Graft Copolymerization of Acrylamide onto Cellulose in Presence of Comonomer Using Ceric Ammonium Nitrate as Initiator

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ABSTRACT: The graft copolymerization of acrylamide (AAm) and ethylmethacrylate (EMA) monomers onto cellulose has been carried out using ceric ammonium nitrate (CAN) as initiator in presence of nitric acid at (25 ± 1)°C and varying feed molarity from 7.5×10^{-2} mol dm^{-3} to 60.0×10^{-2} mol dm^{-3} at fixed feed composition ($f_{AAm} = 0.6$). The graft yield (%G_Y) has shown a linear increasing trend upto a feed molarity of 37.5×10^{-2} mol dm^{-3}. The composition of grafted copolymer chains was found to be constant ($F_{AAm} = 0.56$) during feed molarity variation but shown variations with feed composition (f_{AAm}) and reaction temperature. The grafting parameters have shown increasing trends up to 7.5×10^{-3} mol dm^{-3} concentration of ceric (IV) ions and decreased on further increasing the concentration of ceric (IV) ions beyond 7.5×10^{-3} mol dm^{-3}. The IR and elemental analysis data were used to determine the composition of grafted chains (F_{AAm}) and reactivity ratio of acrylamide (r_1) and ethylmethacrylate (r_2) comonomers. The reactivity ratio for acrylamide (r_1) and ethylmethacrylate (r_2) has been found to be 0.7 and 1.0 respectively, which suggested for an alternate arrangement of average sequence length of acrylamide ($m\bar{M}_1$) and ethylmethacrylate ($m\bar{M}_2$) in grafted chains. The rate of graft copolymerization of comonomers onto cellulose was found to be proportional to square concentration of comonomers and square root to the concentration of ceric (IV) ions. The energy of activation (ΔEa) of graft copolymerization was found to be 9.57 kJ mol^{-1} within the temperature range of 20–50°C. On the basis of experimental findings, suitable reaction steps have been proposed for graft copolymerization of selected comonomers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2546–2558, 2006

Key words: cellulose; graft copolymerization; ceric ions; acrylamide, ethylmethacrylate

INTRODUCTION

Graft copolymerization of vinyl monomers from their binary mixtures is a potential technique to obtain a polymer surface having simultaneous properties of both monomers in comparison with the surface obtained by graft copolymerization using single monomers.[1–5] The grafting with binary mixture of monomers provides an opportunity to prepare tailor made material for specific applications.[6,7] However, in these investigations no systematic analysis of grafting parameters has been reported, as has been carried out using binary mixture of monomers.[8] In these investigations, the concentration dependant monomer–monomer interactions in the reaction mixture have been found to be responsible for controlling the graft yield and the composition of the grafted chains. Because of synergistic effect of the added comonomer, the graft yield (%G_Y), and other grafting parameters have shown improvement, in comparison with graft copolymerization carried out with individual monomers. Investigations have revealed that grafted chains of desired properties can be obtained using suitable combination of monomers and their compositions in the feed.[8] The graft copolymerization of individual monomers has been reported using thermal methods,[7] photosensitizer,[9] magnetic field,[10] radiation,[5,11] redox system[12] and metal chelates.[13,14] But in these methods, the extent of ungrafted homopolymer was usually high as compared with grafted copolymers. But ceric (IV) ions[15,16] initiation has shown a substantial decreasing trend in formation of ungrafted polymers because of direct participation of ceric (IV) ions in formation of active sites onto cellulose backbone through single electron transfer process,[17] which has been presumed to be responsible in promoting the extent of graft copolymerization onto cellulose. However ceric (IV) ions have been reported to be able to create free radicals onto cellulose in presence of sufficient amount of acid[18,19] and the efficiency of ceric (IV) ions has been found to be low in aqueous media because of hydrolysis of ceric (IV) ions. The individual

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grafting of acrylamide[10,20,21] and ethylmethacrylate[22,23] has been reported in the literature but grafting of these monomers using their binary mixtures has not yet studied extensively, hence current studies have been focused to investigate the behavior of acrylamide for grafting onto cellulose in presence of ethylmethacrylate comonomer. To investigate the effect of monomer–monomer interactions, the graft copolymerization has been studied taking different feed compositions and feed molarity and by varying other experimental conditions. The composition of the grafted chains has been determined by IR and elemental analysis and used to estimate the reactivity ratios of acrylamide and ethylmethacrylate.

EXPERIMENTAL

Chemicals

Acrylamide (Loba Chemie, Mumbai, India) was purified by recrystallization from benzene and dried in vacuum desiccator. The ethylmethacrylate (E. Merck, India) was purified by extraction with aqueous sodium chloride-sodium hydroxide solution and was stored below 5°C after drying over sodium sulfate in vacuum desiccator. The cellulose powder (Loba Chemie, Mumbai, India) was washed with methanol, acetone deionized water and finally dried at room temperature. Ceric ammonium nitrate and nitric acid were reagent grade chemicals and used without further purification. The nitrogen gas was passed through alkaline pyrogallol and concentrated sulfuric acid before using it in graft copolymerization.

Graft copolymerizaion

The graft copolymerization of vinyl monomers was carried out by adding 1.0 g of purified cellulose ($M_{\bar{w}} = 4.1 \times 10^5$ g mol^{-1}) in a three-necked round bottom flask containing 100 mL solution of nitric acid (7.5×10^{-2} mol dm^{-3}) and ceric ammonium nitrate (7.5×10^{-3} mol dm^{-3}). The reaction mixture of the flask was thermostat to 25 ± 1°C and stirred vigorously with electrically operated stirrer and purged with N_2 gas for about 15 min to remove dissolved oxygen from the solution. To initiate, the graft copolymerization, a calculated amount of monomer mixture (1.99 g of AAm and 1.32 g of EMA) was added in the reaction flask and supply of nitrogen gas was maintained till graft copolymerization was carried out. The reaction mixture was stirred at a constant rate to avoid the effect of stirring. Finally, the reaction was stopped by adding 5 wt% solution of hydroquinone and product was obtained by precipitating reaction mixture in excess amount of methanol. The precipitate was filtered and washed repeatedly with hot and cold water to remove unpolymerized monomers, ungrafted polymers, and other trapped impurities in grafted cellulose. The purified product was finally dried to a constant weight in vacuum desiccator.

Ceric (IV) ions consumption

To estimate the amount of ceric (IV) ions consumed in graft copolymerization, 5 mL aliquot of reaction mixture was taken out and poured in the beaker containing excess amount of ferrous ammonium sulfate. The amount of ceric (IV) ions consumed in graft copolymerization was determined by back titrating the excess ferrous ammonium sulfate with ceric sulfate in presence of *o*-phenanthraline as indicator.

Extraction of homopolymers

The ungrafted polyacrylamide and polyethylmethacrylate homopolymers were extracted from grafted crude using water and acetonitrile as extractant in Soxhlet Apparatus for about 24 h. The ungrafted homopolymers were obtained by precipitating the extract with methanol and drying the precipitate till constant weight, which ultimately used to calculate other grafting parameters.

Extraction of ungrafted copolymers

The homopolymer-extracted crude was subsequently used to extract the ungrafted poly (AAm-*co*-EMA) using dimethylformamide (DMF) as extractant in Soxhlet apparatus. The extract was precipitated with methanol and filtered. The ungrafted copolymers were characterized for their molecular weight by gel permeation chromatography and their composition was determined by IR and elemental analysis.

