Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Acrylamide-Methylmethacrylate Graft Copolymerization onto Cellulose Using Ceric Ammonium Nitrate

K. C. Gupta[a]; Keerti Khandekar[a]
[a] Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee, U.A., India

To cite this Article Gupta, K. C. and Khandekar, Keerti(2003) 'Acrylamide-Methylmethacrylate Graft Copolymerization onto Cellulose Using Ceric Ammonium Nitrate', Journal of Macromolecular Science, Part A, 40: 2, 155 — 179
To link to this Article: DOI: 10.1081/MA-120017258
URL: http://dx.doi.org/10.1081/MA-120017258

JOURNAL OF MACROMOLECULAR SCIENCE®
Part A—Pure and Applied Chemistry
Vol. 40, No. 2, pp. 155–179, 2003

Acrylamide–Methylmethacrylate Graft Copolymerization onto Cellulose Using Ceric Ammonium Nitrate

K. C. Gupta* **and Keerti Khandekar**

Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee, U.A., India

ABSTRACT

The graft copolymerization of acrylamide (AAm) and methylmethacrylate (MMA) onto cellulose has been carried out from their mixtures using ceric ammonium nitrate (CAN) as initiator in the presence of nitric acid at 25.0 ± 0.1°C. The extent of graft copolymerization of acrylamide onto cellulose has shown a substantial increasing trend in the presence of methylmethacrylate comonomer. On varying the feed molarity from $7.5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ to $60 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, the graft yield has shown a linear increase with grafted chains of almost constant composition ($F_{AAm} = 0.57$). The composition of the grafted chains (F_{AAm}) has been found to be dependent on the feed composition (f_{AAm}) and temperature of reaction mixture. The effect of ceric (IV) ions concentration, reaction time and temperature was also studied and grafting parameters were determined to evaluate the effect of these reaction variables. The grafting parameters have shown an increasing trend up to $8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ concentration of ceric ammonium nitrate at a feed morality of $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ and shown a decreasing trend on further increasing the concentration of ceric ammonium nitrate ($> 8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$) while keeping fixed concentrations of nitric acid ($9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$). The IR and nitrogen percent data were used to determine the composition of the grafted chains (F_{AAM}), which was further used to determine reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2) using the Mayo and Lewis plot. The reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2) were found to be 0.82 and 1.10

---

*Correspondence: K. C. Gupta, Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, U.A., India; E-mail: kcgptfcy@iitr.ernet.in.

DOI: 10.1081/MA-120017258 1060-1325 (Print); 1520-5738 (Online)

www.dekker.com

respectively. This indicated an alternate arrangement of average sequence lengths of acrylamide ($\bar{m}M_1$) and methylmethacrylate ($\bar{m}M_2$) in the grafted chains as the product of reactivity ratios (r_1r_2) was less then unity. The rate of graft copolymerization of comonomers onto cellulose has been found to be dependent on the square concentration of comonomers and square root of the ceric ammonium nitrate concentration. The activation energy (ΔEa) of graft copolymerization was found to be low ($14.36\,\mathrm{kJ\,mol^{-1}}$) within the temperature range of 20°C to 45°C. On the basis of experimental observations, suitable reaction steps for graft copolymerization of acrylamide and methylmethacrylate have been proposed to explain the grafting of these comonomers onto cellulose.

Key Words: Acrylamide; Methylmethacrylate; Ceric ammonium nitrate; Cellulose; Graft copolymerization.

INTRODUCTION

Graft copolymerization of vinyl monomers from their binary mixtures is of special importance to obtain polymers having properties of both monomers in comparison to graft copolymers obtained by the grafting of individual monomers.[1−5] The grafting from binary mixture of monomers has the advantage of introducing grafted chains with tailor made properties for specific applications. The mutual effect of monomers in the reaction mixture controls the fraction of individual monomer in the grafted chains and overall yield of grafting. This synergistic effect of comonomer enhances the fraction of monomer in the graft yield which, otherwise shows poor affinity for grafting onto cellulose. The properties of graft copolymer ultimately depend upon the composition of the monomer in the grafted chains. Hence, this technique of graft copolymerization provides an opportunity to prepare tailor made grafted chains of desired properties by using suitable monomers and their composition in the feed.[6] The graft copolymerization of individual monomers has been carried out using a photosensitizer,[7] magnetic field,[8] radiation,[5,9] redox initiator[10] and metal chelates,[11−12] but in these techniques, the extent of ungrafted homopolymer has been found to be substantially high in comparison to grafted polymers. The ceric (IV) ions[13,15] have shown a substantial decrease in ungrafted polymer due to its participation in the formation of active sites onto cellulose through a single electron transfer process[16] to promote graft copolymerization. The ceric ion (IV) ions create free radicals onto cellulose in the presence of acids,[17−18] but its efficiency is low in aqueous media due to hydrolysis of ceric (IV) ions. The graft copolymerization of acrylamide (AAm)[8,14,19] and methylmethacrylate[20−21] individually onto cellulose has been reported, but using a binary mixture of acrylamide and methylmethacrylate is not available in the literature, therefore, we have focused our interest on investigating the grafting behavior of acrylamide onto cellulose in the presence of methylmethacrylate. The effect of feed composition, feed molarity on graft yield and composition of grafted polymers has been studied systematically and reactivity ratios of grafted monomers were determined using composition of grafted chains estimated by elemental and IR techniques.

EXPERIMENTAL

Chemicals Used

Acrylamide (Loba Chemie, Mumbai, India) was purified by recrystallization from benzene and dried in a vacuum desiccator. The methylmethacrylate (E. Merck, India) was purified by extraction with aqueous sodium chloride–sodium hydroxide solution and after drying over sodium sulfate in a vacuum desiccator, was stored below 5°C. The cellulose powder (Loba Chemie, Mumbai, India) was washed with methanol, acetone, deionized water, and vacuum dried at room temperature. Ceric ammonium nitrate (E. Merck, India) and nitric acid were analytical 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 reaction mixture.

Graft Copolymerization

The graft copolymerization of vinyl monomers was carried out by adding 1.0 g of purified cellulose ($\bar{M}n = 4.1 \times 10^5\,g\,mol^{-1}$) in a three-necked round bottom flask containing a 100 ml solution of nitric acid ($9.0 \times 10^{-2}\,mol\,dm^{-3}$) and ceric ammonium nitrate ($8.0 \times 10^{-3}\,mol\,dm^{-3}$). The three-necked round bottom flask was fitted with an electrically operated stirrer and thermostat to 25.0 ± 0.1°C. The solution was purged with nitrogen gas for about 15 min to remove oxygen from the solution. To initiate the graft copolymerization, a calculated amount of monomer mixture (1.971 g acrylamide and 1.80 g methylmethacrylate) was added into the reaction flask and a supply of nitrogen gas was maintained till graft copolymerization was carried out. To avoid the effect of stirring, the reaction mixture was stirred at a constant rate until graft copolymerization reaction was studied. The reaction was stopped by adding a 5.0% solution (w/w) of hydroquinone, and the reaction products were obtained by precipitating the reaction mixture in an excess of methanol. The precipitated reaction products were filtered and washed repeatedly with hot and cold water to remove unpolymerized monomers, ungrafted polyacrylamide and other impurities trapped in grafted cellulose. Finally, the product was dried in a vacuum desiccator till a constant weight.

Ceric (IV) Ions Consumption

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

Extraction of Homopolymer

The ungrafted polyacrylamide and polymethylmethacrylate was extracted from grafted crude using water and acetonitrile in Soxhlet apparatus for about 24 h. To obtain a homopolymer, the extracts were precipitated in methanol. Finally, the precipitates were dried to a constant weight and used to estimate the grafting parameters.

Extraction of Ungrafted Copolymers

The homopolymer extracted crude was subsequently used to extract the ungrafted ploy (acrylamide–methylmethacrylate) copolymer using dimethylformamide (DMF) as an extractant in a Soxhlet apparatus. The extract was precipitated with methanol and filtered. The ungrafted copolymers were characterized for their molecular weights by gel permeation chromatography (GPC) and their composition was determined by elemental analysis.

Extraction of Ungrafted Cellulose

After extracting the ungrafted homopolymer and copolymers from cellulose crude, the ungrafted cellulose was extracted by keeping grafted cellulose in a cuoxam solution[22] containing 1.2% $NaHSO_3$. The solution was stirred vigorously and after 6 h, the residue was filtered and washed with dilute acetic acid, deionized water, and dried to a constant weight at 50°C.

