in the molecular weight ($\bar{M}_w$) of the grafted and ungrafted chains on increasing the reaction time has clearly indicated that the premature termination of the grafted chains has not taken placed at different intervals of graft copolymerization.

Effect of temperature

The graft copolymerization of acrylamide–methylacrylate comonomers onto cellulose was also studied at dif-

TABLE IV
Effect of Reaction Time on Grafting Parameters at 25°C[a,b,c]

a	Time (min)	% G_T	% C_T	% C_g	% C_{cp}	% C_c	% G_E
	30	338	65.36	61.03	2.37	55.0	92.76
	60	344	69.26	64.50	2.42	56.0	93.12
	120	353	75.49	70.56	2.59	58.0	93.46
	180	355	78.13	73.16	2.72	59.0	93.62
	240	356	80.43	75.32	2.85	60.0	93.64
	300	361	82.68	77.48	3.03	60.5	93.71
	360	363	84.24	79.00	3.07	61.0	93.78
	420	364	85.15	79.87	2.98	61.2	93.79
	480	364	86.75	81.38	2.98	62.0	93.81
	1440	367	89.91	84.41	2.72	63.1	93.88

b	Time (min)	G_F	$N_{gp} \times 10^6$	$N_{cp} \times 10^6$	$\bar{M}_w \times 10^{-3}$ (Gp)	$\bar{M}_w/\bar{M}_n$ (Gp)	$\bar{M}_w \times 10^{-3}$ (Cp)
	30	2.39	3.21	0.48	845	1.93	223
	60	2.48	3.38	0.49	845	1.92	228
	120	2.60	3.67	0.51	861	1.94	235
	180	2.60	3.73	0.53	886	1.96	242
	240	2.61	3.82	0.59	901	1.98	254
	300	2.64	3.89	0.57	966	2.10	261
	360	2.64	3.92	0.57	1000	2.15	269
	420	2.64	3.94	0.55	1020	2.18	277
	480	2.64	4.00	0.54	1034	2.20	285
	1440	2.65	4.08	0.49	1102	2.30	314

[a,b] [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [cellulose] = 1.0 g.

ferent temperatures ranging from 20 to 50°C at constant feed molarity (30.0×10^{-2} mol dm^{-3}), feed composition (f_{AAm} = 0.6), and concentrations of CAN (7.5×10^{-3} mol dm^{-3}) and nitric acid (6.0×10^{-2} mol dm^{-3}). The graft yield (%G), graft conversion (%C_g), and efficiency of grafting (G_E) increased up to 40°C and decreased on further increasing the temperature beyond 40°C (Table Va and Figure 7a). Similar trends in frequency of grafting (G_F) and number of grafted chains (N_{gp}) were noted, as shown in Table Vb. On increasing the temperature beyond 40°C, the cellulose conversion (%C_c) increased (Table Va). This trend is attributed to the oxidative degradation of cellulose at higher temperature. The molecular weights ($\bar{M}_w$) of grafted (Gp) and ungrafted (Cp) copolymers showed a decreasing trend on increasing the temperature that is due to the enhanced rate of chain termination at high temperature (Table Vb). The reactivity ratios of acrylamide (r_1) and methylacrylate (r_2) showed dependence on temperature, which clearly indicates that the reactivity of growing radicals was changed on changing the reaction temperature. This variation in reactivity ratios has shown variation in average sequence lengths ($\bar{m}M_1$ and $\bar{m}M_2$), run number (R), and probability in addition of acrylamide ($P_{AAm, AAm}$), as is clear from the data shown in Table Vc. The values of rate constant (k) of graft copolymerization of acrylamide–methylacrylate comonomers determined as a function of temperature were used to calculate the energy of activation by Arrhenius plot (Figure 7b) as 6.96 kJ mol^{-1}.

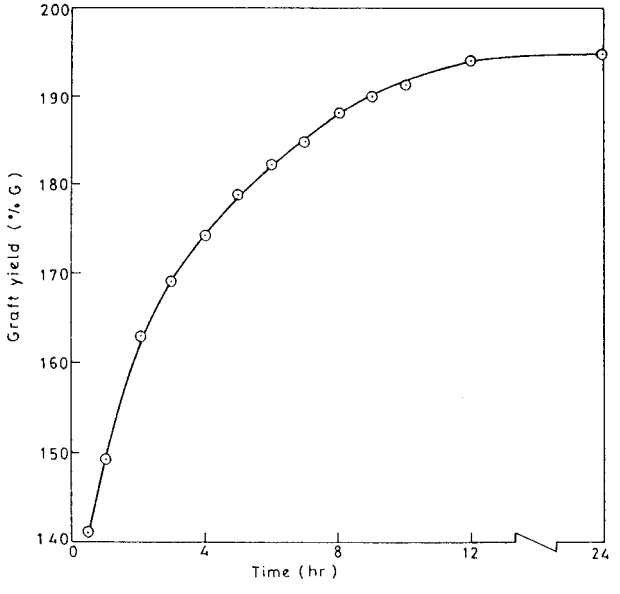


Figure 6 Percent graft yield (%G) as a function of reaction time: [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3},HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] =1.0 g, f_{AAm} = 0.6, temperature = 25°C.