Extraction of ungrafted cellulose

After extracting ungrafted homopolymers and copolymers from grafted crude, the ungrafted cellulose was extracted by keeping grafted cellulose in ammonical solution of copper hydroxide (Cuoxam)[24] containing 1.2 wt% $NaHSO_3$. The solution was stirred vigorously and after 6 h, the residue was washed with dilute acetic acid, deionized water and dried to constant weight at 50°C.

Extraction of grafted copolymers

After extracting the ungrafted polymers and cellulose, the grafted copolymer chains were extracted by hydrolyzing the copolymer grafted cellulose in 7.2 wt% sulfuric acid at 30°C. At the end of 4 h, the hydrolyzing solution was diluted with water to an acid concentration of 4 wt% and refluxed for about 6 h. The grafted copolymers were obtained by precipitating the

extract in methanol. The extracted grafted copolymer chains after purification were characterized for their composition by IR and elemental analysis. The molecular weight of the extracted copolymers was determined by gel permeation chromatography.

Characterization

IR spectra

The IR spectra of pure cellulose and copolymers were recorded with Perkin–Elmer 1600 FTIR Spectrophotometer and used as evidence for grafting of copolymers onto cellulose. The composition of grafted copolymer chains was determined by using percent transmittance at 1664 and 1770 cm^{-1} for carbonyl group (C═O) in acrylamide and ethylmethacrylate, respectively. The optical density ratio (ODR) calculated as percent transmittance using following equation was used to determine the mole fraction of acrylamide (F_{AAm}) and ethylmethacrylate (F_{EMA}) in grafted chains using calibration curve drawn between ODR and composition of known copolymers.

$$\text{ODR} = \frac{\log (\%T_{\text{baseline for EMA}}/\%\ \text{T}_{\text{EMA}})}{\log (\%T_{\text{baseline for AAm}}/\%T_{\text{AAm}})} \quad (1)$$

Elemental analysis

The composition of grafted copolymer chains determined by IR method of analysis, has been verified by determining the percent nitrogen content of grafted chains with Heraeus Carlo Ebra 1108 Elemental Analyzer.

Thermal analysis

Thermal stability of cellulose and grafted cellulose was estimated by recording thermogravimetric (TG) and differential thermogravimetric (DTG) curves using Perkin–Elmer 7.0 Thermal Analyzer System at a heating rate of 10°C min^{-1} under nitrogen atmosphere. The energy of activation (E_a) for thermal decomposition of cellulose and grafted cellulose was determined by taking fraction of sample (α) decomposed at a particular temperature (T) and fitting the data in the following equation.[25]

$$\ln \ln(1-\alpha)^{-1} = \frac{E_a}{RT_s^2}\frac{100}{T_f - T_i}\theta + \text{C} \quad (2)$$

Where, T_i and T_f are the initial and final decomposition temperatures taken at a deviation of 5 wt% from the base line in DTG curve (Fig. 1) and θ is the difference of particular decomposition temperature (T) and temperature of the reference (T_s).

Molecular weight measurements

The molecular weights of polyacrylamide and polyethylmethacylate were determined by viscometric method using following equations

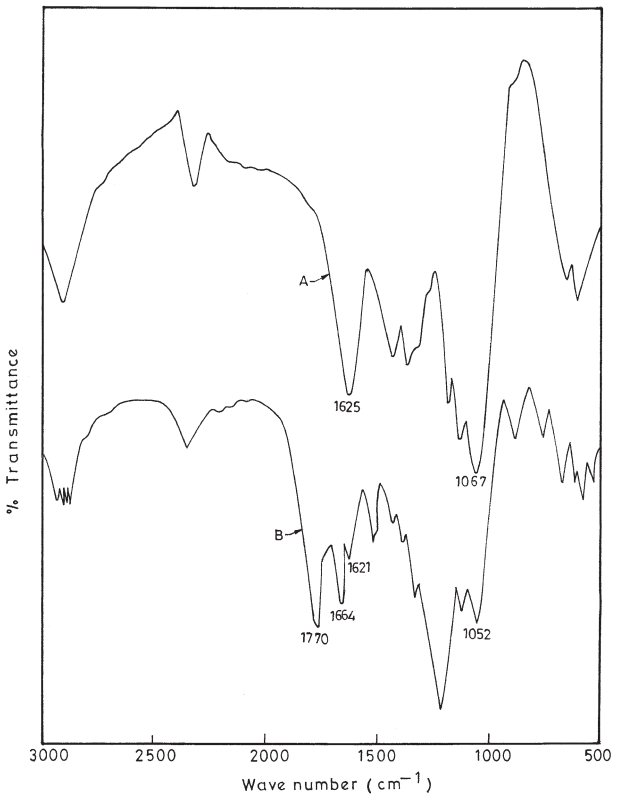
$$[\eta]_{30°C} = 4.75 \times 10^{-4}\ \text{cm}^3\ \text{g}^{-1}\ M_v^{0.50} \quad \text{(iso-PrOH for PEMA)} \quad (3)$$

$$[\eta]_{27°C} = 6.80 \times 10^{-4}\ \text{cm}^3\ \text{g}^{-1}\ M_v^{0.66} \quad (\text{NaNO}_3 \text{ for PAAm}) \quad (4)$$

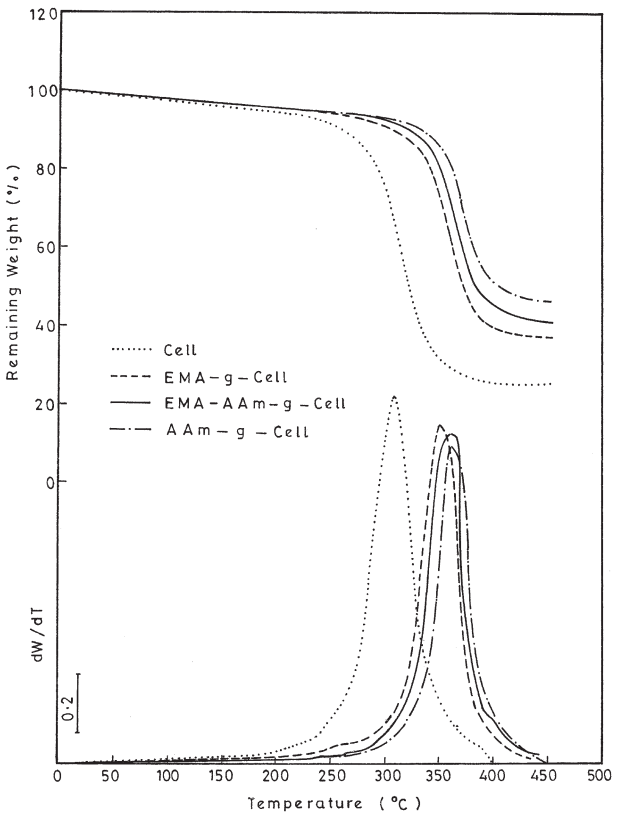
The molecular weights of grafted and ungrafted copolymer were determined by gel permeation chromatograph (PL-GPC-120) equipped with three PL aqua gel columns (PL aqua gel, 40, 60, and 100 μm) in series and UV detector (λ_{max} = 208 nm). A 200 μL copolymer solution of 0.1 mg/mL concentration was loaded and eluted with dimethylformamide at flow rate of 1.0 mL/min at 25°C. The universal calibration curve was recorded using polyacrylamide calibration kit.