Extraction of Grafted Copolymer

After extracting ungrafted polymers and cellulose, the grafted copolymers were extracted by hydrolyzing the copolymer grafted cellulose in 72% sulfuric acid[23] at 30°C. At the end of 4 h, the hydrolyzing solution was diluted with water to an acid concentration of 4% and refluxed for 6 h. The grafted copolymers were obtained by precipitating the extract in methanol. After purification, the copolymers were characterized for their compositions by elemental analysis using a Perkin-Elmer 240C Elemental Analyzer. The molecular weight of the extracted copolymers was determined by gel permeation chromatography (GPC).

Characterization

FTIR-Spectra

The IR Spectra of cellulose and copolymer grafted cellulose recorded with Perkin-Elmer 1600 FTIR Spectrophotometer were used as evidence for grafting of copolymers onto cellulose and to determine the composition of the grafted copolymer chains using a percent transmittance at $1660\,cm^{-1}$ and $1765\,cm^{-1}$ for carbonyl group ($>C{=}O$) in acrylamide and methylmethacrylate respectively. The optical density ratio (ODR) as calculated with percent transmittance using the following equation was used to determine the mole fractions of acrylamide (F_{AAm}) and methylmethacrylate (F_{MMA}) in the grafted copolymer chains using a calibration curve drawn between ODR and a composition of known copolymers.

$$\mathrm{ODR} = \frac{\log(\text{Base line } \%\ T_{1765}/\text{MMA } \%\ T_{1765})}{\log(\text{Base line } \%\ T_{1660}/\text{AAm } \%\ T_{1660})}$$

Elemental Analysis

To verify the composition of grafted copolymer chains determined by infrared spectrum, the nitrogen content of grafted copolymers was determined by a Heraeus Carlo Ebra 1108 elemental analyzer and used to calculate the composition of the grafted chains.

Molecular Weight Measurement

The molecular weights of polyacrylamide and polymethylmethacrylate were determined by viscometric methods using following equations:

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

$$[\eta]_{35°C} = 5.50 \times 10^{-3}\,cm^3\,g^{-1}\ \bar{M}_V^{0.76}\ \text{(for PMMA in CH}_3\text{CH}_2\text{CN)}$$

The molecular weights of grafted and ungrafted copolymers were determined by gel permeation chromatography (PL-GPC-120, UK) equipped with three PL-aqua gel columns (PL-aqua gel 40–60, 10 μm) in a series and a ultra violet detector ($\lambda_{max} = 208\,nm$). A 200 μml copolymer solution of 0.1 mg/ml was loaded and eluted with dimethyl formamide at a flow rate of 1.0 ml/min. at 25°C. The universal calibration curve was recorded using a polymethylmethacrylate calibration kit.

RESULTS AND DISCUSSION

The graft copolymerization of acrylamide in the presence of methylmethacrylate has shown a substantial increase in the graft yield (%G) in comparison to the graft yield found with individual monomers. The methylmethacrylate has shown a synergistic effect on acrylamide, hence, affinity of acrylamide for grafting onto cellulose has increased.[24] The polymer chains grafted onto cellulose from the mixture of acrylamide and methylmethacrylate were copolymeric in nature, which has indicated that there were strong interactions between acrylamide and methylmethacrylate monomers responsible to prevent grafting of a individual monomer onto cellulose. The intensity of interactions between comonomers has shown a significant dependence on the composition of feed

(f_{AAm}) as it is clear from the compositional analysis of grafted chains. The high efficiency of grafting of comonomers onto cellulose has also been attributed to ceric (IV) ions, which were exclusively involved in the formation of radicals at cellulose backbone[16] to facilitate grafting of a monomer rather than in the formation of radicals at monomers to produce ungrafted homopolymer and copolymers in the reaction mixture. However, the efficiency of ceric ammonium nitrate in formation of active radicals at cellulose has been found to be low at relatively low concentration of nitric acid ($<9.0 \times 10^{-2}$ mol dm^{-3}) due to the formation of hydrated ceric (IV) ions, which were less reactive in hydrogen ions abstraction from the cellulose backbone than unhydrated ceric (IV) ions. These investigations have clearly suggested for keeping an excess concentration of nitric acid in the reaction mixture to maintain optimum reactivity of ceric (IV) ions to produce free radicals at the backbone of the cellulose. The IR spectra of poly(acrylamide–methylmethacrylate) copolymer grafted cellulose (Fig. 1B) have shown two additional

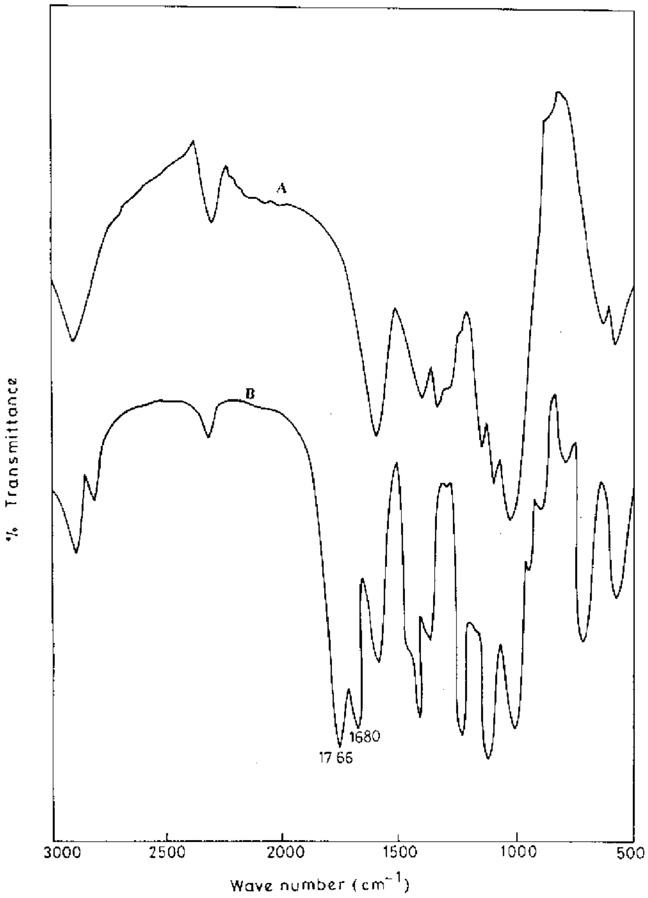

Figure 1. FTIR spectra of cellulose (A) and poly(acrylamide–co-methylmethacrylate) copolymer grafted cellulose(B).

absorption bands at 1766 cm^{-1} and 1680 cm^{-1} in comparison to pure cellulose (Fig. 1A), which corresponds to an ester carbonyl group of methylmethacrylate and carbamide group of acrylamide (Fig. 1B), hence provided strong proof for the presence of both monomers onto cellulose. Acrylamide and methylmethacrylate monomers were present as repeating units in grafted copolymers onto cellulose since no grafted chain was purely of individual monomer. The optical density ratio (ODR) of hydrolyzed copolymer chains has been used to verify the composition of grafted chains, which was also determined by percent nitrogen content in grafted chains. The thermogravimetric analysis (TGA) of pure cellulose, cellulose grafted with polyacrylamide or polymethylmethacrylate and cellulose grafted with poly(acrylamide–methylmethacrylate) copolymers has clearly indicated a substantial increase in thermal stability of cellulose on the grafting of monomers (Fig. 2). The DTGA curves of cellulose and grafted cellulose (Fig. 2) have indicated a shift in temperature of maximum decomposition rate (T_{max}) from 317°C (pure cellulose) to 350°C (poly acrylamide grafted cellulose). The decomposition temperature of cellulose grafted with poly(acrylamide–methylmethacrylate) copolymer has been found to be higher (337°C) than that of pure cellulose (317°C) and cellulose grafted with polymethylmethacrylate (328°C). These thermal data have clearly indicated a substantial variation in thermal stability of the cellulose on graft copolymerization of monomers. To gain further insight into the mechanism and factors which controlled the composition and extent of grafting of comonomers onto cellulose, the graft copolymerization of acrylamide–methylmethacrylate comonomers has been carried out at different feed molarity, feed compositions and reaction times and the effect of these variables on grafting

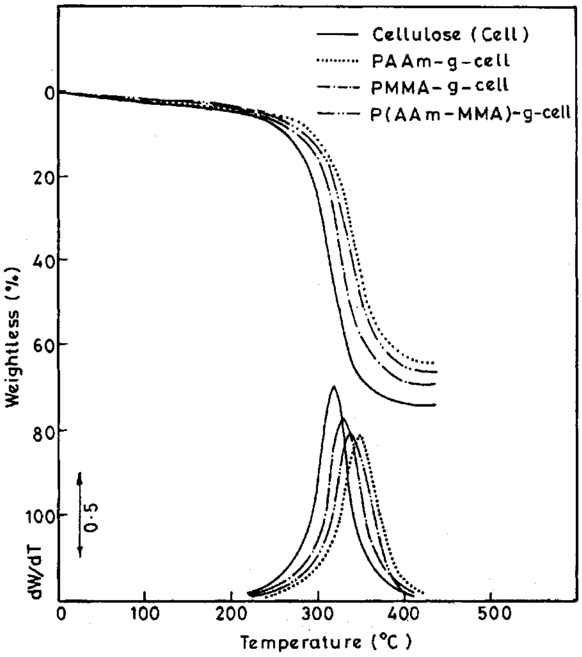

Figure 2. TGA and DTGA curves of cellulose and grafted cellulose.

parameters have been evaluated to optimize experimental conditions for maximum graft yield.