Thus, on the basis of experimental observations, the following reaction steps have been proposed for graft copolymerization of the binary mixture of acrylamide–methylacrylate comonomers onto cellulose in the presence of CAN as initiator.

TABLE V
Effect of Temperature on Grafting Parameters[a,b,c]

a	Temperature (°C)	% G_T	% C_T	% C_g	% C_{cp}	% C_c	% G_E
	20	343	67.09	62.33	2.59	55.0	92.90
	25	344	69.26	64.50	2.42	56.0	93.12
	30	351	71.42	67.09	2.07	56.5	93.93
	35	353	74.45	70.56	1.73	58.0	94.76
	40	357	77.05	73.59	1.29	59.0	95.50
	50	325	74.45	70.99	1.55	62.0	95.35

b	Temperature (°C)	G_F	$N_{gp} \times 10^6$	$N_{cp} \times 10^6$	$\bar{M}_w \times 10^{-3}$ (Gp)	$\bar{M}_w/\bar{M}_n$ (Gp)	$\bar{M}_w \times 10^{-3}$ (Cp)
	20	2.41	3.23	0.517	935	2.10	261
	25	2.48	3.38	0.486	845	1.92	228
	30	2.61	3.58	0.495	855	1.98	226
	35	2.69	3.83	0.510	893	2.10	230
	40	2.86	4.06	0.537	920	2.20	223
	50	2.66	4.02	0.494	939	2.30	221

c	Temperature (°C)	% Cellulose in graft	% Branches in graft	F_{AAm}	% N	$\bar{m}M_1$	$\bar{m}M_2$	R	$P_{AAm,AAm}$
	20	28.21	71.79	0.52	9.31	1.68	2.06	53.47	0.48
	25	27.32	72.68	0.55	9.92	1.79	1.87	54.64	0.49
	30	26.71	73.29	0.55	9.92	1.96	1.80	53.19	0.54
	35	26.24	73.76	0.54	9.67	1.82	1.90	53.76	0.51
	40	25.76	74.24	0.52	10.20	1.68	2.05	53.61	0.48
	50	26.13	73.87	0.47	8.29	1.42	2.49	51.15	0.41

[a,b,c] [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [cellulose] = 1.0 g, time = 60 min; $\bar{m}M_1$ and $\bar{m}M_2$ are the average sequence lengths of AAm and MA monomers in the grafted copolymer chains (Gp); respectively.

Radical Formation:

$$\text{Cell—H} + \text{Ce(IV)} \xrightarrow{k} \underset{(\text{R}^{\cdot})}{\text{Cell}^{\cdot}} + \text{Ce(III)} + \text{H}^{+} \quad (4)$$

Initiation:

$$\text{R}^{\bullet} + \text{AAm} \xrightarrow{k_i} \text{R—AAm}^{\cdot}\text{—} \quad (5)$$

$$\text{R}^{\bullet} + \text{MA} \xrightarrow{k_i} \text{R—MA}^{\cdot}\text{—} \quad (6)$$

Propagation:

$$\text{R—(AAm)}_{n-1}\text{—AAm}^{\cdot}\text{—} + \text{AAm} \xrightarrow{k_p} \text{R—(AAm)}_n\text{—AAm}^{\cdot}\text{—} \quad (7)$$

$$\text{R—(MMA)}_{m-1}\text{—MA}^{\cdot}\text{—} + MA \xrightarrow{k_p} \text{R—(MA)}_m\text{—MA}^{\cdot}\text{—} \quad (8)$$

$$\text{R—(AAm)}_{n-1}\text{—AAm}^{\cdot}\text{—} + \text{MA} \xrightarrow{k_p} \text{R—(AAm)}_n\text{—MA}^{\cdot}\text{—} \quad (9)$$

$$\text{R—(MA)}_{m-1}\text{—MA}^{\cdot}\text{—} + \text{AAm} \xrightarrow{k_p} \text{R—(MA)}_m\text{—AAm}^{\cdot}\text{—} \quad (10)$$