RESULTS AND DISCUSSION

The graft copolymerization of acrylamide in presence of ethylmethacrylate has shown a substantial increase in graft yield ($\%G_Y$) in comparison with graft yield ($\%G_Y$) found with individual acrylamide. Because of the synergistic effect of ethylmethacrylate on acrylamide, the extent of overall grafting has also increased considerably.[26] Because of strong interactions between acrylamide and ethylmethacrylate, the chains grafted onto cellulose were purely copolymeric in nature, which has provided a strong support that grafting of individual monomer in presence of comonomer was inhibited in present system. The intensity of interactions between comonomers has found to be dependent on composition of feed (f_{AAm}) as clear from the observed variations in composition of the grafted chains. The high efficiency of grafting of selected comonomers onto cellulose has also been attributed to ceric (IV) ions, which involved exclusively in the formation of radicals at cellulose backbone[18] and facilitated the grafting of comonomers than formation of ungrafted homopolymers and copolymers. At a relatively low concentration of nitric acid ($<7.5 \times 10^{-2}$ mol dm^{-3}), the number of active sites formed at cellulose backbone was low because of the formation of hydrated ceric (IV) ions, which were less active in hydrogen ions abstraction from cellulose backbone in comparison to unhydrated ceric (IV) ions. These observations have clearly suggested that keeping excess concentration of nitric acid in the reaction mixture, the reactivity of ceric (IV) ions is maintained to produce free radicals at the backbone of cellulose. The IR spectrum [Fig.



(a)



(b)

1(a)] of poly(acrylamide-*co*-ethylmethacrylate) copolymers grafted onto cellulose has shown two additional absorption bands at 1770 and 1664 cm^{-1} in comparison with that of pure cellulose, which correspond to ester caronyl group of ethylmethacrylate and carbamide group of acrylamide, hence provided an evidence for the presence of both monomers onto cellulose. Since no grafted chain was consisted of individual monomer, hence acrylamide and ethylmethacrylate monomers were together responsible to form grafted chains onto cellulose. The ODR of hydrolyzed copolymer chains has been used to verify the composition of grafted chains obtained by elemental analysis. The thermogravimetric analysis (TGA) of pure cellulose, cellulose grafted with polyacrylamide or polyethylmethacrylate and poly (acrylamide-*co*-ethylmethacrylate) copolymers has indicated a substantial increase in thermal stability of cellulose on grafting [Fig. 1(b)]. The DTGA curves of cellulose and grafted cellulose [Fig. 1(b)] have indicated a shift in temperature of maximum decomposition rate (T_{max}) from 320°C for pure cellulose to 374°C for polyacrylamide-grafted cellulose. The decomposition temperature (T_i) of cellulose grafted with poly (acrylamide-*co*-ethylmethacrylate) copolymers has been found to be higher (235°C) than that of pure cellulose (190°C) and cellulose grafted with polyethylmethacrylate (232°C). These thermal data have indicated a substantial variation in thermal stability of cellulose on graft copolymerization of comonomers. The energy of activation (E_a) for decomposition of pure cellulose and grafted cellulose has been determined from the slope of curve (Fig. 2) drawn between ln ln $(1 - \alpha)^{-1}$ Versus $(T - T_s)$ using eq. 2.

The energy of activation for decomposition of cellulose has increased from 202.33 kJ mol^{-1} for pure cellulose (Fig. 2, curve A) to 283.80 kJ mol^{-1} and 275.97 kJ mol^{-1} on individual grafting of acrylamide (Fig. 2, curve D) and ethylmethacrylate (Fig. 2, curve B) monomers respectively, but energy of activation for decomposition of cellulose grafted with comonomers was 278.99 kJ mol^{-1} [Fig. 2(C)], which lies in between the energies observed for cellulose grafted either with ethylmethacrylate or with acrylamide monomer. This has clearly indicated that grafting of acrylamide and ethylmethacrylate comonomers has contributed significantly to increase the thermal stability of cellulose and cellulose grafted with only ethylmethacrylate monomer.

Figure 1 (a) FT-IR spectra of (curve A) cellulose and (curve B) poly (acrylamide-*co*-ethylmethacrylate) grafted cellulose (G_Y-340%). (b) TGA and DTGA curves of cellulose and grafted cellulose (G_Y-340%).

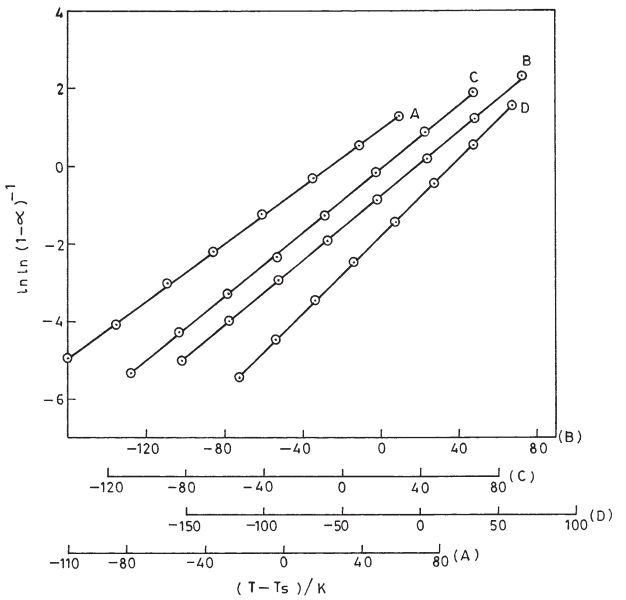
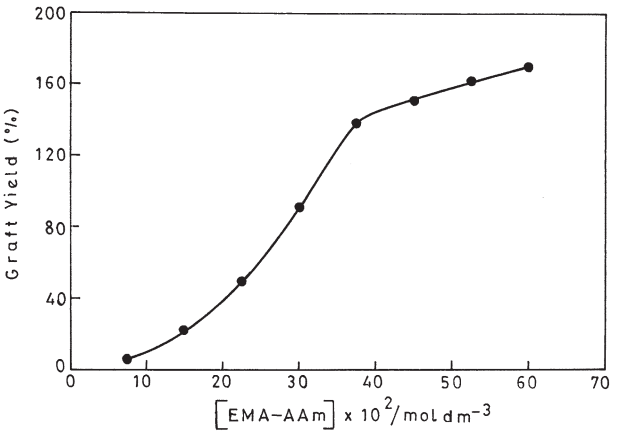


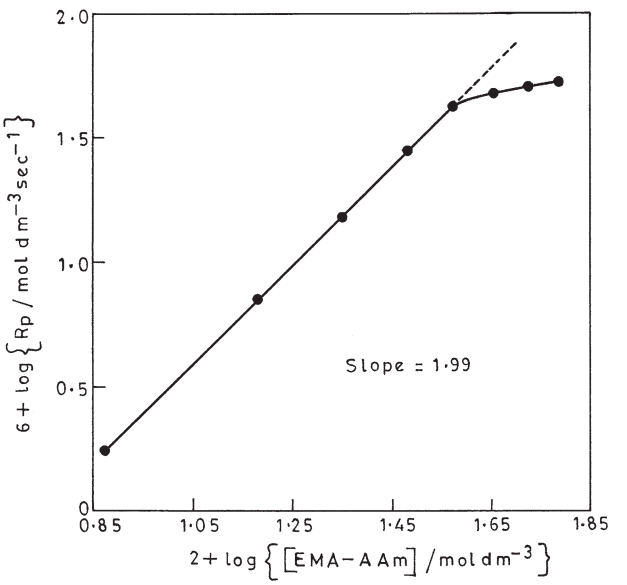
Figure 2 Energy of activation for decomposition of pure cellulose and grafted cellulose (G_Y-340%).