Effect of Feed Molarity

In order to evaluate the effect of concentration of monomers on grafting parameters at a constant monomer–monomer interactions, the graft copolymerization was studied at different feed molarity ranging from $7.5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ to $60.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ at constant concentration of ceric ammonium nitrate ($8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$) and nitric acid ($9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) at 25°C. During feed molarity variation, the composition of feed was kept constant ($f_{AAm} = 0.6$) so that monomer–monomer interactions remained almost constant. The percent graft yield (%G) has shown a steep rise up to $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ concentration of comonomers (Fig. 3a). A similar trend has been shown by the true grafting (%G_T) and efficiency of grafting (%G_E) as is clear from the data shown in Table 1a. However, on further increase in feed molarity beyond $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, the grafting parameters have not shown a linear trend as was observed at low feed molarity ($< 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$). The decreasing trend in percent graft conversion (%Cg) and efficiency of grafting (%G_E) at high feed molarity ($> 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) is due to the increase in formation of ungrafted homopolymer and copolymers. The increasing trend in graft yield (%G), true grafting (%G_T), percent graft conversion (%Cg) and efficiency of grafting (%G_E) up to $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ of the feed molarity was due to substantial consumption of monomers in the inception and growth of polymeric chains onto cellulose backbone. But deviation from a linear increase in these parameters at high feed molarity ($> 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) was due to the increase in viscosity of the medium, which retarded the rate of diffusion of comonomers from a solution phase to the active sites onto the cellulose. The retardation in extent of grafting at high feed molarity ($> 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) was also due to the decrease in swelling effect of solvent on cellulose and steric hindrance offered by chains which were already grafted onto cellulose. The combined effect of these factors at high feed molarity ($> 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) resulted in production of more grafted chains at the surface than inside the cellulose matrix. On increasing the feed molarity, the number (Ng) and frequency (G_F) of grafted chains has increased (Tables 1a and 1b). The molecular weights ($\bar{M}w$) of the grafted chains have shown an increasing trend up to $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ of feed molarity and have shown a decreasing trend on increasing feed molarity beyond $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ (Table 1b). The molecular weight dispersity ($\bar{M}_w/\bar{M}_n$) of grafted chains has improved up to a feed molarity of $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ (Table 1b). The variation in molecular weight dispersity ($\bar{M}_w/\bar{M}_n$) at high feed molarity ($> 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) was due to a decrease in the rate of diffusion of comonomer molecules to the active sites on growing chains at cellulose backbone. The percentage of grafted chains has shown an increasing trend on increasing feed molarity from $7.5 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ to $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ due to the growth of grafted chains and the formation of new side chains onto cellulose, but decreased on further increasing the feed molarity beyond $45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ (Table 1b). The composition of the grafted chains during feed molarity variation was constant which has clearly indicated that during feed molarity variation, the monomer–monomer interactions have remained constant. The rate of graft copolymerization (R_P) determined

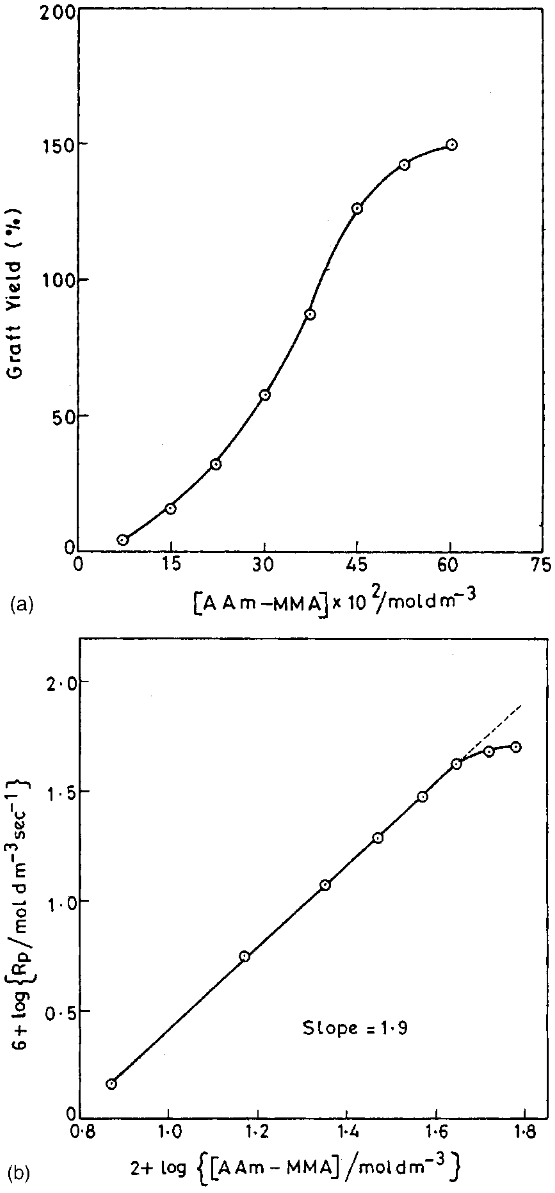

Figure 3. (a) Graft yield (%G) as a function of feed molarity. [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO$_3$] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min, Temp. 25°C. (b) Log–log plot between Rp vs. [AAm–MMA]. [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO$_3$] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min., Temp. 25°C. (c) Ceric (IV) ions consumption as a function of feed molarity (B) and reaction time (A). $f_{AAm} = 0.6$, [HNO$_3$] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Temp. 25°C. [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}(A).

(*continued*)

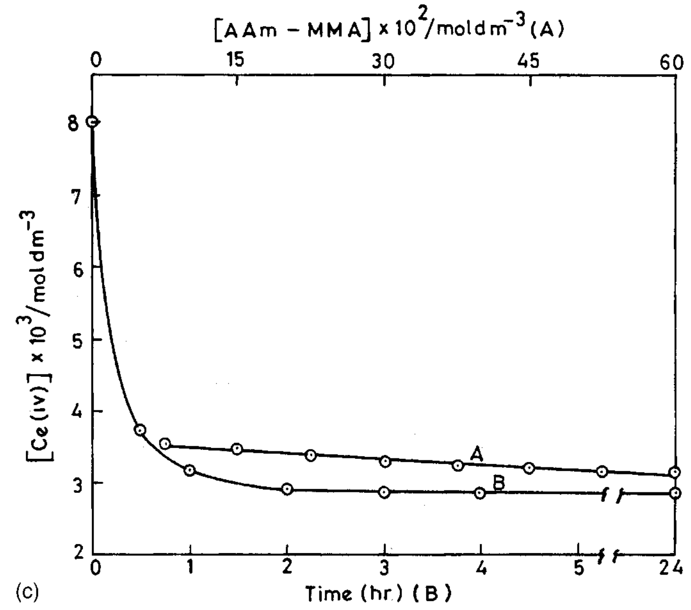

Figure 3. Continued.

at different feed molarity has been used to draw a plot between log Rp vs. feed molarity to determine the dependence of the grafting rate on feed molarity (Fig. 3b). The slope of this plot was 1.90, which has shown a second order dependence of the reaction rate on the feed molarity (Fig. 3b). On varying the feed molarity from $7.5 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$ to $60.0 \times 10^{-2}\,\text{mol}\,\text{dm}^{-3}$, the rate of ceric (IV) ions disappearance was almost constant, which provided evidence that ceric (IV) ions were not directly involved in the formation of active sites onto comonomers, otherwise the rate of ceric (IV) ions consumption must have been affected on varying the feed molarity (Fig. 3c). The ungrafted homopolymer and

Table 1a. Effect of comonomer concentration on grafting parameters at 25°C.

