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

Graft Copolymerization on to Cellulose Using Binary Mixture of Monomers

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

To cite this Article Gupta, K. C. , Sahoo, Sujata and Khandekar, Keerti(2007) 'Graft Copolymerization on to Cellulose Using Binary Mixture of Monomers', Journal of Macromolecular Science, Part A, 44: 7, 707 — 719
To link to this Article: DOI: 10.1080/10601320701352688
URL: http://dx.doi.org/10.1080/10601320701352688

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2007) **44**, 707–719

ISSN: 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320701352688

Graft Copolymerization on to Cellulose Using Binary Mixture of Monomers

K. C. GUPTA, SUJATA SAHOO, and KEERTI KHANDEKAR

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

Received December, 2006, Accepted February, 2007

The graft copolymerization of acrylonitrile (AN) and ethyl acrylate (EA) comonomers onto cellulose has been carried out using ceric ammonium nitrate (CAN) as an initiator in the presence of nitric acid at 35 ± 0.1°C. The addition of ethyl acrylate as comonomer has shown a significant effect on overall and individual graft copolymerization of acrylonitrile on cellulose. The graft yield ($\%G_Y$) and other grafting parameters viz. true grafting ($\%G_T$), graft conversion ($\%C_G$), cellulose number (Ng) and frequency of grafting (G_F) were evaluated on varying the concentration of comonomers from $6.0–30.0 \times 10^{-1}$ mol dm^{-3} and ceric (IV) ions concentration from $2.5–25 \times 10^{-3}$ mol dm^{-3} at constant feed composition (f_{AN} 0.6) and constant concentration of nitric acid (7.5×10^{-2} mol dm^{-3}) in the reaction mixture. The graft yield ($\%G_Y$) and other grafting parameters were optimal at 15×10^{-1} mol dm^{-3} concentration of comonomers and at 10×10^{-3} mol dm^{-3} concentration of ceric ammonium nitrate. The graft yield ($\%G_Y$) and composition of grafted chains (F_{AN}) was optimal at a feed composition (f_{AN}) of 0.6. The energy of activation (Ea) for graft copolymerization has been found to be 16 kJ mol^{-1}. The molecular weight (Mw) and molecular weight distribution (Mw/Mn) of grafted chains was determined by GPC and found to be optimum at 15×10^{-1} mol dm^{-3} concentration of comonomer in the reaction mixture. The composition of grafted chains (F_{AN}) determined by IR method was used to calculate the reactivity ratios of monomers, which has been found to be 0.62 (r_1) and 1.52 (r_2), respectively for acrylonitrile (AN) and ethyl acrylate (EA) monomers used for graft copolymerization. The energy of activation for decomposition of cellulose and grafted cellulose was determining by using different models based on constant and different rate (β) of heating. Considering experimental observations, the reaction steps for graft copolymerization were proposed.

Keywords: acrylonitrile; ethyl acrylate; cellulose; graft copolymerization

1 Introduction

Cellulose is a natural biopolymer and its properties have been modified by cross-linking, substitution and by grafting with suitable monomers (1, 2). The graft copolymerization of acrylonitrile onto cellulose has shown significant effect on its hydrophobic and thermal stability. The individual graft copolymerization of acrylonitrile onto cellulose was low (3); hence, efforts have also been made for its graft copolymerization onto cellulose in a dispersed phase (4). The photoinitiated individual graft copolymerization of acrylonitrile and other vinyl monomers onto cellulose has also been reported in homogeneous conditions (5), but graft copolymerization of acrylonitrile in presence of comonomers is rarely reported. Similarly, the individual graft copolymerization of ethyl acrylate and other vinyl monomers onto carboxy methylcellulose (CMC) has been studied (6) but it has shown poor grafting onto cotton fabric in presence of redox system in comparison to acrylamide, methyl methacrylate monomers (7) and other vinyl monomers (8). The individual graft copolymerization of ethyl acrylate onto cellulose in presence of ceric (IV) ions has also been reported (9), but its effect on graft copolymerization of acrylonitrile onto cellulose not yet reported. Similarly the individual graft copolymerization of vinyl monomers onto cellulose (10–12) and other polymeric material (13, 14) is reported substantially but graft copolymerization of acrylonitrile and other monomers in presence of comonomer is reported recently (15). The presence of a comonomer in the reaction mixture has shown a significant effect on graft copolymerization of monomer, which otherwise has shown a poor affinity for grafting in absence of comonomer. The binary graft copolymerization has provided opportunities to control the composition of grafted chains to obtain cellulose for specific applications (16, 17). The graft copolymerization in presence of radiation (18, 19), redox systems (20) and metal chelates (21, 22) has favored the formation of ungrafted polymers in comparison to grafted polymers but ceric (IV)

Address correspondence to: K. C. Gupta, Polymer Research Laboratory, Department of Chemistry, Indian Institute of Technology, Roorkee 667, India. Tel.: +91 1332 285325; Fax: +91 1332 273560; E-mail: kcgptfcy@iitr.ernet.in

ions initiated graft copolymerization has provided significant improvement on grafting of monomers due to the formation of sufficient number of active sites on cellulose backbone through single electron transfer process (23). However, the activity of ceric (IV) ions was high in acidic media in comparison to basic media (24, 25). In present investigations, efforts have been made to study the graft copolymerization of acrylonitrile onto cellulose in presence of ethyl acrylate by varying the feed molarity, feed composition and other experimental conditions to identify the effect of ethyl acrylate comonomer on graft copolymerization of acrylonitrile on cellulose. Finally the grafted cellulose was characterized for the variation in thermal stability in comparison to cellulose grafted with individual monomers and with mixture of acrylonitrile and ethyl acrylate. The effect of feed composition on reactivity and sequence length of monomers in the grafted chains has been planned to be studied using acrylonitrile and ethyl acrylate comonomer system for graft copolymerization on to cellulose.

2 Experimental

2.1 Chemicals

Acrylonitrile and ethyl acrylate monomers (E. Merck, India) were purified by extracting with aqueous sodium chloride-sodium hydroxide solutions and after drying purified monomers in vacuum desiccator on sodium sulfate, the monomers were stored below 5°C. The cellulose powder (Loba Chemie, Mumbai, India) was washed with methanol, acetone deionized water and dried finally at room temperature. Ceric ammonium nitrate (CAN) and nitric acid were reagent grade chemicals and used without further purification. The nitrogen gas was passed through alkaline pyrogallol and sulfuric acid before using in graft copolymerization.