Effect of feed molarity

To study the effect of concentration of comonomers on grafting, the graft copolymerization was studied by varying the feed molarity from 7.5×10^{-2} to 60.0×10^{-2} mol dm^{-3} at constant concentration of ceric ammonium nitrate (7.5×10^{-3} mol dm^{-3}) and nitric acid (7.5×10^{-2} mol dm^{-3}). During feed molarity variation, the feed composition was kept constant ($f_{AAm} = 0.6$) to keep monomer–monomer interactions constant. On varying the feed molarity there has been a steep rise in percent graft yield (%G_Y) up to 37.5×10^{-2} mol dm^{-3} of feed molarity [Fig. 3(a)]. Similar trend has been shown by true grafting (%G_T) and efficiency of grafting (%G_E) as clear from the data shown in Table I. However, on further increase in feed molarity beyond 37.5×10^{-2} mol dm^{-3}, the grafting parameters have not shown linear increasing trend as was observed at low feed molarity ($<37.5 \times 10^{-2}$ mol dm^{-3}). The decreasing trend in percent graft conversion (%C_g) and efficiency of grafting (%G_E) at high feed molarity ($>37.5 \times 10^{-2}$ mol dm^{-3}) was due to the increase in formation of ungrafted homopolymer and copolymer. The increasing trend in percent graft conversion (%C_g), efficiency of grafting (%G_E), and true grafting (%G_T) up to 37.5×10^{-2} mol dm^{-3} of feed



(a)



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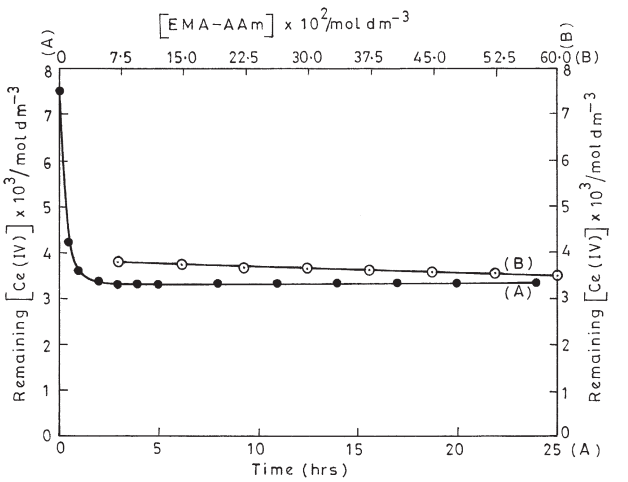


(c)

Figure 3 (a) Graft yield (%G_Y) as a function of feed molarity. $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %. (b) Log–log plot between R_p Versus [AAm–EMA], $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %. (c) Ceric ions consumption as a function of feed molarity and reaction time. [AAm–EMA]. $f_{AAm} = 0.6$, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %

TABLE I
Effect of [AAm–EMA] on Grafting Parameters

[AAm–EMA] × 10^2 mol dm^{-3}	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
7.5	240	10.76	8.18	31.0	76.05	0.24
15.0	248	20.26	16.63	35.0	82.09	0.77
22.5	272	29.54	24.75	40.0	83.76	1.22
30.0	298	30.30	34.39	48.0	87.50	1.85
37.5	336	46.83	41.69	54.5	89.03	2.44
45.0	333	44.08	38.03	58.0	86.28	2.54
52.5	329	49.89	34.99	61.0	70.13	2.62
60.0	328	52.74	32.13	62.0	60.93	2.78

[AAm–EMA] × 10^2 mol dm^{-3}	$N_g \times 10^6$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%Branches	%Cellulose
7.5	0.18	294	1.95	14.84	85.16
15.0	0.66	330	1.90	38.60	61.40
22.5	1.18	414	1.87	55.00	45.00
30.0	2.16	420	1.85	65.47	34.53
37.5	3.25	425	1.82	71.69	28.31
45.0	3.58	422	1.86	72.25	27.75
52.5	3.90	415	1.89	72.65	27.35
60.0	4.20	405	1.93	73.28	26.72

$f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt%.

molarity was due to the substantial consumption of monomers in inception and growth of polymeric chains onto cellulose backbone but deviation from linearity in these parameters at high feed molarity (>37.5×10^{-2} mol dm^{-3}) was due to the substantial increase in viscosity of medium, which has retarded the rate of diffusion of comonomers from solution phase to active sites onto cellulose. The retardation in extent of grafting at high feed molarity (>37.5×10^{-2} mol dm^{-3}) was also due to decrease in degree of swelling of cellulose because of excess amount of monomers in the solution and due to the steric hindrance offered by chains already grafted onto the cellulose.

The combined effect of all these factors at high feed molarity (> 37.5×10^{-2} mol dm^{-3}) has increased the grafting of comonomers more at the surface than the matrix of the cellulose. On increasing feed molarity, the frequency (G_F) and number (N_g) of grafted chains have also shown an increasing trend (Table I). The molecular weight ($M_{\bar{w}}$) of the grafted chains has increased up to a feed molarity of 37.5×10^{-2} mol dm^{-3} and then after a decreasing trend was shown by all grafting parameters (Table I).

The percentage of grafted chains onto cellulose has increased up to a feed molarity of 37.5×10^{-2} mol dm^{-3}, which was due to the growth of grafted chains and due to the formation of new side chains (Table I).

The composition of grafted chains during feed molarity variation has remained almost constant (F_{AAm} = 0.56), which has given an indication that during feed molarity variation, the monomer–monomer interactions remained almost constant, otherwise the chain composition would have been different. The rate of graft copolymerization (R_p) determined at different feed molarity has been used to draw a log–log plot between R_p versus feed molarity to order of reaction rate of grafting on feed molarity [Fig. 3(b)]. The slope of the log–log plot was found to be 1.99, indicating a second order dependence of reaction rate on feed molarity. On varying the feed molarity from 7.5×10^{-2} to 37.5×10^{-2} mol dm^{-3}, the rate of ceric (IV) ions disappearance was almost constant [Fig. 3(c)], which indicated that ceric (IV) ions have not involved directly in the formation of active sites on monomers, otherwise the rate of ceric (IV) ions consumption would have been affected on varying the feed molarity [Fig. 3(c)]. The ungrafted homopolymers and copolymers found in reaction mixture were formed exclusively by the transfer of activity of cellulose grafted chains to the comonomers and not due to the direct interactions of ceric (IV) ions to create active sites on comonomers present in the reaction mixture.