[AAm–MMA] × 10^2 mol dm^{-3}	% G_T	% C_T	% C_g	% C_c	% G_E	G_F
7.5	225	9.70	7.03	32	71.67	0.27
15.0	230	15.80	12.06	35	80.10	0.72
22.5	250	21.50	17.74	38	82.05	1.18
30.0	251	27.84	23.38	45	84.00	1.60
37.5	282	33.33	28.32	49	84.10	1.88
45.0	334	39.55	33.89	52	85.71	2.38
52.5	324	53.00	32.71	57	61.73	2.52
60.0	322	58.87	30.04	59	51.03	2.56

[CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO$_3$] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

Table 1b. Effect of comonomer concentration on grafting parameters at 25°C.

[AAm–MMA] $\times 10^2$ mol dm^{-3}	$N_g \times 10^6$	$\bar{M}_w \times 10^{-3}$ g mol^{-1} (G_P)	$\bar{M}_w/\bar{M}_n$, (G_P)	% Branches in grafted polymer	% Cellulose in grafted polymer
7.5	0.209	205	1.96	11.85	88.15
15.0	0.615	255	1.88	30.97	69.03
22.5	1.100	298	1.76	46.48	53.52
30.0	1.760	330	1.68	56.31	43.69
37.5	2.240	390	1.62	64.10	35.90
45.0	3.040	415	1.60	70.79	29.21
52.5	3.500	405	1.78	71.36	28.64
60.0	3.740	398	2.10	71.63	28.37

[CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

copolymer were formed in the reaction mixture by the chain transfer process of growing grafted chains onto cellulose and not due to the formation of active sites on monomer molecules by direct interactions of ceric (IV) ions.

Effect of Feed Composition

The graft yield (%G) and composition of the grafted chains onto cellulose have also been evaluated by varying feed composition (f_{AAm}) at constant feed molarity (45.0×10^{-2} mol dm^{-3}), ceric ammonium nitrate concentration (8.0×10^{-3} mol dm^{-3}) and nitric acid (9.0×10^{-2} mol dm^{-3}) at 25°C. To compare the effect of addition of comonomers, the individual graft yield (%G) of acrylamide and methylmethacrylate onto cellulose was also estimated at the same feed molarity (45.0×10^{-2} mol dm^{-3}). The graft yield (%G) and other grafting parameters for acrylamide–methylmethacrylate comonomers as a function of feed composition (f_{AAm}) are shown in Fig. 4a and Table 2. The methylmethacrylate has shown a high affinity for grafting (%G) in comparison to

Table 2a. Effect of feed composition (f_{AAm}) on grafting parameters at 25°C.

f_{AAm}	% G_T	% C_T	% C_g	% C_c	% G_E	G_F
0.00	314	27.33	23.33	49.5	85.36	2.25
0.20	294	27.36	22.88	50.0	83.62	2.04
0.40	315	33.18	28.15	51.0	84.84	2.21
0.60	334	39.55	33.89	52.0	85.71	2.39
0.80	283	32.12	25.46	49.0	79.28	2.11
1.00	266	24.73	16.90	42.0	68.35	2.00

[AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell.] = 1.0 g, Time = 60 min.

Table 2b. Effect of feed composition (f_{AAm}) on grafting parameters at 25°C.

f_{AAm}	$N_g \times 10^6$	$\bar{M}_w \times 10^3$ g mol^{-1} (G_P)	$\bar{M}_w/\bar{M}_n$ (G_P)	% Branches in grafted polymer	% Cellulose in grafted polymer
0.00	2.72	385	2.20	67.96	32.04
0.20	2.49	390	1.92	65.99	34.01
0.40	2.74	408	1.86	68.71	31.29
0.60	3.04	415	1.60	70.79	29.21
0.80	2.51	350	1.88	64.23	35.77
1.00	2.04	265	2.10	56.25	43.75

[AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell.] = 1.0 g, Time = 60 min.

acrylamide (Fig. 4a). The extent of the percent graft yield (%G) increased on increasing the mole fraction of the acrylamide (f_{AAm}) from 0.2 to 0.6 and on further increasing the mole fraction of acrylamide (f_{AAm}) beyond 0.6, the graft yield (%G) has shown a substantial decreasing trend (Fig. 4a). Similar trends have been shown by true grafting (%G_T), percent conversion (%Cg), efficiency (%G_E) and frequency of grafting (G_F) as is evident from the data shown in Table 2a. The number of grafted chains (Ng) has also decreased on a high fraction of acrylamide ($f_{AAm} > 0.6$) in the feed (Table 2b). The total conversion (%C_T) and cellulose conversion (%C_c) have shown dependence on feed composition (Table 2a). The decreasing trend in all these parameters on taking acrylamide beyond $f_{AAm} > 0.6$ has indicated that acrylamide has low affinity for grafting onto cellulose in comparison to methylmethacrylate monomer. The initial increase in the graft yield (%G) and other grafting parameters within the mole fraction of acrylamide (f_{AAm}) from 0.2 to 0.6 has been due to the synergistic effect of methylmethacrylate onto acrylamide so that the extent of acrylamide mole fraction in the grafted chains has increased. In this range of feed composition, the acrylamide–methylmethacrylate interactions are stronger in comparison to acrylamide–acrylamide interactions, hence, growing chains with methylmethacrylate as an active center prefer to combine with acrylamide monomer which resulted in an increase in graft yield (%G) and other grafting

Table 2c. Compositional data of grafted polymer chains on cellulose at 25°C.

f_{AAm}	F_{AAm}	%N	$\bar{m}M1$	$\bar{m}M2$	$P_{(AAm,AAm)}$	R
0.00	—	—	—	—	0.00	—
0.20	0.19	2.87	1.20	5.56	0.17	29.59
0.40	0.39	6.16	1.55	2.73	0.35	46.73
0.60	0.57	9.54	2.08	1.83	0.55	51.15
0.80	0.76	13.66	3.61	1.35	0.77	40.32
1.00	1.00	19.72	—	—	1.00	—

[AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell.] = 1.0 g. $\bar{m}M_1$ and $\bar{m}M_2$ are the average sequence lengths of AAm and MMA monomers in the grafted copolymer chains (G_P).

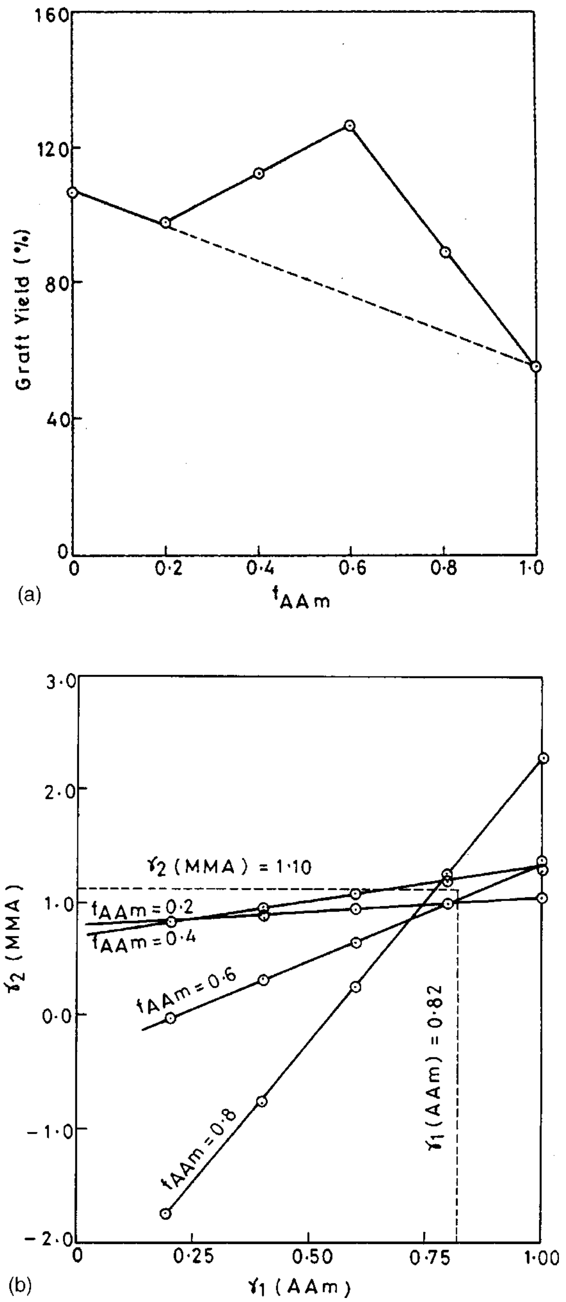

Figure 4. (a) Graft yield (%G) as a function of feed composition (f_{AAm}). [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 60 min., Temp. 25°C. (b) Mayo and Lewis plot for reactivity ratios. [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 60 min, Temp. 25°C.