2.2 Graft Copolymerizaion

The graft copolymerization of acrylonitrile and ethyl acrylate on to cellulose was carried out by dispersing 1.0 g purified cellulose ($\bar{M}w = 2.5 \times 10^5\ g\ mol^{-1}$) in a three-necked round bottom flask containing 100 mL solution of ceric ammonium nitrate ($10.0 \times 10^{-3}\ mol\ dm^{-3}$) in nitric acid ($7.5 \times 10^{-2}\ mol\ dm^{-3}$). The reaction mixture was thermostat to 35 ± 0.1°C and stirred vigorously with an electrically operated stirrer and purged with N_2 gas for about 15 min for removing the dissolved oxygen from the solution to prevent the deactivation of radicals in the reaction mixture. To initiate the graft copolymerization, a calculated amount of monomers (6.88 g of AN and 4.59 g of EA) was added dropwise in a reaction flask for maintaining the feed molarity of $15 \times 10^{-1}\ mol\ dm^{-3}$ and feed composition (f_{AN}) of 0.6 as at this feed molarity and composition, the graft yield and composition of grafted chains was optimal. To prevent the deactivation of radicals, a constant supply of nitrogen in the reaction flask was ensured and to avoid the effect of stirring on graft copolymerization, the reaction mixture was stirred at a constant speed of 1200 rpm. Finally, the reaction was stopped by adding 5 mL (5 wt%) hydroquinone and precipitated in an excess volume of methanol. The resultant precipitate was filtered and washed repeatedly with hot and cold water to remove monomers, ungrafted polymers and other impurities, which were stick to the surface of grafted cellulose. Finally the grafted cellulose was dried at 60°C to a constant weight in vacuum oven and used for extraction of ungrafted and grafted polymers.

2.3 Extraction of Homopolymers

The ungrafted polyacrylonitrile and polyethylacrylate formed during graft copolymerization were extracted from grafted cellulose crude using dimethyl formamide (DMF) as extractant in Soxhlet Apparatus for about 24 h. The extracted homopolymers were precipitated in methanol/water mixture (1:1 v/v) and dried to a constant weight in vacuum oven. The amount of homopolymers so obtained was used in calculation of grafting parameters.

2.4 Extraction of Ungrafted Copolymers

The homopolymer extracted cellulose crude was subsequently used to extract the ungrafted poly(acrylonitrile-co-ethyl acrylate) with tetrahydrfuran (THF) in Soxhlet apparatus for 30 h. The extracted copolymers were precipitated in methanol/water mixture (1:1 v/v) and vacuum dried till a constant weight after washing repeatedly with deionized water. The ungrafted copolymers subsequently were characterized for their molecular weight by gel permeation chromatography and the composition of grafted copolymers was determined with IR and elemental analysis.

2.5 Extraction of Ungrafted Cellulose

After extracting the ungrafted homopolymers and copolymers from grafted cellulose, the ungrafted cellulose was extracted by keeping grafted cellulose in ammonical solution of copper hydroxide (Cuoxam) containing 1.2 wt% $NaHSO_3$ (26). The solution was stirred vigorously and after 6 h, the residue was washed with dilute acetic acid, deionized water and dried to a constant weight at 50°C.

2.6 Extraction of Grafted Copolymers

After extracting the ungrafted polymers and cellulose, the grafted polymer chains were extracted by hydrolyzing the grafted cellulose in 7.2 wt% sulfuric acid at 30°C. At the end of 6 h, the hydrolyzing solution was diluted with water to 4 wt% concentration of acid and then refluxed for about 6 h to ensure the complete hydrolysis of grafted cellulose. The grafted polymers were obtained by precipitating the extract in excess methanol. The graft copolymers after

purification were characterized for their composition by IR and elemental analysis and for molecular weight by gel permeation chromatography.

2.7 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 a 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.

2.8 Characterization

2.8.1 IR spectra

The IR spectra of pure cellulose and grafted copolymers were recorded with a 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 2240 cm^{-1} for cyano group (>CN) of acrylonitrile and at 1760 cm^{-1} for carboxyl group (>C═O) of ethyl acrylate. The optical density ratio (ODR) of grafted polymers was determined using following equation to estimate the mole fraction of acrylonitrile (F_{AN}) and ethyl acrylate (F_{EA}) in grafted chains using calibration curve drawn between ODR and composition of known copolymers.

$$\mathrm{ODR} = \frac{\log(\%T_{\text{base line}}/\%T_{EA})}{\log(\%T_{\text{base line}}/\%T_{EA})} \tag{1}$$

2.8.2 Elemental Analysis

The composition of grafted polymers was determined by IR analysis, which was further verified by determining the content of nitrogen in grafted chains using Heraeus Carlo Ebra 1108 Elemental Analyzer.

2.8.3 Thermal Analysis

Thermal stability of cellulose and grafted cellulose was estimated by recording thermogravimetric (TG) and differential thermogravimetric (DTG) curves using a Perkin-Elmer 7.0 Thermal Analyzer System at a heating rate of 10°C/min under nitrogen atmosphere. The TG and DTG curves were also recorded at different heating rates (β) and energy of activation of decomposition (Ea) was determined using a temperature of a maximum rate of decomposition (T_m) obtained at different rates of heating (β) in the Kissinger method (27) and using temperature (T_α) for the decomposition of fixed fraction of the grafted cellulose analyzed at different rates of heating (β) in Flynn and Wall method (28). These experiments were repeated for determining the energy of activation for decomposition (Ea) for pure cellulose and cellulose grafted with individual and a mixture of monomers using Equations (2) and (3).

$$\frac{d(\ln \beta/T_m{}^2)}{d(\ln/T_m)} = -\frac{Ea}{R} \quad \text{(Kissinger method)} \tag{2}$$

$$\frac{d\log\beta}{d(1/T_\alpha)} = -0.45\frac{Ea}{R} \quad \text{(Flynn and Wall method)} \tag{3}$$

2.8.4 Molecular Weight Measurements

The molecular weight of cellulose, poly(acrylonitrile) and poly(ethyl acrylate) were determined by a viscometric method using Equations (4–6).

$$[\eta]_{25_c^\alpha} = 38.5 \times 10^3 \mathrm{cm}^3\,\mathrm{g}^{-1} M_v^{0.76} \quad \text{(Cellulose in cadoxen)} \tag{4}$$

$$[\eta]_{20_c^\alpha} = 46.6 \times 10^3 \mathrm{cm}^3\,\mathrm{g}^{-1}\,M_v^{0.71} \quad \text{(PAN in DMF)} \tag{5}$$

$$[\eta]_{30_c^\alpha} = 27.7 \times 10^{-3} \mathrm{cm}^3\,\mathrm{g}^{-1}\,M_v^{0.67} \quad \text{(PEA in benzene)} \tag{6}$$

The molecular weights of grafted and ungrafted polymer were determined by gel permeation chromatograph (PL-GPC-120, UK) equipped with three PL aqua gel columns (PL aqua gel, 40, 60, 100 μm) in series and UV detector ($\lambda_{max} = 208$ nm). A 200 μmL copolymer solution of 0.1 mg/mL concentration 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 calibration kit of poly(acrylamide).

The graft copolymerization of comonomers has been carried out at different feed molarity and compositions and varying other experimental conditions. Finally, the experimental data were used to evaluate the following parameters for graft copolymerization.