Effect of feed composition

The graft yield ($\%G_Y$) and composition of grafted chains (F_{AAm}) onto cellulose have been determined as a function of feed composition (f_{AAm}) at constant concentration of CAN (7.5×10^{-3} mol dm^{-3}), nitric acid (7.5×10^{-2} mol dm^{-3}), and comonomers (37.5×10^{-2} mol dm^{-3}) at a reaction temperature of 25°C. The individual grafting of acrylamide and ethylmethacrylate onto cellulose was also carried out at same feed

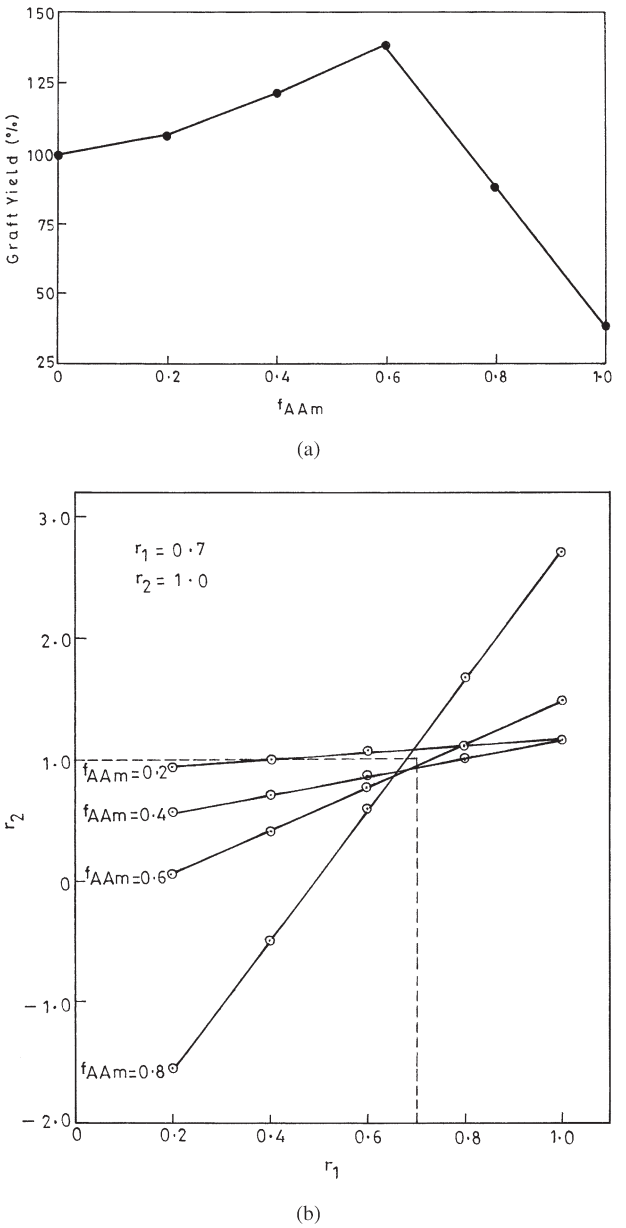


Figure 4 (a) Graft yield (%G_Y) as a function of feed composition. [AAm–EMA] = 37.5 × 10^{-2} mol dm^{-3}, [Ce(IV)] = 7.5 × 10^{-3} mol dm^{-3}, [HNO_3] = 7.5 × 10^{-2} mol dm^{-3}, Time = 60 min, Temp. = 25°C, [Cell] = 1 wt %. (b) Mayo and Lewis plot for reactivity ratios. [AAm–EMA] = 37.5 × 10^{-2} mol dm^{-3}, [Ce(IV)] = 7.5 × 10^{-3} mol dm^{-3}, [HNO_3] = 7.5 × 10^{-2} mol dm^{-3}, Time = 60 min., Temp. = 25°C, [Cell] = 1 wt %.

molarity (37.5 × 10^{-2} mol dm^{-3}) to compare the effect of addition of comonomer on the extent of graft yield (%G_Y) of individual monomer onto cellulose. The graft yield (%G_Y) and other grafting parameters for acrylamide and ethyl methacrylate comonomers as a function of feed composition are shown in Figure 4(a) and Table II. The ethylmethacrylate has shown a high affinity for grafting (99%) when compared with acrylamide (38%) as shown in Figure 4(a). The extent of percent graft yield (%G_Y) has increased on increasing the mole fraction of acrylamide (f_{AAm}) from 0.2 to 0.6 and shown a substantial decreasing trend in graft yield (%G_Y) on further increase in mole fraction beyond 0.6. Same trend has been observed with true grafting (%G_T), percent conversion (%C_g), efficiency (%G_E), and frequency of grafting (G_F), as evident from the data shown in Table II. The number of grafted chains (N_g) has also shown a decreasing trend on taking high mole fraction (>0.6) of acrylamide in the feed. The total conversion (%C_T) and cellulose conversion (%C_c) were found to be dependant on feed composition (f_{AAm}). The decreasing trend in grafting parameters at high mole fraction of acrylamide ($f_{AAm} > 0.6$) has given a clear indication that acrylamide was having low affinity for grafting onto cellulose in comparison with pure ethylmethacrylate monomer.

The initial increasing trend in graft yield (%G_Y) and other grafting parameters (Table II) within the range of mole fraction of acrylamide (f_{AAm}) from 0.2 to 0.6 has been due to the synergistic effect of ethylmetacrylate onto acrylamide. In this range of feed composition, the intermolecular interactions between acrylamide–ethylmethacrylate comonomers have been assumed to be stronger than the intramolecular interactions between acrylamide–acrylamide monomer or ethylmethacrylate–ethylmethacrylate monomers, hence the growing chains with terminal ethylmethacrylate has preferred to combine with acrylamide monomer than with ethylmethacrylate monomer, which has ultimately increased the graft yield (%G_Y) and other grafting parameters. The molecular weight ($M_{\bar{w}}$) and number of grafted chains (N_g) have also increased on increasing the mole fraction of acrylamide from 0.2 to 0.6 (Table II). This has been verified by IR and elemental analysis of grafted chains (Table II). The data obtained on composition of grafted chains were used to calculate the reactivity ratios of acrylamide (r_1) and ethylmethacrylate (r_2) by Mayo and Lewis plot[27] [Fig. 4(b)]. The reactivity ratio of acrylamide and ethylmethacrylate has been found to be 0.7 and 1.0 respectively, which has clearly indicated that acrylamide has low reactivity for grafting onto cellulose in comparison with ethylmethacrylate, hence grafted chains were having low fraction of acrylamide (F_{AAm}) in comparison with feed (f_{AAm}).

The average sequence lengths of acrylamide ($m\bar{M}_1$) have increased on increasing the mole fraction of acrylamide in the feed (Table II), whereas average sequence lengths of ethylmethacrylate ($m\bar{M}_2$) in the chains were shown a reverse trend (Table II). The probability of addition of acrylamide ($P_{AAm\text{-}AAm}$) during variation in feed composition has shown a continuous increasing trend but run number (R) was increased only upto 0.6 mol fraction of acrylamide in the feed and then after shown a decreasing trend on increasing the mole fraction of acrylamide (f_{AAm}) be-

TABLE II
Effect of Feed Composition (f_{AAm}) on Grafting Parameters

f_{AAm}	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
0.0	314	26.43	23.16	48.0	87.61	2.18
0.2	312	30.63	26.83	50.0	87.60	2.15
0.4	319	37.74	33.33	52.0	88.32	2.30
0.6	336	46.83	41.69	54.5	89.03	2.44
0.8	283	35.84	29.31	48.9	81.77	2.12
1.0	206	22.93	14.28	45.0	62.29	1.33

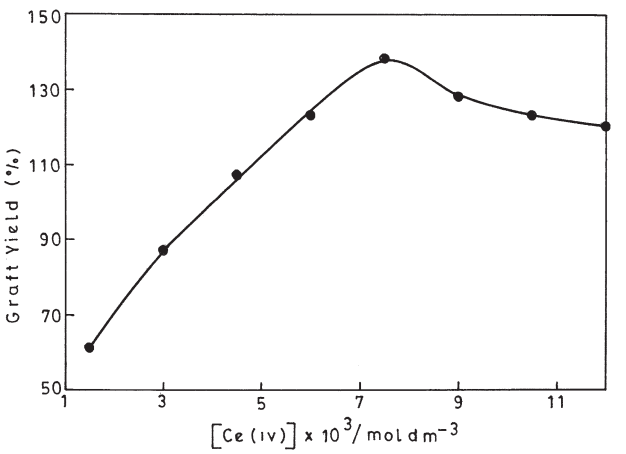
f_{AAm}	$N_g \times 10^6$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%Branches	%Cellulose
0.0	2.55	388	2.08	67.35	32.65
0.2	2.62	405	1.99	67.95	32.05
0.4	2.92	415	1.93	69.94	30.06
0.6	3.25	425	1.82	71.69	28.31
0.8	2.52	347	1.87	64.15	35.85
1.0	1.46	260	1.94	45.78	54.22

[AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %.