parameters. The molecular weight and number of grafted chains (Ng) have also increased on increasing the mole fraction of the acrylamide in the feed from 0.2 to 0.6 (Table 2b). This has been verified from the IR and nitrogen content in the grafted chains (Table 2c). The compositional data of grafted chains were used to calculate the reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2) (Fig. 4b) by Mayo and Lewis plot.[25] The reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2) have been found to be 0.82 and 1.10, respectively which clearly indicated that acrylamide has low reactivity in comparison to methylmethacrylate. Hence, grafted chains had a low fraction of the acrylamide (F_{AAm}) in comparison to feed (f_{AAm}) (Table 2c). The average sequence lengths of acrylamide ($\bar{m}M_1$) in the grafted chains have increased on increasing the mole fraction of acrylamide in the feed (Table 2c), whereas, average sequence lengths of methylmethacrylate ($\bar{m}M_2$) in the chains have shown a decreasing trends which is due to the high mole fractions of the acrylamide in the grafted chains (Table 2c). The probability of the addition of acrylamide ($P_{AAm,AAm}$) during feed composition variation has shown a continuous increasing trend, but the run number (R) has increased only up to a 0.6 mole fraction of acrylamide in the feed and decreased on increasing the mole fraction (f_{AAm}) of acrylamide beyond 0.6. The product of reactivity ratios (r_1r_2) is less than unity (0.90), which has indicated that the average sequence lengths of acrylamide ($\bar{m}M_1$) in the grafted chains are arranged in an alternate fashion. These investigations have clearly indicated that the composition of the grafted chains depends upon the reactivity of the monomer used for grafting and also onto the composition of the feed used during graft copolymerization.

Effect of Ceric (IV) Ions Concentration

The effect of ceric (IV) ions concentration on graft copolymerization of acrylamide and methylmethacrylate comonomer has been studied at different concentrations of ceric ammonium nitrate ranging from $2.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ to $12.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ at constant feed molarity ($45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) and nitric acid ($9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) at 25°C. The composition of the feed was also kept constant ($f_{AAm} = 0.6$). The graft yield (%G) and other grafting parameters as a function of ceric ammonium nitrate are shown in Fig. 5a and Table 3. The percent graft yield (%G) has shown an increasing trend up to $8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ concentration of ceric (IV) ions and has shown a sharp decreasing trend on increasing the ceric ammonium nitrate concentration beyond $8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. 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 up to $8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ concentration of ceric ammonium nitrate (Table 3a). The initial increasing trend in graft yield (%G) and other grafting parameters is due to the formation of sufficient number of ceric (IV) ions in the reaction mixture at $9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ concentration of nitric acid which is ultimately consumed in the formation of active sites onto the cellulose to facilitate the graft copolymerization of comonomer. With a higher concentration of ceric ammonium nitrate ($> 8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$), the decreasing trend in graft yield (%G) and other grafting parameters has been attributed to the decrease in ratio of nitric acid to ceric ammonium nitrate, hence ceric (IV) ions undergo hydrolysis which are inefficient to form active sites onto cellulose. This is clear from the decreasing

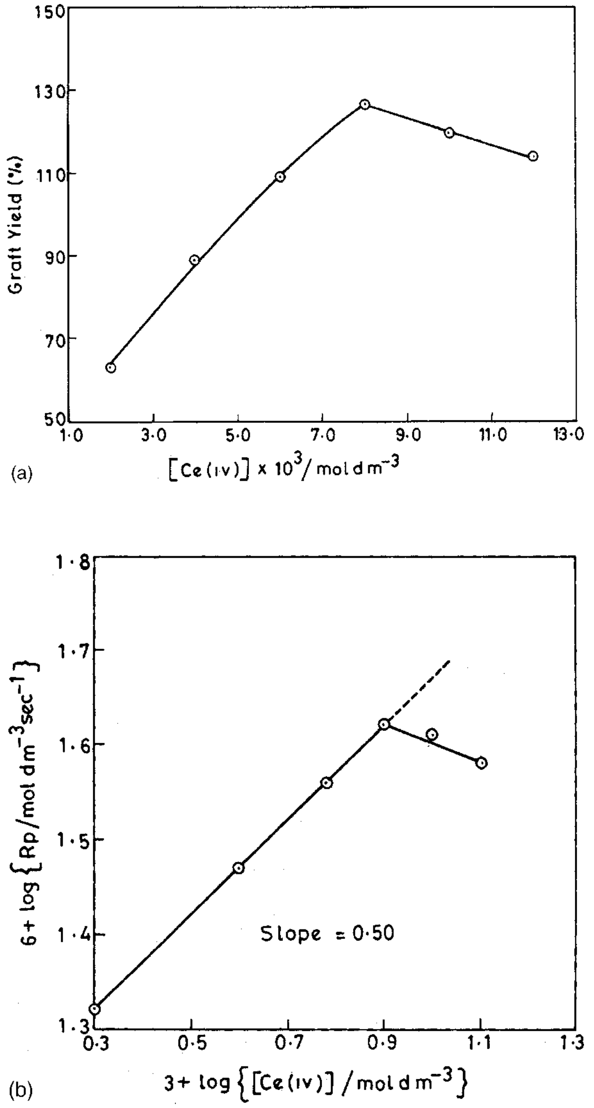

Figure 5. (a) Graft yield (%G) as a function of [CAN]. [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 60 min, Temp. 25°C. (b) Log–log plot between Rp vs. [CAN]. [AAm–MMA] = 45.0×10^{-2} mol dm^{3}, $f_{AAm} = 0.6$, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 60 min, Temp. 25°C.

trend in a number of grafted chains (N_g) at a high concentration of ceric ammonium nitrate ($> 8.0 \times 10^{-3}$ mol dm^{-3}). At high concentration of ceric ammonium nitrate ($> 8.0 \times 10^{-3}$ mol dm^{-3}), the cellulose conversion (%C_c) has also shown a decreasing trend which is an indication that ceric (IV) ions have not created active sites onto cellulose to enhance the consumption of cellulose by graft copolymerization (Table 3a).

Table 3a. Effect of [CAN] on grafting parameters at 25°C.

[CAN] $\times 10^3$ mol dm^{-3}	% G_T	%C_T	% C_g	% C_c	% G_E	G_F
2	262	20.98	16.95	45	80.76	1.22
4	301	28.38	23.81	47	83.88	1.70
6	318	34.70	29.32	50	84.49	2.10
8	334	39.55	33.89	52	85.71	2.38
10	329	38.20	32.02	51	83.80	2.34
12	328	37.40	30.67	50	82.01	2.29

[AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

The molecular weight of grafted chains has shown a continuous decreasing trend on increasing the concentration of ceric ammonium nitrate, which has indicated that ceric (IV) ions have also participated in the termination reaction with growing chains. This chain termination process is more predominant with hydrated ceric (IV) ions. The percentage of comonomer in grafted cellulose has also decreased above a 8.0×10^{-3} mol dm^{-3} concentration of ceric ammonium nitrate, which is clear from the data shown in Table 3b. The decreasing trend in grafting parameters at a high concentration of ceric ammonium nitrate ($> 8.0 \times 10^{-3}$ mol dm^{-3}) has also been attributed to steric hindrance created by grafted chains at the cellulose which have reduced the rate of diffusion of ceric (IV) ions from solution phase to the cellulose to produce active sites onto the cellulose, hence, the extent of grafting has shown a decreasing trend. The logarithmic plot drawn between log Rp vs. concentration of ceric ammonium nitrate (Fig. 5b) has given a linear curve with a slope of 0.50. This has indicated that the rate of graft copolymerization is proportional to a square root concentration of ceric ammonium nitrate (Fig. 5b).

Table 3b. Effect of [CAN] on grafting parameters at 25°C.