Graft yield ($\%G_Y$): as weight percent of grafted polymer in comparison to initial weight of cellulose.

Graft conversion ($\%C_G$): as weight percent of grafted polymers onto cellulose used initially for graft copolymerization.

True grafting ($\%G_T$): as weight percent of grafted polymers to the weight of cellulose consumed in graft copolymerization.

Cellulose conversion (%Cc): as weight percent of cellulose, which was actually used in grafting.

Efficiency of grafting ($\%G_E$): as weight percent of total polymer, which was grafted onto cellulose.

Grafting frequency (G_F): as number of grafted chains per mole of cellulose.

Grafted chains (Ng): as the total number of polymer chains grafted on cellulose.

3 Results and Discussion

The graft copolymerization of acrylonitrile onto cellulose in the presence of ethyl acrylate has been found to be high in comparison to the individual graft copolymerization of

acrylonitrile. The increase in individual grafting of acrylonitrile and overall grafting in presence of comonomer has been attributed to the synergistic effect shown by ethyl acrylate comonomer on acrylonitrile by forming a complex with acrylonitrile and by modifying the cellulose-acrylonitrile interactions, which have contributed significantly in increasing the individual grafting of acrylonitrile as well as the overall grafting of comonomers on to the cellulose (29). The acrylonitrile and ethyl acrylate comonomers interactions have been considered responsible for the formation of purely copolymeric grafted chains onto cellulose, otherwise there was a possibility to obtain grafted chains of individual monomer onto the cellulose in the present system. The extent of acrylonitrile and ethyl acrylate comonomers interactions has been found to be dependent on feed composition (f_{AN}) as clear from the variations in composition (F_{AN}) of grafted chains on varying the feed composition (f_{AN}). The application of ceric (IV) ions has also been considered as one of the factors for increasing the graft yield ($\%G_Y$) of comonomer onto cellulose (Scheme 1) due to the formation of sufficient active sites on cellulose back bone (24) and inhibiting the formation of homopolymers.

The homopolymers in the reaction mixture were formed due to the transfer of activity of growing chains to the monomers however, the probability of such chain transfer activity was low in the present comonomer system, hence, the amount of ungrafted homopolymers and copolymers was low in comparison to the amount of grafted copolymers. At high concentration of nitric acid ($>7.5 \times 10^{-2}$ mol dm^{-3}), the ceric (IV) ions were more efficient in forming active sites onto cellulose backbone because the hydration of ceric (IV) ions was prevented at high concentration of nitric acid.

The IR spectrum (Figure 1B) of poly(acrylonitrile-co-ethyl acrylate) grafted cellulose has shown two additional absorption bands at 1734 cm^{-1} and 2228 cm^{-1} in comparison to pure cellulose (Figure 1A), which corresponds to the ester carbonyl group of ethyl acrylate and cyano group of acrylonitrile, hence, this provided evidence for the grafting of both monomers onto the cellulose. The analysis of hydrolyzed grafted chains has clearly indicated that all grafted chains were copolymeric in nature, which has further provided evidence to take for granted that acrylonitrile and ethyl acrylate monomers were interacting strongly with each other before their grafting on cellulose, which inhibited the individual grafting of monomer onto the cellulose. The optical density ratio (ODR) of grafted polymers (Equation (1)) was used to determine the composition of grafted chains with a calibration curve drawn between ODR and composition of known copolymers. The composition of grafted copolymers was verified further form elemental analysis. The thermogravimetric analysis (TGA) of pure cellulose and cellulose grafted with poly(acrylonitrile) or poly(ethyl acrylate) or poly(acrylonitrile-co-ethyl acrylate) has been used to record percent weight loss at different temperatures (Figure 2) and to determine the energy of activation (Ea) for decomposition using Equations (2) and (3). To compare the thermal stability of cellulose and cellulose grafted with mixture of monomers, the cellulose samples grafted with individual monomers were also analyzed by TGA and DTGA. The analysis of thermograms (Figure 2) has clearly indicated that the thermal stability of cellulose was increased on individual grafting of acrylonitrile, ethyl acrylate and their mixtures. The DTGA curves of cellulose and grafted cellulose (Figure 2B) have shown a shift in temperature of maximum rate of decomposition (T_m) from 340°C for pure cellulose to 408°C for poly (acrylonitrile) grafted cellulose. The temperature of maximum rate of decomposition (T_m) of cellulose grafted with poly (acrylonitrile-co-ethyl acrylate) has been found to be higher (373°C) than with pure cellulose (340°C) and cellulose grafted with poly (ethyl acrylate) (360°C), which was a clear indication for the increase in thermal stability of cellulose on grafting either individual monomer or on grafting the mixture of monomers.

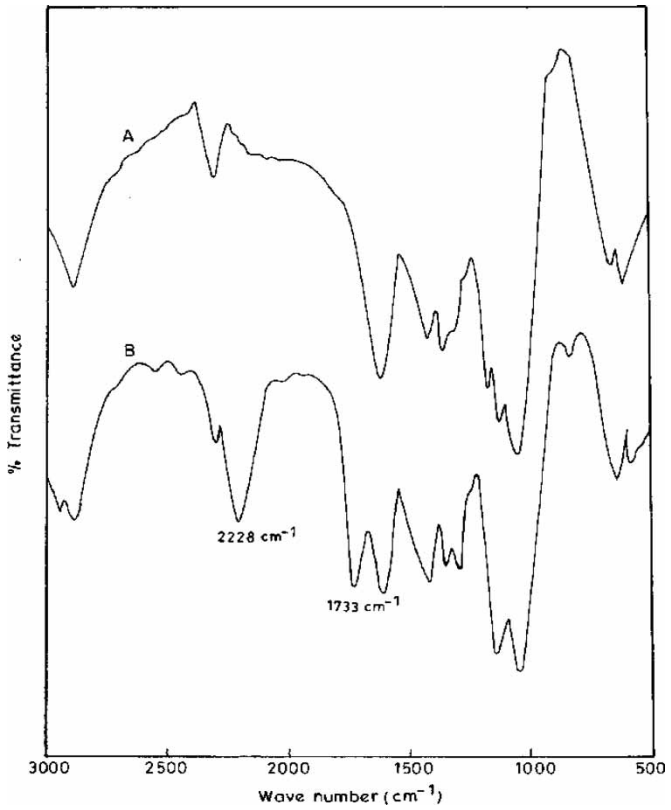
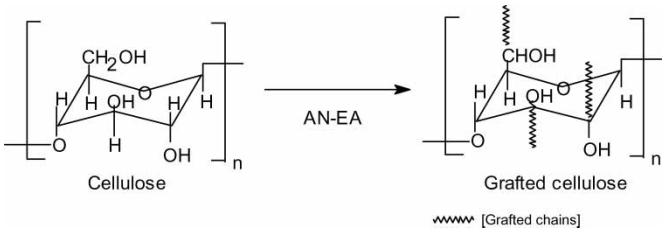


Fig. 1. FT-IR spectra of cellulose (A) and poly(acrylonitrile-co-ethyl acrylate) grafted cellulose (B).