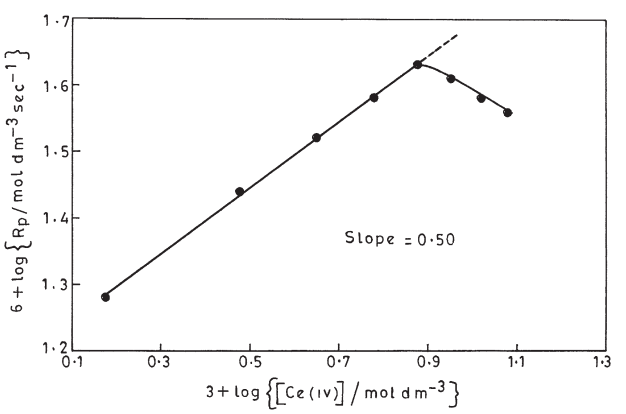
yond 0.6. The product of monomer reactivity ratios ($r_1 r_2$) has been found to be less then unity (0.7), which has indicated that acrylamide monomer blocks ($m\bar{M}_1$) in grafted chains were arranged in alternate fashion. These investigations have clearly indicated that composition of grafted chains was dependant on reactivity ratio of monomers and composition of feed used for graft copolymerization.

Effect of ceric (IV) ions concentration

The effect of ceric (IV) ions concentration on graft copolymerization of acrylamide and ethylmethacrylate comonomers has been studied at different concentrations of ceric ammonium nitrate ranging from 1.5 $\times 10^{-3}$ mol dm^{-3} to 12.0 $\times 10^{-3}$ mol dm^{-3} at constant feed molarity (37.5 $\times 10^{-2}$ mol dm^{-3}) and composition (f_{AAm} = 0.6). To maintain the activity of ceric (IV) ions, the concentration of nitric acid in the reaction mixture was kept in access (7.5 $\times 10^{-2}$ mol dm^{-3}). The graft yield ($\%G_Y$) and other grafting parameters determined as a function of ceric (IV) ions concentration were shown in Figure 5a and Table III. The percent graft yield ($\%G_Y$) has shown an increasing trend upto 7.5 $\times 10^{-3}$ mol dm^{-3} concentration of ceric (IV) ions and shown a decreasing trend on increasing the concentration of ceric (IV) ions beyond 7.5 $\times 10^{-3}$ mol dm^{-3}. The true grafting ($\%G_T$), total conversion ($\%C_T$), graft conversion ($\%C_g$), efficiency ($\%G_E$), and frequency of grafting (G_F) have also shown a similar trend upto 7.5 $\times 10^{-3}$ mol dm^{-3} concentration of ceric (IV) ions (Table III). The initial increasing trend in graft yield ($\%G_Y$) and other grafting parameters is due to the sufficient numbers of ceric (IV) ions in the reaction mixture at 7.5 $\times 10^{-2}$ mol dm^{-3} concentration of nitric acid, which were ultimately consumed in the



(a)



(b)

Figure 5 (a) Graft yield ($\%G_Y$) as function of [Ce(IV)]. [AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %. (b) Log–log plot between R_p Versus [Ce(IV)]. [AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, f_{AAm} = 0.6, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %.

TABLE III
Effect of [Ce(IV)] on Grafting Parameters

[Ce(IV)] $\times 10^3$ mol dm^{-3}	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
1.5	283	22.06	18.83	42.0	81.33	1.26
3.0	325	30.81	26.28	44.0	85.29	1.77
4.5	331	37.46	32.33	48.0	86.99	2.02
6.0	333	42.29	37.16	51.5	87.86	2.25
7.5	336	46.83	41.69	54.5	89.03	2.44
9.0	330	44.41	38.67	53.0	87.07	2.37
10.5	329	44.11	37.16	52.0	84.24	2.33
12.0	328	43.81	36.25	51.4	82.76	2.32

[Ce(IV)] $\times 10^3$ mol dm^{-3}	$N_g \times 10^6$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%Branches	%Cellulose
1.5	1.29	470	1.93	59.22	40.78
3.0	1.89	460	1.92	66.41	33.59
4.5	2.37	452	1.88	69.03	30.97
6.0	2.83	435	1.84	70.49	29.51
7.5	3.25	425	1.82	71.69	28.31
9.0	3.06	418	1.85	70.72	29.28
10.5	2.96	415	1.87	70.29	29.71
12.0	2.90	413	1.89	70.01	29.99

[AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{\mathrm{AAm}} = 0.6$, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, Temp = 25°C, [Cell] = 1 wt %.

formation of active sites onto cellulose, which have facilitated the graft copolymerization of selected comonomers. On higher concentration of ceric (IV) ions (>7.5×10^{-3} mol dm^{-3}), the decreasing trend in graft yield ($\%G_Y$) and other grafting parameters has been attributed to the decrease in ratio of nitric acid to ceric (IV) ions concentration, hence ceric (IV) ions became inactive due to hydrolysis.

This is clear from the decreasing trend with number of grafted chains (N_g) at high concentration of ceric ammonium nitrate (>7.5×10^{-3} mol dm^{-3}). At high concentration of ceric (IV) ions (>7.5×10^{-3} mol dm^{-3}), the cellulose conversion has also shown a decreasing trend, which is indicative that ceric (IV) ions were inactive in creating active sites onto cellulose, and consequently the consumption of cellulose ($\%C_c$) by graft copolymerization has decreased (Table III). The molecular weight ($M_{\bar{w}}$) of grafted chains has shown a continuous decreasing trend on increasing the concentration of ceric ammonium nitrate, which has indicated that ceric (IV) ions at high concentration have participated in chain termination reaction.

The chain termination process was more predominant with hydrated ceric (IV) ions. The percentage of polymers in grafted cellulose has also decreased at high (7.5×10^{-3} mol dm^{-3}) concentration of ceric (IV) ions, as clear from the data shown in Table III. The decreasing trend in grafting parameters at high concentration of ceric (IV) ions (>7.5×10^{-3} mol dm^{-3}) has also been attributed to steric hindrance created by chains already grafted at cellulose, which reduced the rate of diffusion of ceric (IV) ions from solution phase to cellulose, hence the extent of grafting has shown a decreasing trend. The logarithmic plot drawn between log R_p versus concentration of ceric (IV) ions [Fig. 5(b)] has given a linear curve with a slope of 0.5, indicating square root dependence of rate of graft copolymerization on concentration of ceric (IV) ions.