[CAN] $\times 10^3$ mol dm^{-3}	$N_g \times 10^6$	$\bar{M}_w \times 10^{-3}$ g mol^{-1} (G_P)	$\bar{M}_w/\bar{M}_n$ (G_P)	% Branches in grafted polymer	% Cellulose in grafted polymer
2	1.34	469	2.30	58.33	41.67
4	1.94	455	2.10	65.31	34.69
6	2.56	425	1.88	68.55	31.45
8	3.04	415	1.60	70.79	29.21
10	2.91	408	2.16	70.00	30.00
12	2.80	398	2.20	69.51	30.49

[AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

Effect of Reaction Time

The effect of different variables on grafting parameters has been studied at a fixed time of graft copolymerization (60 min), but recording grafting parameters as a function of reaction time is also equally important in comparison to other variations. To study the effect of reaction time on grafting parameters, the grafted samples were collected at different times of graft copolymerization at constant feed molarity (45.0×10^{2} mol dm^{-3}), ceric ammonium nitrate (8.0×10^{-3} mol dm^{-3}), nitric acid (9.0×10^{-2} mol dm^{-3}) and feed composition ($f_{AAm} = 0.6$) and were analyzed for various grafting parameters as shown in Fig. 6 and Table 4. The graft yield (%G) and other grafting parameters have shown a substantial increasing trend up to 8 h of graft copolymerization and after 8 h, the value of these parameters became almost constant (Fig. 6 and Table 4a). The increasing trend in graft yield (%G) 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 the cellulose. This is clear from the increasing trend in number (N_g) and frequency (G_F) of grafted chains onto cellulose (Table 4b) and from the increasing trend in true grafting (%G_T), percent conversion (%C_g) and efficiency of grafting (%G_E). After 8 h, the grafting parameters have shown a insignificant increase in their values (Table 4a), which has been attributed to the decrease in rate of diffusion of comonomer from the solution phase to the cellulose due to the decrease in activity of comonomers in the reaction mixture of graft copolymerization. The steric hindrance offered by grafted chains has retarded the extent of grafting after 8 h of graft copolymerization. The grafted chains obtained at different

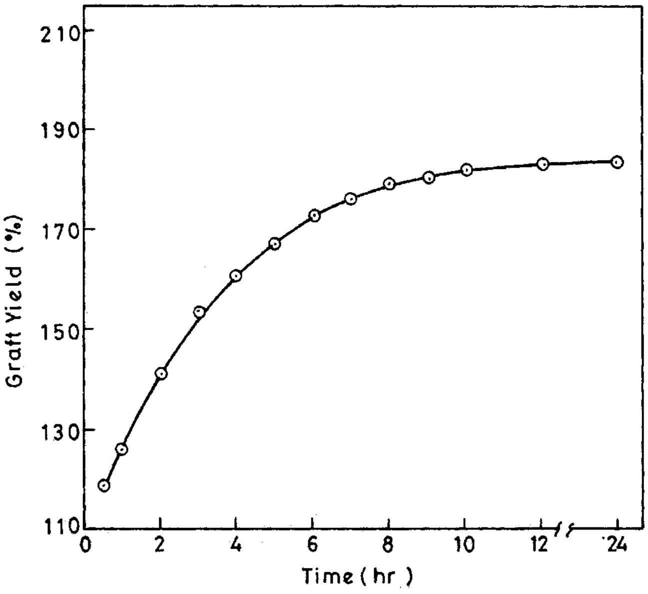

Figure 6. Graft yield (%G) as a function of reaction time. [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell.] = 1.0 g, $f_{AAm} = 0.6$, Temp. 25°C.

Table 4a. Effect of reaction time on grafting parameters at 25°C.

Time (min.)	% G_T	% C_T	% C_g	% C_c	% G_E	G_F
30	329	37.40	32.01	51.0	85.61	2.33
60	334	39.55	33.89	52.0	85.71	2.39
120	350	44.12	37.93	53.5	85.98	2.49
180	352	47.62	41.16	55.9	86.44	2.50
240	354	50.04	43.31	57.5	86.56	2.55
300	356	51.71	44.93	58.5	86.89	2.56
360	360	53.40	46.56	59.3	87.15	2.576
420	361	54.24	47.35	59.8	87.30	2.58
480	361.9	55.10	48.16	60.4	87.40	2.581
540	363	55.39	48.43	60.5	87.42	2.583
600	363.8	55.96	48.96	60.8	87.50	2.59
720	364	56.25	49.23	60.9	87.52	2.60
1440	365	56.55	49.50	61.0	87.53	2.60

[AAm–MMA] $= 45.0 \times 10^{-2}$ mol dm^{-3}, [CAN] $= 8.0 \times 10^{-3}$ mol dm^{-3}, [HNO$_3$] $= 9.0 \times 10^{-2}$ mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] $= 1.0$ g.

intervals of reaction time were of high molecular weight and have shown variation in molecular weight dispersity beyond 8 h (Table 4b). After 8 h, the weight average molecular weight of the grafted chains has increased substantially in comparison to the number average molecular weight, hence, molecular weight dispersity has increased

Table 4b. Effect of reaction time on grafting parameters at 25°C.

Time (min.)	$N_g \times 10^6$	$\bar{M}_w \times 10^{-3}$ g mol^{-1} (G_P)	$\bar{M}_w/\bar{M}_n$ (G_P)	% Branches in grafted polymer	% Cellulose in grafted polymer
30	2.90	410	1.62	70.00	30.00
60	3.04	415	1.60	70.79	29.21
120	3.24	435	1.62	72.49	27.51
180	3.40	450	1.63	73.24	26.76
240	3.57	451	1.63	73.68	26.32
300	3.64	454	1.63	74.06	25.94
360	3.71	466	1.64	74.47	25.53
420	3.768	467	1.64	74.67	25.36
480	3.80	470	1.66	74.77	25.33
540	3.81	472	1.98	74.84	25.16
600	3.84	473	2.10	74.96	25.04
720	3.86	474	2.22	75.03	24.97
1440	3.88	474	2.30	75.10	24.90

[AAm–MMA] $= 45.0 \times 10^{-2}$ mol dm^{-3}, [CAN] $= 8.0 \times 10^{-3}$ mol dm^{-3}, [HNO$_3$] $= 9.0 \times 10^{-2}$ mol dm^{-3}, $f_{AAm} = 0.6$, [Cell.] $= 1.0$ g.

beyond 8 h of graft copolymerization. These investigations have clearly indicated that the optimum rate of graft copolymerization and molecular weight dispersity could be obtained by maintaining a constant supply of comonomer in the reaction mixture so that the molecular weight and compositional heterogeneity of grafted chains could be avoided. The effect of reaction time was also studied on the rate of ceric (IV) ions disappearance during graft copolymerization of comonomers onto cellulose. The rate of ceric (IV) ions was very high during the initial 60 min of graft copolymerization as it is clear from curve B in Fig. 3c. After 60 min, the ceric (IV) ions consumption was almost negligible, which indicated that ceric (IV) ions were consumed only in the formation of active sites onto cellulose during the initial one hour of graft copolymerization. Hence after 1 h, the concentration of ceric (IV) ions has not changed substantially. The retardation in the rate of ceric (IV) ions disappearance after 1 h has also been attributed to the decrease in the rate of diffusion of ceric (IV) ions from the solution phase to the cellulose matrix due to the hindrances created by grafted chains onto the cellulose. The increasing trend in molecular weight of the grafted chains as a function of reaction time is an indication that ceric (IV) ions have not participated in the premature termination of the grafting chains on cellulose and growth of grafted chains was continued until the supply of comonomers was maintained.