Sch. 1. Grafting of comonomers on cellulose.

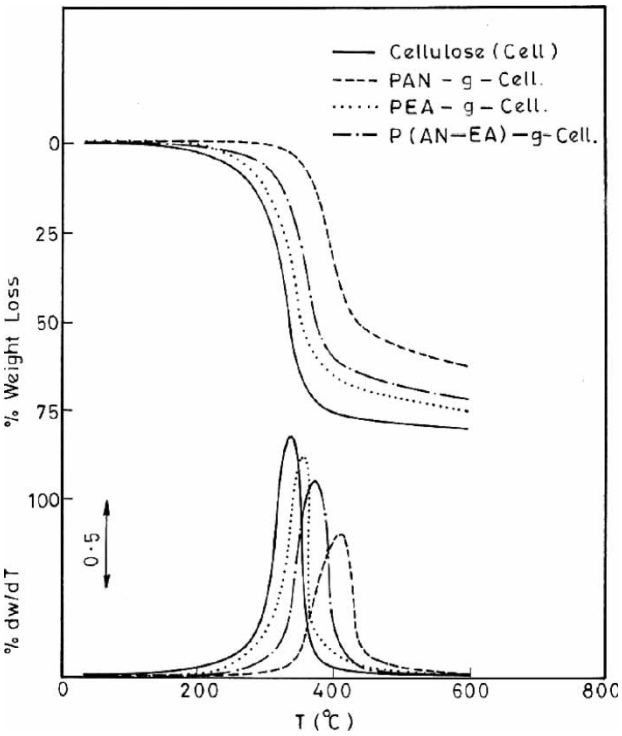


Fig. 2. TGA and DTGA curves of cellulose and grafted cellulose.

The energy of activation (Ea) for decomposition of pure cellulose and cellulose grafted with individual or a mixture of monomers has been determined by drawing plots (Figure 3) between ln β/T_m^2 vs. $1/T_m$ using the Kissinger method (Equation (2)) and by drawing plots (Figure 4) between log β vs. $1/T_\alpha$ using the Flynn and Wall method (Equation (3)). These plots have clearly indicated an increasing trend on energy of activation for decomposition from pure cellulose

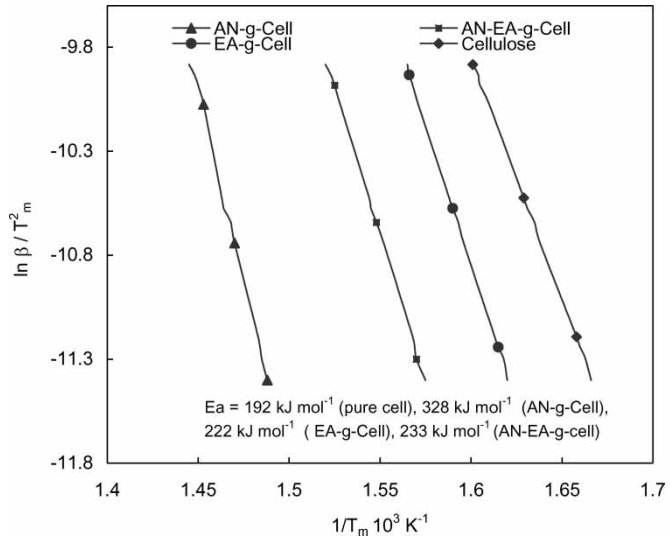


Fig. 3. Kissinger plots for the determination of energy of activation for decomposition of pure cellulose and grafted cellulose at different heating rate.

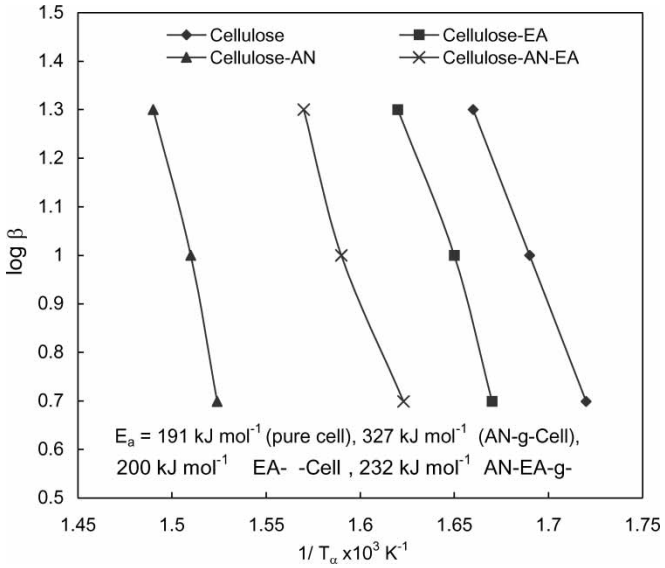


Fig. 4. Flynn and Wall plots for determination of energy of activation for decomposition of pure cellulose and grafted cellulose at different heating rate.

to the cellulose grafted with individual and the mixture of monomers. The energy of activation for decomposition of cellulose and grafted cellulose determined by the Kissinger method (Figure 3) was almost close to the values obtained with the Flynn and Wall method (Figure 4), which has given an indication that both methods are applicable in determining the energy of activation (Ea) for decomposition of pure cellulose and grafted cellulose.

The extent of monomer grafting onto cellulose has been determined at different experimental conditions, which showed a significant effect on grafting parameters due to the variations in concentration of monomers in the reaction mixtures and due to the variations in monomer-monomer interactions as analyzed by evaluating various grafting parameters during experimental variations.

3.1 Effect of Feed Molarity

To study the effect of feed molarity on graft copolymerization of acrylonitrile and ethyl acrylate onto cellulose, the feed molarity was varied from $6.0 - 30 \times 10^{-1}$ mol dm^{-3} at constant feed composition (f_{AN}, 0.6) keeping constant concentration of ceric (IV) ions (100×10^{-3} mol dm^{-3}) and nitric acid (7.50×10^{-2} mol dm^{-3}). On varying the feed molarity from 6.0×10^{-1} mol dm^{-3} to 21.0×10^{-1} mol dm^{-3}, the graft yield ($\%G_Y$) was increased linearly but after 21.0×10^{-1} mol dm^{-3} concentration of comonomer, there was a substantial decrease in graft yield (Figure 5). The efficiency of grafting ($\%G_E$), graft conversion ($\%C_G$), true grafting ($\%G_T$) and other grafting parameters such as frequency (G_F) and number of grafted chains (Ng) have also shown almost similar trends as found with the graft yield (Table 1a and b). The decreasing trend in graft yield and