Effect of reaction time

The effect of different variables on graft copolymerization of comonomers has been studied at fixed time interval of graft copolymerization but recording grafting parameters as a function of reaction time is also of paramount importance. To study the effect of reaction time on grafting parameters, the grafted samples were collected at different reaction time intervals at constant concentration of comonomers (37.5×10^{-2} mol dm^{-3}), ceric (IV) ions (7.5×10^{-3} mol dm^{-3}), nitric acid (7.5×10^{-2} mol dm^{-3}), and fixed feed composition ($f_{\mathrm{AAm}} = 0.6$) were analyzed for various grafting parameters at 25 °C as shown in Figure 6 and Table IV. The graft yield ($\%G_Y$) and other grafting parameters have increased substantially upto a reaction time of 6 h and beyond that the value of these parameters has becomes almost constant (Fig. 6 and Table IV). The increasing trend in graft yield ($\%G_Y$) and other grafting parameters on increasing the reaction time was due to the formation of new chains and due to the increase in size of growing chains onto cellulose. This is evident from the increasing trend in number (N_g) and frequency (G_F) of grafted chains onto cellulose (Table IV) and from increasing trend in other grafting

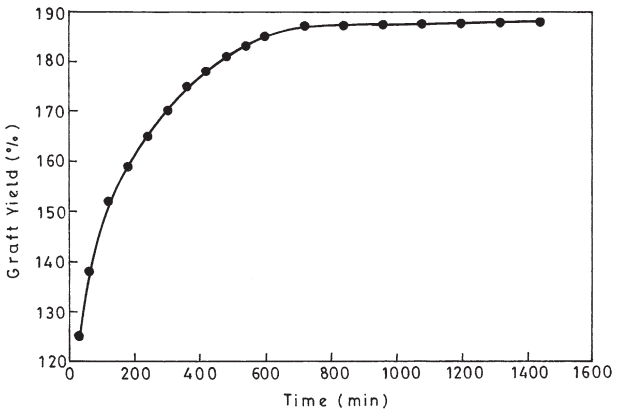


Figure 6 Graft yield (%G_Y) as a function on reaction time. [AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Temp = 25°C, [Cell] = 1 wt %.

parameters such as true grafting (%G_T), percent conversion (%C_g), and efficiency of grafting (%G_E). After 6 h, the value of grafting parameters increased insignificantly (Table IV), which has been attributed to the decrease in rate of diffusion of comonomers from solution phase to cellulose due to the decrease in activity of comonomers in the reaction mixture.

The steric hindrance offered by grafted chains after 6 h has been assumed to be reasonably high in preventing the further growth of the chains onto the cellulose. The weight of grafted chains has shown an increasing trend on increasing the reaction time (Table IV). These investigations have clearly indicated that optimum rate of graft copolymerization could be obtained by maintaining a constant supply of monomer in the reaction mixture so that molecular weight and molecular weight heterogeneity in grafted chains could be avoided. The effect of reaction time was also studied on rate of ceric (IV) ions disappearance during graft copolymerization of comonomers. The rate of ceric (IV) ions disappearance was very high during initial first hour and after that ceric (IV) ions consumption was almost negligible [Fig. 3(c)], which has indicated that ceric (IV) ions were mainly consumed in the formation of active sites onto cellulose during initial first hour and after that ceric (IV) ions consumption has decreased to zero.

The retardation in rate of ceric (IV) ions disappearance after 1 h has also been attributed to the decrease

TABLE IV
Effect of Reaction Time on Grafting Parameters

Time (min)	%G_T	%C_T	%C_G	%C_C	%G_E	G_F
30	324	42.90	37.76	53.0	88.03	2.35
60	336	46.83	41.69	54.5	89.03	2.44
120	351	51.36	45.92	55.8	89.41	2.55
180	354	53.47	48.03	57.0	89.83	2.56
240	357	55.35	49.85	58.5	90.06	2.56
300	358	56.95	51.36	58.9	90.18	2.58
360	360	58.61	52.87	59.7	90.21	2.59
420	362	59.57	53.77	60.2	90.26	2.60
480	363	60.54	54.68	60.7	90.32	2.61
540	364	61.18	55.29	61.0	90.37	2.61
600	364	61.81	55.89	61.4	90.42	2.62
720	366	62.45	56.49	61.5	90.47	2.63
1440	367	62.75	56.80	61.6	90.51	2.63

Time (min)	$N_g \times 10^6$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%Branches	%Cellulose
30	3.03	412	1.79	70.22	29.78
60	3.25	425	1.82	71.69	28.31
120	3.47	438	1.84	73.15	26.85
180	3.56	446	1.86	73.61	26.39
240	3.64	453	1.87	73.83	26.17
300	3.70	459	1.88	74.27	25.73
360	3.76	465	1.89	74.56	25.44
420	3.81	467	1.89	74.73	25.27
480	3.86	469	1.90	74.89	25.11
540	3.87	473	1.90	75.00	25.00
600	3.90	474	1.90	75.08	24.92
720	3.92	476	1.90	75.25	24.75
1440	3.95	476	1.90	75.32	24.68

[AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Temp = 25°C, [Cell] = 1 wt %.

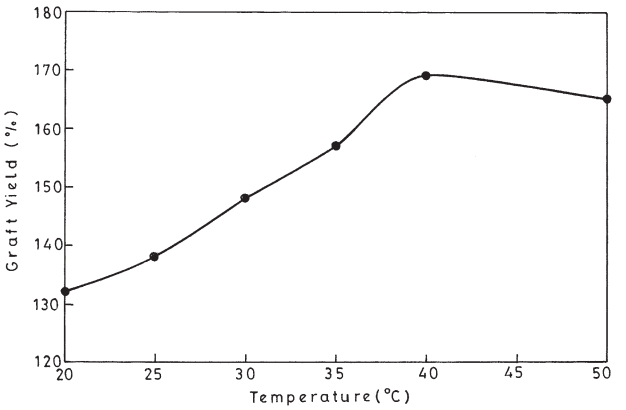
in rate of diffusion of ceric (IV) ions from solution phase to cellulose matrix due to the hindrances created by grafted chains formed already onto the surface of cellulose.

The increasing trend in molecular weight of grafted chains as a function of reaction time has been an indicative that ceric (IV) ions were not involved in termination of grafting chains implanted onto cellulose and grafted chains were allowed to grow continuously till the supply of comonomers from the reaction mixture was maintained.

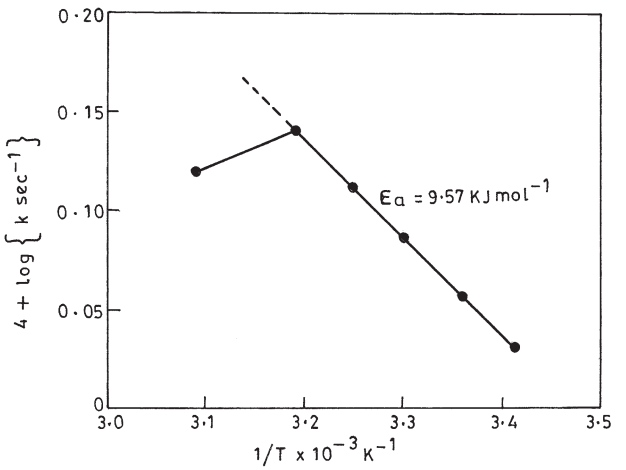
Effect of temperature

The graft copolymerization of acrylamide and ethylmethacrylate comonomers onto cellulose has also been studied at different temperatures ranging from 20 to 50°C at constant feed molarity (37.5×10^{-2} mol dm^{-3}) and constant concentration of CAN (7.5×10^{-3} mol dm^{-3}), and nitric acid (7.5×10^{-2} mol dm^{-3}) at fixed feed composition ($f_{AAm} = 0.6$). The graft yield ($\%G_Y$) and other grafting parameters have shown an increasing trend up to 40°C (Fig. 7(a) and Table V) that is due to the increase in rate of diffusion of comonomers from solution phase to the active sites onto the cellulose. The increase in reaction temperature has also increased the degree of swelling of cellulose, which facilitated the transport of comonomers inside the cellulose matrix to effect the grafting onto trapped reactive sites in the cellulose matrix, which were lying dormant at low temperature. This is evident from the observed increasing trend in cellulose consumption ($\%C_C$) (Table V) and number of grafted chains (N_g) (Table V) on increasing the temperature of reaction mixture. However increasing trend in consumption of cellulose beyond 40°C was attributed to the oxidative degradation of cellulose. The molecular weight of grafted chains has shown a decreasing trend on increasing the temperature, which was due to the increase in rate of chain termination and transfer processes at high temperature. The increase in temperature of graft copolymerization has shown a substantial effect on reactivity ratios (Table V) of acrylamide (r_1) and ethylmethacrylate (r_2). The reactivity ratio of acrylamide (r_1) has increased upto 30°C and after that it has shown a decreasing trend whereas ethylmethacrylate has shown a reverse trend, i.e., the value of reactivity ratio has decreased upto 30°C and further increasing the temperature beyond 30°C the reactivity ratio has increased.