Effect of Temperature

The graft copolymerization of acrylamide and methylmethacrylate comonomers onto cellulose has also been studied at different temperatures ranging from 20°C to 50°C at constant feed molarity (45.0×10^{-2} mol dm^{-3}), constant concentration of ceric ammonium nitrate (8.0×10^{-3} mol dm^{-3}) and nitric acid (9.0×10^{-2} mol dm^{-3}) at constant feed composition ($f_{AAm} = 0.6$). The graft yield (%G) and other grafting parameters have shown an increasing trend up to 40° C (Fig. 7a and Table 5), which is due to the increase in the rate of diffusion of comonomers from solution phase to the active sites onto 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 cellulose matrix which were lying unutilized at low temperature. This is evident from the increasing trend in cellulose consumption (%C_c) (Table 4a) and number of grafted chains (N_g) (Table 4b) on increasing the temperature of the reaction mixture. The increasing trend in cellulose consumption beyond 40°C was due to the oxidative degradation of the cellulose. The molecular weights of the grafted chains have shown a continuous decreasing trend on increasing the temperature, which is due to the increase in chain termination and transfer process at high temperature. The increase in temperature of graft copolymerization has shown a substantial effect on reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2). The reactivity ratio of the acrylamide (r_1) has increased up to 30°C (Table 5c) and has shown a decreasing trend beyond 30°C whereas, the reactivity ratio of methylmethacrylate (r_2) has shown an opposite trend in comparison to acrylamide. The variation in reactivity ratios has resulted in variation in average sequence lengths of acrylamide ($\bar{m}M_1$) and methylmethacrylate ($\bar{m}M_2$) in the grafted polymer chains. The variation in reactivity of acrylamide is also evident from the variation in probability of the addition of acrylamide

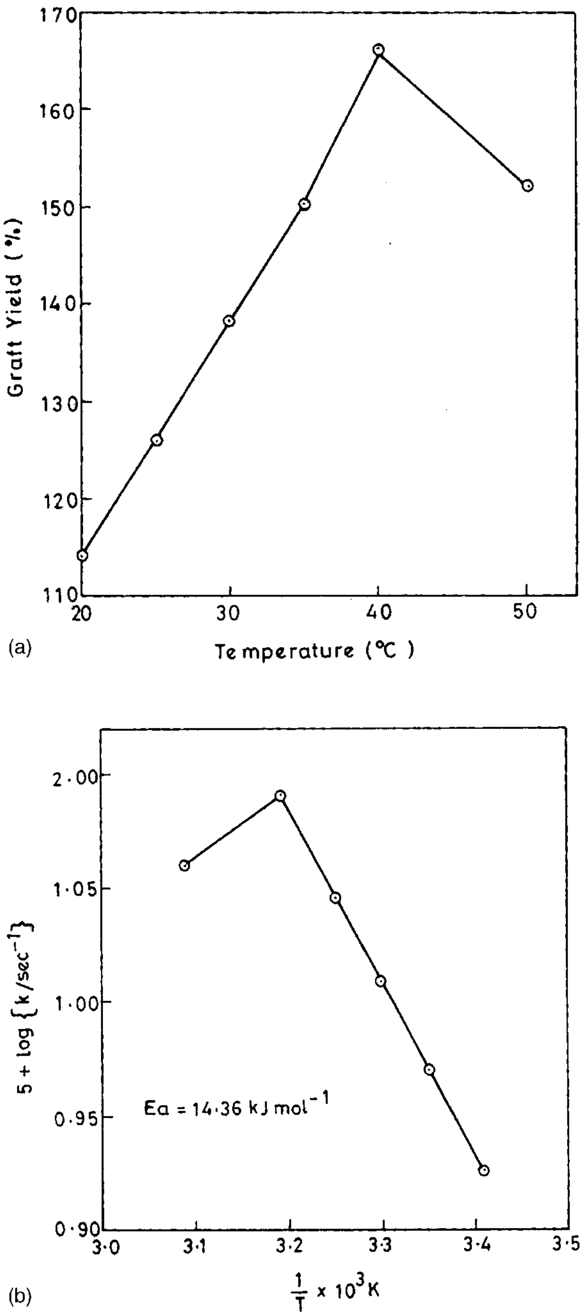

Figure 7. (a) Effect of temperature on graft yield (%G). [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, f_{AAm} = 0.6, Time = 60 min. (b) Arrhenius plot between log k vs. 1/T. [AAm–MMA] = 45.0×10^{-2} mol dm^{-3}, [CAN] = 8.0×10^{-3} mol dm^{-3}, [HNO_3] = 9.0×10^{-2} mol dm^{-3}, [Cell] = 1.0 g, f_{AAm} = 0.6, Time = 60 min.

Table 5a. Effect of temperature on grafting parameters.

Temperature (°C)	% G_T	% C_T	% C_g	% C_c	% G_E	G_F
20	328	36.59	30.67	50.0	83.82	2.21
25	334	39.55	33.89	52.0	85.71	2.38
30	349	42.24	37.12	53.0	87.89	2.64
35	350	44.93	40.35	55.5	89.82	2.82
40	355	48.96	44.66	58.5	91.20	3.02
50	320	45.06	40.89	60.0	90.74	2.80

$[\mathrm{AAm{-}MMA}] = 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{CAN}] = 8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{HNO_3}] = 9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, $f_{\mathrm{AAm}} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

($P_{\mathrm{AAm,AAm}}$) to the growing chains. The variation in reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2) has also resulted in a variation of the run number (R) of the grafted chains (Table 5c). The rate constants of graft copolymerization determined at different temperatures were used to determine the activation energy of graft copolymerization by drawing the Arrhenius plot (Fig. 7b), which has been found to be comparatively low ($14.36\,\mathrm{kJ\,mol^{-1}}$) for the grafting of comonomers onto cellulose.

Thus, on the basis of experimental observations, the following reaction steps have been proposed for graft copolymerization of acrylamide and methylmethacrylate onto cellulose in the presence of ceric ammonium nitrate as initiator.

Radical formation:

$$\mathrm{Cell{-}H} + \mathrm{Ce(IV)} \xrightarrow{k} \underset{(\mathrm{R}^{\cdot})}{\mathrm{Cell}^{\cdot}} + \mathrm{Ce(III)} + \mathrm{H}^{+} \tag{1}$$

Initiation:

$$\mathrm{R}^{\cdot} + \mathrm{AAm} \xrightarrow{k_i} \mathrm{R} - \mathrm{AAm}^{\cdot} - \tag{2}$$

$$\mathrm{R}^{\cdot} + \mathrm{MMA} \xrightarrow{k_i} \mathrm{R} - \mathrm{MMA}^{\cdot} - \tag{3}$$

Table 5b. Effect of temperature on grafting parameters.

Temperature (°C)	$N_g \times 10^6$	$\bar{M}_w \times 10^{-3}$ $\mathrm{g\,mol^{-1}}$ (G_P)	$\bar{M}_w/\bar{M}_n$ (G_P)	% Branches in grafted polymer	% Cellulose in grafted polymer
20	2.70	422	1.62	69.51	30.49
25	3.04	415	1.60	70.79	29.21
30	3.41	405	1.64	72.25	27.75
35	3.81	394	1.68	72.99	27.01
40	4.26	389	1.76	73.94	26.06
50	4.03	377	1.86	71.70	28.30

$[\mathrm{AAm{-}MMA}] = 45.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{CAN}] = 8.0 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$, $[\mathrm{HNO_3}] = 9.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$, $f_{\mathrm{AAm}} = 0.6$, [Cell.] = 1.0 g, Time = 60 min.

Table 5c. Effect of temperature on composition of grafted polymer chains on cellulose.

Temperature (°C)	F_{AAm}	$\bar{m}M_1$	$\bar{m}M_2$	r_1	r_2	$P_{(AAm,AAm)}$	R
20	0.54	1.89	2.04	0.76	1.22	0.53	50
25	0.57	2.08	1.83	0.82	1.10	0.55	51
30	0.58	2.20	1.70	0.86	0.98	0.56	51
35	0.56	2.02	1.83	0.81	1.05	0.55	52
40	0.55	1.95	1.91	0.77	1.13	0.53	41
50	0.52	1.74	2.15	0.68	1.26	0.50	51

$[AAm{-}MMA] = 45.0 \times 10^{-2}\,mol\,dm^{-3}$, $[CAN] = 8.0 \times 10^{-3}\,mol\,dm^{-3}$, $[HNO_3] = 9.0 \times 10^{-2}\,mol\,dm^{-3}$, $f_{AAm} = 0.6$, $[Cell.] = 1.0\,g$, Time $= 60\,min$. $\bar{m}M_1$ and $\bar{m}M_2$ are the average sequence lengths of AAm and MMA monomers in the grafted copolymer chains (G_P).