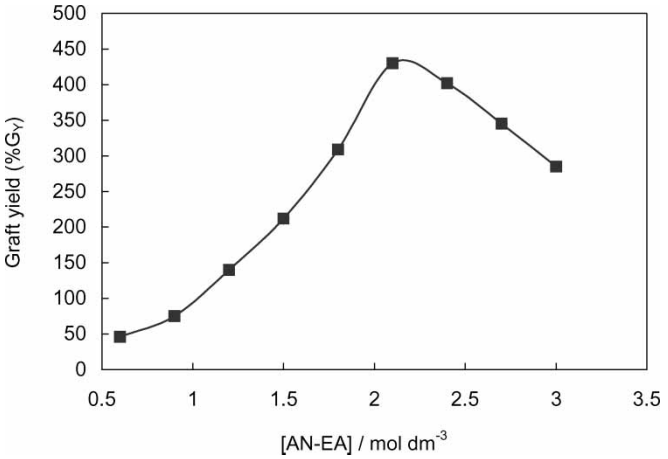


Fig. 5. Graft yield (%G_Y) as a function of feed molarity. [Ce (IV)] $= 10 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Time $=$120 min, Temp. $= 35^{\circ}$C, $f_{AN} = 0.6$ [Cell] $= 1$ wt%.

other grafting parameters at high feed molarity ($>21.0 \times 10^{-1}$ mol dm^{-3}) was due to the increase in solution viscosity and the increase in steric hindrances at the cellulose surface, which has reduced the access of monomer-monomer complex to the active sites on the cellulose backbone, hence, the graft yield and other grafting parameters have decreased at high feed molarity. The molecular weight of grafted chains has increased on increasing the feed molarity from $6.0-30.0 \times 10^{-1}$ mol dm^{-3}, which was due to the continuous increase in chain length of grafted polymers without any significant chain transfer process within the studied range of feed molarity. The molecular weight distribution has been found to be low at 15×10^{-1} mol dm^{-3} concentration of comonomers as is clear from the molecular weight distribution curves recorded for grafted chains obtained at different feed molarity (Figure 6). At high feed molarity (30×10^{-1} mol dm^{-3}), the molecular weight distribution was high (Table 1b and Figure 6), which indicated that at high feed molarity, the growth of polymer chains was predominating compared to the inception of new polymer chains at cellulose backbone. But at low feed molarity (6.0×10^{-1} mol dm^{-3}), the inception and growth of polymer chain took place simultaneously; hence molecular weight distribution was low at low feed molarity (Table 1b and Figure 6). The weight percent of grafted chains has shown an increasing trend up to 21×10^{-1} mol dm^{-3} concentration of comonomers, which was due to the continuous growth of grafted chains and due to the inception of new chains on cellulose backbone. But at high feed molarity ($>21 \times 10^{-1}$ mol dm^{-3}), the decreasing trend in weight percentage of grafted chains was due to the decrease in rate of graft copolymerization of comonomers on growing chains (Table 1b). During feed molarity variations, the composition of grafted chains remained constant (F_{AN}, 0.49), which was an indication that during feed molarity variation, the interactions between acrylonitrile and ethyl acrylate remained constant, otherwise the observed composition of grafted chains would have been different on varying the feed molarity.

The rate of graft copolymerization (Rp) of comonomer has been determined at different feed molarity and used to determine the order of reaction on concentration of comonomers by drawing a log-log plot between Rp vs. feed molarity (Figure 7). The slope of the log-log plot was found to be 2.08, indicating a second order dependence of reaction rate on feed molarity. On varying the feed molarity from 6.0×10^{-1} mol dm^{-3} to 30×10^{-1} mol dm^{-3}, the rate of ceric (IV) ions disappearance has remained almost constant (Figure 8), which has clearly indicated that the ceric (IV) ions were not involved directly in the formation of active sites onto monomers, otherwise the rate of ceric (IV) ions consumption would have been affected on varying the feed molarity (Figure 8). The formation of ungrafted homopolymers and copolymers in the reaction mixture has been assumed due to the transfer of activity of grafted chains to the comonomers in the reaction mixture and the formation of radicals on monomers by the direct interactions of ceric (IV) ions has been discarded on the basis of trend shown by ceric (IV) ions disappearance during feed molarity variations.

3.2 *Effect of Feed Composition*

The effect of feed composition on graft yield and other grafting parameters has been studied by taking different

Table 1a. Effect of [AN-EA] on grafting parameters

[AN-EA] $\times$ 10/mol dm^{-3}	%G_T	%C_T	%C_G	%C_C	%G_E	G_F
6.0	256	19.1	10.02	41.0	51.80	1.12
9.0	265	20.9	10.90	48.0	52.20	1.49
12.0	336	28.8	15.25	55.0	53.10	2.25
15.0	420	34.0	18.48	60.0	54.40	2.87
18.0	560	39.5	22.44	62.0	56.90	3.69
21.0	715	46.8	26.77	65.0	57.20	4.35
24.0	697	43.4	21.89	63.0	50.20	4.29
27.0	667	39.8	16.70	58.0	41.80	4.24
30.0	587	37.2	12.41	56.0	33.30	3.85

[Ce (IV)] $=10.0 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, $f_{AN} = 0.6$, Time $= 120$ min, Temp. $= 35^{\circ}$C, [Cell] $= 1$ wt%.

Table 1b. Effect of [AN-EA] on grafting parameters

[AN-EA] × 10/ mol dm^{-3}	Ng × 10^{6}	$\bar{M}w \times 10^{-3}$	$\bar{M}w/\bar{M}n$	%Branches	%Cellulose
6.0	1.84	445	1.78	53	47
9.0	2.86	448	1.71	61	39
12.0	4.95	452	1.60	72	28
15.0	6.88	462	1.50	83	17
18.0	9.14	591	1.75	87	13
21.0	11.30	722	1.90	87	13
24.0	10.80	714	1.92	86	14
27.0	9.86	700	2.00	86	14
30.0	8.64	1023	3.10	84	16

[Ce (IV)] =10.0 × 10^{-3} mol dm^{-3}, [HNO_3] = 7.5 × 10^{-2} mol dm^{-3}, f_{AN} = 0.6, Time = 120 min, Temp. = 35°C, [Cell] = 1 wt%.