The variation in the values of reactivity ratio has affected the average sequence length of acrylamide ($m\bar{M}_1$) and ethylmethacrylate ($m\bar{M}_2$) in grafted chains. This variation in reactivity of monomer on increasing the temperature is evident from the observed variation in probability of combination of acrylamide monomer ($P_{AAm\text{-}AAm}$) to the growing chains with terminal acrylamide monomer. The variation in reactivity ratio of acrylamide and ethylmethacrylate has controlled the run number (R) of grafted chains (Table V).



(a)



(b)

Figure 7 a Effect of temperature on graft yield ($\%G_Y$). [AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, [Cell] = 1 wt %. (b) Arrhenius plot between log k Versus $1/T$. [AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, [Cell] = 1 wt %.

The rate constant of graft copolymerization determined at different temperatures has been used to determine the energy of activation of graft copolymerization by drawing Arrhenious Plot [Fig. 7(b)], which has been found to be 9.57 kJ mol^{-1} for grafting of comonomers onto cellulose.

Thus on the basis of these experimental observations, the following reaction steps have been proposed for graft copolymerization of acrylamide and ethylmethacrylate.

Radical formation:

$$\text{Cell-H} + \text{Ce(IV)} \xrightarrow{k} \underset{\text{R}}{\text{Cell}^{\cdot}} + \text{Ce(III)} + \text{H}^{+} \qquad (5)$$

TABLE V
Effect of Temperature on Grafting Parameters

Temp (°C)	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
20	332	45.92	39.88	53.7	87.42	2.29
25	336	46.83	41.69	54.5	89.03	2.44
30	351	49.54	44.71	55.0	90.24	2.61
35	353	51.66	47.43	56.7	91.28	2.71
40	356	55.29	51.06	58.9	92.34	2.81
50	324	54.08	49.85	62.5	92.18	2.64

Temp (°C)	$N_g \times 10^6$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	%Branches	%Cellulose
20	3.00	440	1.85	71.08	28.92
25	3.25	425	1.82	71.69	28.31
30	3.50	422	1.87	72.91	27.09
35	3.74	420	1.90	73.47	26.53
40	4.05	417	1.94	74.16	25.84
50	4.01	411	1.98	72.53	27.47

Temp (°C)	F_{AAm}	$\overline{m}\ M_1$	$\overline{m}\ M_2$	r_1	r_2	$P_{AAm\text{-}AAm}$	R
20	0.52	1.72	2.14	0.66	1.24	0.50	51.80
25	0.56	1.88	1.79	0.70	1.00	0.51	54.50
30	0.57	2.08	1.75	0.82	0.99	0.55	52.22
35	0.55	1.96	1.89	0.78	1.10	0.54	51.95
40	0.54	1.86	2.00	0.74	1.17	0.53	51.83
50	0.49	1.54	2.36	0.56	1.30	0.46	51.28

[AAm–EMA] = 37.5×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Ce(IV)] = 7.5×10^{-3} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 60 min, [Cell] = 1 wt %.

Initiation:

$$R^{\cdot} + AAm \xrightarrow{k_i} R—AAm^{\cdot} - \quad (6)$$

$$R^{\cdot} + EMA \xrightarrow{k_i} R—EMA^{\cdot} - \quad (7)$$

Propagation:

$$R—(AAm)_{n-1}^{\cdot} + AAm \xrightarrow{k_p} R—(AAm)_n^{\cdot} - \quad (8)$$

$$R—(EMA)_{m-1}^{\cdot} + EMA \xrightarrow{k_p} R—(EMA)_m^{\cdot} - \quad (9)$$

$$R—(AAm)_n^{\cdot} - + EMA \xrightarrow{k_p} R—(AAm)_n—EMA^{\cdot} - \quad (10)$$

$$R—(EMA)_m^{\cdot} - + AAm \xrightarrow{k_p} R—(EMA)_m—AAm^{\cdot} - \quad (11)$$

Termination:

$$R—(AAm)_n—EMA^{\cdot} - + -^{\cdot}EMA—(AAm)_n—R \xrightarrow{k_{tc}}$$

$$R—(AAm)_n(EMA)_m—(AAm)_n—R \quad (12)$$

$$R—(EMA)_m—AAm + AAm—(EMA)_m—R \xrightarrow{k_{tc}}$$

$$R—(EMA)_m—(AAm)_n—(EMA)_m—R \quad (13)$$

$$R—(AAm)_n—EMA^{\cdot} - + -^{\cdot}AAm—(EMA)_m—R \xrightarrow{k_{tc}}$$

$$R—(AAm)_nEMAAAM(EMA)_mR \quad (14)$$

Oxidative termination:

$$R^{\cdot} + Ce(IV) \xrightarrow{k_t} \text{Oxidation product} + Ce(III) + H^+ \quad (15)$$

Where n and $\bar{m}$ are the average sequence lengths of acrylamide ($m\bar{M}_1$) and ethylmethacrylate ($m\bar{M}_2$) blocks in the grafted polymer chains. The values of these average sequence lengths ($m\bar{M}_1$ and $m\bar{M}_2$) have varied on varying the feed composition and reaction temperature.

CONCLUSIONS

The presence of ethylmethacrylate comonomer in the reaction mixture has increased the extent of grafting onto cellulose because of synergistic effect of ethylmethacrylate. The graft yield ($\%G_Y$) and other grafting parameters have shown dependence on the concentration of ceric (IV) ions, while keep-

ing optimum concentration of nitric acid in reaction mixture. The ceric (IV) ions have also shown a substantial reduction in formation of ungrafted homopolymers and copolymers. The grafting parameters obtained under different experimental conditions have been determined and variations in their values have been explained successfully. The thermal analysis of cellulose and grafted cellulose has indicated a substantial increase in thermal stability of cellulose on graft copolymerization of comonomers. The molecular weight of grafted chains determined by gel permeation chromatography has also shown dependence on concentration of ceric (IV) ions, feed molarity and feed composition. The composition of grafted chains determined by IR and elemental analysis has been used to determine the reactivity ratios of acrylamide (r_1) and ethylmethacrylate (r_2). On the basis of product of reactivity ratios (r_1r_2), the arrangement of average sequence lengths of acrylamide ($m\bar{M}_1$) and ethylmethacrylate ($m\bar{M}_2$) in the grafted chains has been predicted. The presence of comonomer has also reduced the individual grafting of monomer due to strong monomer–monomer interactions, which allowed the formation of alternate blocks of monomers in the grafted chains.

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