Termination:

$$\text{R—(AAm)}_n\text{—MA}^{\cdot}\text{—} + \text{—}^{\cdot}\text{MA—(AAm)}_n\text{—R} \xrightarrow{k_{tc}} \text{R—(AAm)}_n\text{—MA—MA—(AAm)}_n\text{—R} \quad (11)$$

$$\text{R—(MA)}_m\text{—AAm}^{\cdot}\text{—} + \text{—}^{\cdot}\text{AAm—(MA)}_m\text{—R} \xrightarrow{k_{tc}} \text{R—(MA)}_m\text{—AAm—AAm—(MA)}_m\text{—R} \quad (12)$$

$$\text{R—(AAm)}_n\text{—MA}^{\cdot}\text{—} + \text{—}^{\cdot}\text{AAm—(MA)}_m\text{—R} \xrightarrow{k_{tc}} \text{R—(AAm)}_n\text{—MA—AAm—(MA)}_m\text{—R} \quad (13)$$

Oxidative termination:

$$\text{R}^{\bullet} + \text{Ce (IV)} \xrightarrow{k_o} \text{Oxidation product} + \text{Ce (III)} + \text{H}^{+} \quad (14)$$

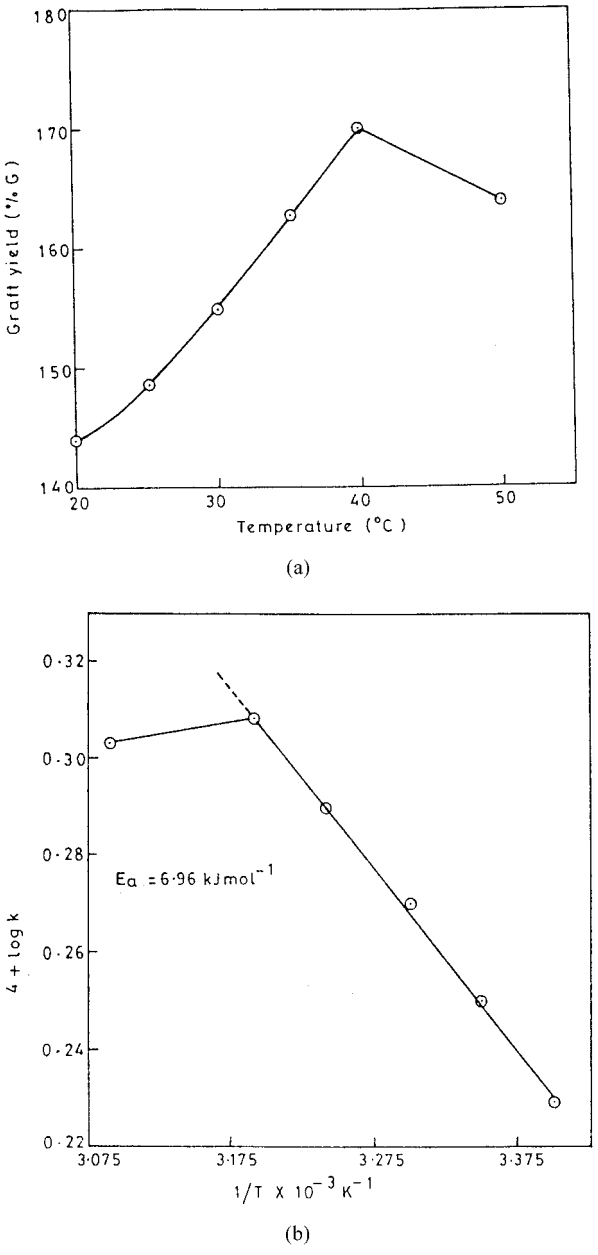


Figure 7 (a) Effect of temperature on percent graft yield (%*G*): [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, $f_{AAm} = 0.6$, time = 60 min. (b) Arrhenius plot of log k versus $1/T$: [AAm-MA] = 30.0×10^{-2} mol dm^{-3}, [CAN] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 6.0×10^{-2} mol dm^{-3}, [cellulose] = 1.0 g, $f_{AAm} = 0.6$, time = 60 min.

where n and m are the average sequence lengths of acrylamide ($\bar{m}M_1$) and methylacrylate ($\bar{m}M_2$) blocks in the grafted copolymer chains, respectively. The values of these average sequence lengths ($\bar{m}M_1$ and $\bar{m}M_2$) varied on varying the feed composition, temperature, and concentration of nitric acid in the reaction mixtures.

CONCLUSIONS

Ceric ammonium nitrate has a high efficiency for graft copolymerization of the acrylamide–methylacrylate comonomers onto cellulose without significant formation of homopolymers. The synergistic effect of comonomers has a significant effect on graft yield and other grafting parameters. The composition of the grafted copolymers varies on varying the feed composition and reaction temperature. The graft yield also has a dependence on the concentrations of CAN and nitric acid.

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