mole factions of acrylonitrile (f_{AN}) in the reaction mixture at constant feed molarity (15 × 10^{-1} mol dm^{-3}) and constant concentration of ceric (IV) ions (10 × 10^{-3} mol dm^{-3}) and nitric acid (7.5 × 10^{-2} mol dm^{-3}) at 35°C (Table 2 and Figure 9). The individual grafting of acrylonitrile and ethyl acrylate onto cellulose was also carried out at the same feed molarity (15 × 10^{-1} mol dm^{-3}) to compare the effect of the addition of comonomer on graft yield and other grafting parameters. The individual graft yield of ethyl acrylate onto cellulose was 360%, whereas acrylonitrile has shown a graft yield of 102% at constant feed molarity (15 × 10^{-1}mol dm^{-3}) and other experimental conditions. The graft yield and other grafting parameters in the presence of ethyl acrylate has shown an increasing trend on increasing the mole fraction of acrylonitrile (f_{AN}) from 0.2 to 0.8 in the reaction mixture but has shown a sharp decreasing trend on increasing the mole fraction of acrylonitrile beyond 0.8 (Table 2 and Figure 9). A maximum graft yield of 240% was obtained at a mole fraction of 0.8 of acrylonitrile (f_{AN}), which was significantly high in comparison to the graft yield observed with pure acrylonitrile (102%) at same feed molarity (Figure 9). The value of true grafting (%G_T), graft conversion (%C_G), efficiency of grafting (%G_E) and number of chains grafted per mole of cellulose (G_F) was maximum at 0.8 mole fraction of acrylonitrile in the reaction mixture (Table 2b). The number of grafted chains (Ng) and weight percent of grafted chains onto cellulose has increased till 0.8 mole fraction of acrylonitrile in the feed (Table 2b), but has decreased on increasing the mole fraction of acrylonitrile beyond 0.8. The inter molecular interactions between comonomers were considered to be responsible for the observed positive trends in the graft yield and other grafting parameters but beyond 0.8 mole fraction of acrylonitrile, the intra molecular interactions of acrylonitrile dominated over inter molecular interactions, hence the synergistic effect of added ethyl acrylate onto acrylonitrile has decreased, which resulted in decrease in affinity of grafting of acrylonitrile on to cellulose. The total conversion (%C_T) and cellulose conversion (%Cc) have also shown dependence on feed composition.

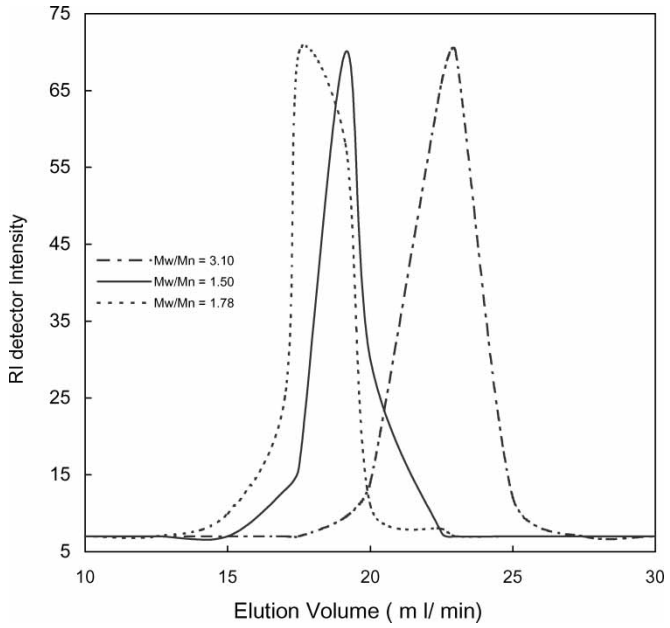


Fig. 6. Gel permeation chromatogram for the grafted chains obtained during feed molarity variation.

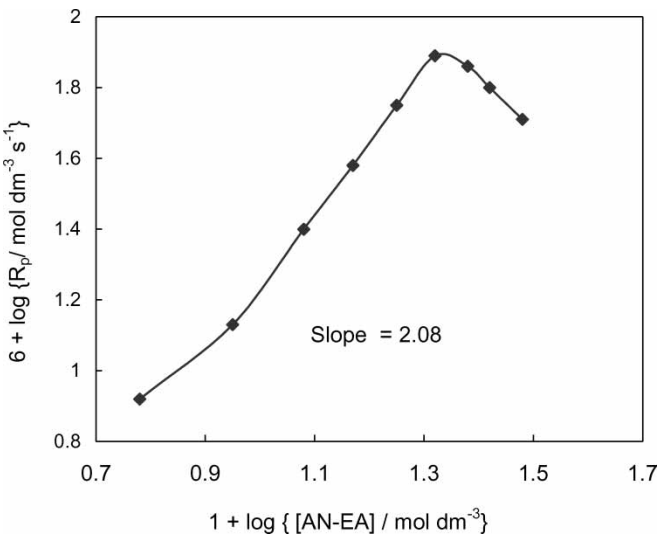


Fig. 7. Log-log plot between Rp vs. [AN-EA], f_{AN} = 0.6, [Ce (IV)] = 10 × 10^{-3} mol dm^{-3}, [HNO_3] = 7.5 × 10^{-2} mol dm^{-3}, Time = 120 min, Temp. = 35°C.

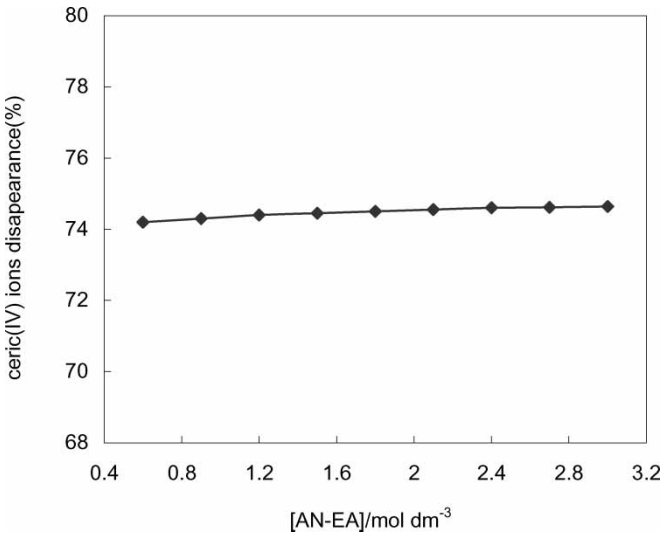


Fig. 8. Effect of feed molarity on ceric ions disappearance, $[HNO_3] = 7.5 \times 10^{-2}$ mol dm^{-3}, Time = 120 min, Temp. = 35°C, $f_{AN} = 0.6$, [Cell] = 1 wt%.