Propagation:

$$R - (AAm)_{n-1}{-}AAm^{\cdot} - +AAm \xrightarrow{k_p} R - (AAm)_n - AAm^{\cdot}- \tag{4}$$

$$R - (MMA)_{m-1}{-}MMA^{\cdot} - +MMA \xrightarrow{k_p} R - (MMA)_m{-}MMA^{\cdot}- \tag{5}$$

$$R - (AAM)_{n-1}{-}AAm^{\cdot} - +MMA \xrightarrow{k_p} R - (AAm)_n{-}MMA^{\cdot}- \tag{6}$$

$$R - (MMA)_{m-1}{-}MMA^{\cdot} - +AAm \xrightarrow{k_p} R - (MMA)_m{-}AAm^{\cdot}- \tag{7}$$

Termination:

$$\begin{aligned} &R(AAm)_nMMA^{\cdot}- \\ &\quad + -^{\cdot}MMA(AAm)_nR \xrightarrow{k_{tc}} R(AAm)_nMMA{-}MMA(AAm)_nR \end{aligned} \tag{8}$$

$$\begin{aligned} &R(MMA)_mAAm^{\cdot}- \\ &\quad + -^{\cdot}AAm(MMA)_mR \xrightarrow{k_{tc}} R(MMA)_mAAm{-}AAm(MMA)_mR \end{aligned} \tag{9}$$

$$\begin{aligned} &R(AAm)_nMMA^{\cdot}- \\ &\quad + -^{\cdot}AAm(MMA)_mR \xrightarrow{k_{tc}} R(AAm)_nMMA{-}AAm(MMA)_mR \end{aligned} \tag{10}$$

Oxidative termination:

$$R^{\cdot} + Ce(IV) \xrightarrow{k_g} Oxidation\ \ product + Ce(III) + H^{+} \tag{11}$$

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

CONCLUSION

The presence of methylmethacrylate comonomer in the reaction mixture has increased the extent of graft copolymerization of the acrylamide onto cellulose due to its synergistic effect. The ceric (IV) ions have shown a significant effect on graft yield and other grafting parameters. The ceric (IV) ions have shown a substantial reduction in formation of ungrafted homopolymer and copolymers. The values of various grafting parameters under different experimental conditions have been evaluated and variations in their value have been explained successfully. The thermal investigations of cellulose and grafted cellulose have indicated a substantial increase in thermal stability on graft copolymerization of the monomers onto the cellulose. The molecular weights of the grafted chains have been determined by gel permeation chromatography. The compositional analysis of grafted chains by IR and percent nitrogen content has been used to calculate the reactivity ratios of acrylamide (r_1) and methylmethacrylate (r_2). The product of reactivity ratios of acrylamide and methylmethacrylate (r_1r_2) has been found to be less than unity; hence average sequence lengths of acrylamide ($\bar{m}M_1$) and methylmethacrylate ($\bar{m}M_2$) in grafted chains were arranged in alternate fashion. The energy of activation for graft copolymerization has been found to be reasonably low due to the cooperative effect of comonomers used for graft copolymerization onto cellulose. Thus it has been observed that graft copolymerization of acrylamide onto cellulose has been improved due to a synergistic effect of methylmethacrylate in the reaction mixture. The presence of the comonomer has also reduced the individual grafting monomer due to strong monomer–monomer interactions, which allowed the formation of alternate blocks of monomer in the grafted chains.

ACKNOWLEDGMENTS

Financial assistance from UGC, New Delhi is thankfully acknowledged. The authors are also thankful to I.I.T. Roorkee for providing facilities to complete this work.

REFERENCES

1. Uchida, E.; Uyama, Y.; Ikada, Y. Antistatic properties of surface modified polyester fabrics. Text. Res. J. **1991**, *61*, 483.
2. Mares, E.; Arther, J.C.; Harris, J.A. Soil release and textile properties of cotton/polyester-poly(methacrylic acid) copolymer fabrics. Text. Res. J. **1976**, *46*, 983.
3. Swason, C.L.; Shogren, R.L.; Fanta, G.F.; Imam, S.H. Starch plastic materials—preparation, physical properties and biodegradability (a review of recent USDA research). J. Environ. Polym. Degrad. **1993**, *1*, 155.
4. Estella, B.; Enrico, M.; Laura, R. Free radical grafting onto cellulose in homogeneous conditions-I. Modified cellulose acrylonitrile system. Carbohydr. Polym. **1998**, *36*, 313.

5. Kubota, H.; Fukushima, Y.; Kuwabara, S. Factors affecting the liquid phase photografting of acrylic acid on cellulose and its derivatives. Eur. Polym. J. **1997**, *33*, 61.
6. El-Salmawi, K.; El-Naggar, A.M.; Attia, S.E. Investigation of synergism during radiation graft copolymerization of binary mixtures of vinyl monomers onto different textiles fabrics by a dyeing method. Polym. Int. **1997**, *44*, 181.
7. Abdul-Razik, E.A.; Ali, M.M.; Sahran, A.A.; Abdulsalam, N.M.; Ahmad, M.; Abdul Beri, E.M. Photo-induced graft copolymerization of acrylamide, acrylonitrile, 4-vinylpyredine and isobutylmethacrylate onto cellulose in homogenous media. Mansoura Sci. Bull. A Chem. **1997**, *24*, 155.
8. Chiriac, A.P.; Neamtu, I.; Cazacu, G.; Siminescu, C.I.; Razmani, G. An investigation of grafting of cellulose powder with acrylamide under a magnetic field. Angew. Macromol. Chem. **1997**, *246*, 1.
9. Kubota, H.; Shibara, M. Photografting of *N*-isopropylacrylamide on cellulose and temperature responsive character of resulting grafted cellulose. React. Funct. Polym. **1998**, *37*, 219.
10. Hebeish, A.; El-Rafie, M.H.; Khalil, E.M.; Abdul Hafiz, S.A. Effect of degradative treatments on cotton graft copolymers part-II. Hypochlorite oxidation of polyacrylamide-cotton graft copolymers. Cell. Chem. Technol. **1986**, *20*, 629.
11. Gupta, K.C.; Gupta, S.K. Grafting of *N*,*N*′-methylenebisacrylamide onto silk fibers using the vandylacetylacetone complex in aqueous medium. J. Appl. Polym. Sci. **1987**, *33*, 2849.
12. Gupta, K.C.; Sahoo, S. Graft copolymerization of 4-vinylpyredine onto cellulose using Co(III) acetylacetonate complex in aqueous medium. Cellulose **2001**, *8*, 233.
13. Okiemen, F.E.; Idehen, K.I. Studies in the graft copolymerization of vinyl monomers on cellulosic materials. J. Appl. Polym., Sci. **1989**, *37*, 1253.
14. Egboh, S.H.O.; Akonwu, L.N. Graft copolymerization of acrylamide onto cellulose acetate initiated by ceric ions. Acta Polym. **1991**, *42*, 279.
15. Tsubokawa, N.; Lida, T.; Takayama, T. Modification of cellulose powder surface by grafting of polymers with controlled molecular weight and narrow molecular weight distribution. J. Appl. Polym. Sci. **2000**, *75*, 515.
16. Mansaur, O.Y.; Nagaty, A. Grafting of synthetic polymers to natural polymers by chemical processes. Prog. Polym. Sci. **1985**, *11*, 91.
17. Mino, G.; Kaizerman, S. A new method for preparation of graft copolymers polymerization initiated by ceric ion redox systems. J. Polym. Sci. **1960**, *31*, 242.
18. Gao, J.; Tian, R.; Zhang, L.C. Graft copolymerization of vinyl monomers onto starch initiated by transition metal-thiourea redox system. J. Polym. Sci. **1996**, *14*, 163.
19. Oprea, S.; Dumitriu, S.; Bulacovschi, V. Grafting of acrylamide and acrylonitrile on some celluloses. Cell. Chem. Technol. **1979**, *11*, 3.
20. Zaharn, M.K. Graft copolymerization of methyl methacrylate and other vinyl monomers onto cotton fabric using ferrous cellulose tricarbonate-*N*-bromosuccinamide redox initiated system. J. Appl. Polym. Sci. **1996**, *62*, 49.
21. Hebeish, A.; El-Rafie, M.H.; Zaharn, M.K. Pentavalent vanadium ion-cellulose thiocarbonate redox system induced grafting of methylmethacrylate and other vinyl monomers onto cotton fabric. J. Appl. Polym. Sci. **1993**, *50*, 2099.

22. Jayame, G.; Lang, F. In *Methods in Carbohydrate Chemistry*; Whither, R.L., Eds.; Academic Press: New York, **1969**; Vol. *3*, 77.
23. Nishioka, N.; Matsumoto, Y.; Yumen, T.; Manmae, K.; Kosai, K. Homogenous graft copolymerization of vinyl monomers onto cellulose in the dimethylsulfoxide-paraformaldehyde solvent system IV. 2-Hydroxyethyl methacrylate. Polym. J. **1986**, *18*, 323.
24. Brockway, C.E. Grafting of poly(vinyl acetate) to granular corn-starch. J. Polym. Sci. **1968**, *24*, 139.
25. Mayo, F.R.; Lewis, F.M. Copolymerization I. A basis for comparing the behavior of monomers in copolymerization; the copolymerization of styrene and methylmetacrylate. J. Am. Chem. Soc. **1944**, *66*, 1594.

Received July 8, 2002
Revised September 9, 2002