The variation in graft yield and other grafting parameters with feed composition has provided enough evidence to consider the contributions of monomer-monomer interactions in controlling the grafting parameters (Tables 2a and b) and composition of grafted chains (Table 2c). The mole fractions of acrylonitrile in the grafted chains (F_{AN}) has increased on increasing the mole fraction of acrylonitrile (f_{AN}) in the feed, which was due to synergistic effect shown by ethyl acrylate monomer onto acrylonitrile. The molecular weight ($\bar{M}w$) and its distribution have also shown a significant variation on varying the feed composition (Table 2b). The composition of grafted chains determined by IR method was verified further by elemental analysis and used to calculate the reactivity ratios of acrylonitrile (r_1) and ethyl acrylate (r_2) with Mayo and Lewis plot (30). The reactivity ratio of acrylonitrile and ethyl acrylate has been found to be 0.62 and 1.52, respectively (Figure 10), which clearly indicated that acrylonitrile was having low reactivity for grafting onto cellulose in comparison to ethyl acrylate, hence, the fraction of acrylonitrile (F_{AN}) in the grafted chains was low in comparison to the mole fraction of acrylonitrile used in the feed (f_{AN}). The effect of feed composition on average sequence length of acrylonitrile ($\bar{m}M_1$) and ethyl acrylate ($\bar{m}M_2$) has also been analyzed, which has shown an increasing trend for the sequence length of acrylonitrile on increasing the mole fraction of acrylonitrile in the feed, whereas the average sequence length of ethyl acrylate in the chains has decreased with the increase in mole fraction of acrylonitrile in the feed (Table 2c). The probability of addition of acrylonitrile ($P_{AN\text{-}AN}$) and ethyl acrylate ($P_{EA\text{-}EA}$) on growing chains ending with acrylonitrile and ethyl acrylate was also determined (Table 2c), from which it was clear that the increase in sequence length of acrylonitrile in the grafted chains was due to the increase in probability of addition of acrylonitrile on growing chains ending with acrylonitrile than to the chains ending with ethyl acrylate and vice-versa. However, the growth of the acrylonitrile sequence length was checked after reaching a certain length and then after, the activity of chain was increased for the addition of ethyl acrylate monomer. The variation in priority for the addition of acrylonitrile and ethyl acrylate was due to the reactivity ratio of acrylonitrile (r_1) and ethyl acrylate (r_2), which provided an alternate arrangement of the sequence length of acrylonitrile ($\bar{m}M_1$) and ethyl acrylate ($\bar{m}M_2$) in the grafted chains as the product of reactivity ratios of monomers ($r_1 \cdot r_2$) was less than unity. The run number (R) in grafted chains obtained at different feed molarity was also determined, which has shown an increasing trend till 0.6 mole fraction of acrylonitrile, but on increasing the mole fraction of acrylonitrile beyond 0.6, the run number was decreased (Table 2c). This was due to the substantial increase in average sequence length of acrylonitrile (3.60) on increasing the mole fraction of acrylonitrile beyond 0.6 (Table 2c). These investigations have given indications that the feed composition can be used to control the composition of the grafted chains.

3.3 *Effect of Ceric (IV) Ions Concentration*

The graft copolymerization of acrylonitrile and ethyl acrylate has also been studied by varying the concentration of ceric (IV) ions form $2.5-25 \times 10^{-3}$ mol dm^{-3} at constant feed molarity (15×10^{-1}mol dm^{-3}) and composition (f_{AN}, 0.6). During ceric (IV) ions concentration variation, the concentration of nitric acid was kept in excess (7.5×10^{-2} mol dm^{-3}) so that the activity of ceric (IV) ions in the reaction mixture was maintained. The graft yield

Table 2a. Effect of feed composition (f_{AN}) on grafting parameters

f_{AN}	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
0.0	539	54.5	31.30	72.0	57.70	3.01
0.2	351	24.2	11.70	52.0	48.50	2.20
0.4	368	28.3	14.90	58.0	52.80	2.46
0.6	420	34.0	18.40	60.0	54.40	2.86
0.8	448	36.9	20.90	62.00	55.00	3.08
1.0	267	39.9	8.89	55.00	29.70	1.59

[AN-EA] = 15×10^{-1} mol dm^{-3}, [Ce (IV)] = 10×10^{-3} mol dm^{-3}, $[HNO_3] = 7.5 \times 10^{-2}$ mol dm^{-3}, Time = 120 min, Temp. = 35°C, [Cell] = 1 wt%.

Table 2b. Effect of feed composition (f_{AN}) on grafting parameters

f_{AN}	Ng $\times 10^6$	$\bar{M}w \times 10^{-3}$	$\bar{M}w/\bar{M}n$	%Branches	%Cellulose
0.0	8.67	1245	3.00	82.0	18.0
0.2	4.57	451	1.53	72.0	28.0
0.4	5.71	457	1.52	75.0	25.0
0.6	6.88	462	1.50	78.0	22.0
0.8	7.64	722	2.30	80.0	20.0
1.0	3.51	928	3.20	65.0	35.0

[AN-EA] $=15 \times 10^{-1}$mol dm^{-3}, [Ce (IV)] $=10 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Time $= 120$ min, Temp. $= 35°$C, [Cell] $= 1$ wt%.

Table 2c. Effect of feed composition (f_{AN}) on grafting parameters

f_{AN}	F_{AN}	$\%N_2$	$\bar{m}M_1$	$\bar{m}M_1\ M_2$	$P_{AN\text{-}AN}$	R
0.0	0.00	0.00	—	—	—	—
0.2	0.14	2.09	1.16	7.16	0.14	24.04
0.4	0.30	4.92	1.43	3.31	0.30	42.19
0.6	0.49	9.00	1.97	2.02	0.49	50.12
0.8	0.72	15.32	3.60	1.38	0.72	40.16
1.0	1.00	26.42	—	—	1.00	—

[AN-EA] $=15 \times 10^{-1}$ mol dm^{-3}, [Ce (IV)] $=10 \times 0^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Time $= 120$ min, Temp. $= 35°$C, [Cell] $= 1$ wt%.

was initially increased from 98% to 245% on increasing the ceric (IV) ions concentration from 2.5×10^{-3}mol dm^{-3} to 12.5×10^{-3} mol dm^{-3}, but on further increasing the concentration of ceric (IV) ions beyond 12.5×10^{-3}mol dm^{-3}, the graft yield was decreased. Similar trends were shown by true grafting, total conversion, graft conversion, efficiency and frequency of grafting within the concentration range of ceric (IV) ions (Table 3). The initial increasing trend in graft yield and other grafting parameters was due to the formation of a sufficient number of active sites on cellulose backbone by ceric (IV) ions, which facilitated the polymer chains inception on cellulose backbone. However, on increasing the concentration of ceric (IV) ions beyond 12.5×10^{-3} mol dm^{-3}, the available nitric acid in the reaction mixture might have become low, which caused a decrease in activity of ceric (IV) ions due to hydration of ceric (IV) ions, hence the number of active sites on cellulose backbone was decreased significantly, which decreased the graft yield and other grafting parameters.

The molecular weight of grafted chains has shown a continuous decreasing trend on increasing the concentration of ceric (IV) ions. This was due to the inception of new chains

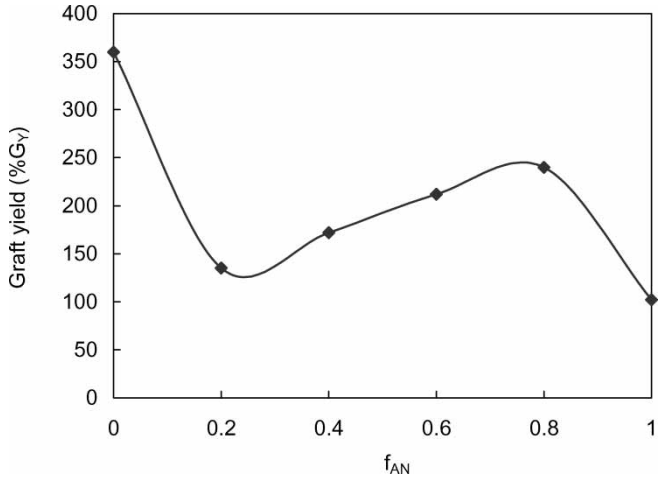


Fig. 9. Effect of feed composition on graft yield (%G_Y). [AN-EA] $= 15 \times 10^{-1}$ mol dm^{-3}, [Ce (IV)] $= 10 \times 10^{-3}$mol dm^{-3}, [HNO_3] $=7.5 \times 10^{-2}$ moldm^{-3}, Time $=120$ min., Temp. $= 35°$C, [Cell] $=$ wt%.

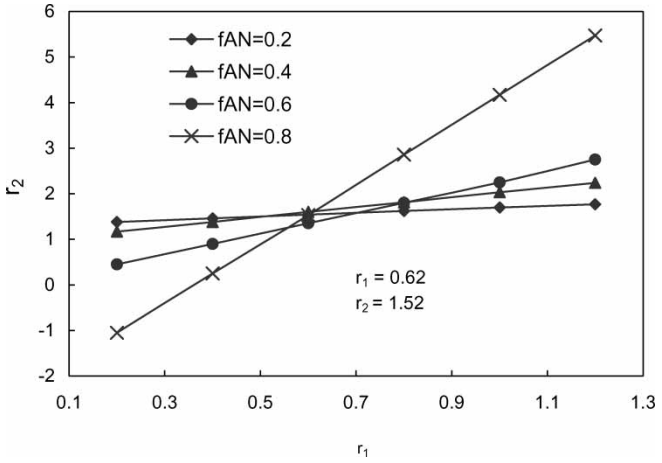


Fig. 10. Mayo and Lewis plot for reactivity ratios. [AN-EA] $= 15 \times 10^{-1}$ mol dm^{-3}, [Ce(IV)] $= 10 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Time $= 120$ min, Temp. $=$ 35°C, [Cell] $= 1$ wt%.

Table 3. 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
2.5	288	18.54	8.50	51.0	46.00	1.41
5.0	331	26.30	12.70	57.0	48.50	1.92
10.0	420	34.00	18.40	60.0	54.40	2.87
12.5	453	40.50	22.60	65.0	56.00	3.42
15.0	447	38.40	21.30	63.0	55.60	3.37
20.0	417	32.50	17.40	58.0	53.70	3.13
25.0	362	27.00	13.40	55.0	49.80	2.63

[AN-EA] = 15×10^{-1} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, $f_{AN} = 0.6$, Time = 120 min, Temp. = 35°C, [Cell] = 1 wt%.

on cellulose backbone and due to immature growing chain termination on cellulose backbone. The participation of ceric (IV) ions in the termination process was more predominant at high concentration ($>12.5 \times 10^{-3}$ mol dm^{-3}) of ceric (IV) ions. This is further clear from the trend shown by the frequency of grafted chains (G_F) on cellulose backbone during the concentration variation of ceric (IV) ions (Table 3). At a high concentration of ceric (IV) ions ($>12.5 \times 10^{-3}$ mol dm^{-3}), the cellulose conversion ($\%C_C$) was decreased. This was due to a decrease in activity of ceric (IV) ions to create active sites on cellulose backbone, otherwise conversion of cellulose would have continued to increase on increasing the concentration of ceric (IV) ions (Table 3). The termination of growing chains was predominant with hydrated ceric (IV) ions. The dependence of rate of graft copolymerization (Rp) on concentration of ceric (IV) ions has been determined by drawing a plot (Figure 11) between log Rp vs. log [Ce (IV)]. The plot was initially linear with a slope of 0.53, indicating a square root dependence of grafting rate on concentration of ceric (IV) ions.

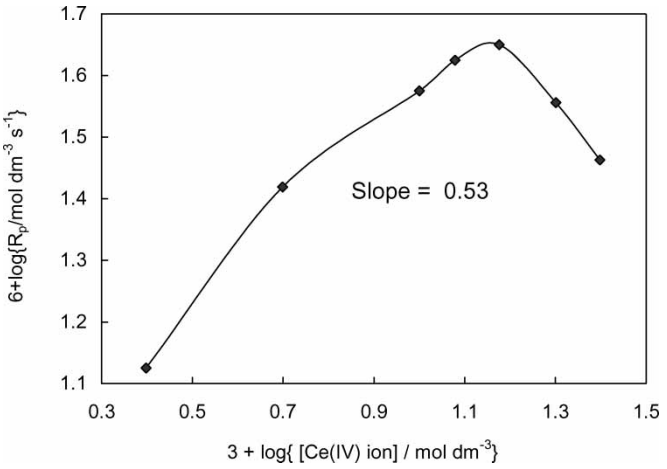


Fig. 11. Effect of ceric (IV) ions concentration on graft yield ($\%G_Y$). [AN-EA] = 15×10^{-1} mol dm^{-3}, [HNO_3] = 7.5×10^{-2} mol dm^{-3}, Time = 120 min, $f_{AN} = 0.6$, Temp. = 35°C, [Cell] = 1 wt%.

3.4 Effect of Reaction Time

During feed molarity and feed composition variations, the graft yield and other grafting parameters were determined at fixed time intervals (120 min), hence, to study the effect of reaction time, the graft yield and other grafting parameters were determined at different time intervals while keeping constant feed molarity (15×10^{-1}mol dm^{-3}) and feed composition (f_{AN}, 0.6). During reaction time variation, the concentration of ceric (IV) ions (10×10^{-3} mol dm^{-3}) and nitric acid (7.5×10^{-2} mol dm^{-3}) was also kept constant. The graft yield and other grafting parameters have increased substantially within a period of 6 h and after that, the increase in graft yield and other grafting parameters was marginal (Table 4). The graft yield was 405% within a period of 6 h and reached 450% in 24 h.

The increasing trend in graft yield and other grafting parameters on increasing the reaction time was due to the inception and growth of polymer chains on active sites formed by ceric (IV) ions on cellulose backbone. On increasing the reaction time, the frequency of grafted chains (G_F) onto cellulose was also increased (Table 4), which was a clear indication that the increase in graft yield and other grafting parameters was due to growth of polymer chains and due to the inception of new polymer chains on cellulose backbone by ceric (IV) ions The increase in percent conversion of cellulose was more evidence for assuming the formation of new active sites on cellulose back bone on increasing the reaction time (Table 4). This increasing trend in the number of active sites on cellulose backbone has also influenced true grafting ($\%G_T$), graft conversion ($\%C_G$) and efficiency of grafting ($\%G_E$) in addition to graft yield and cellulose conversion (Table 4). After 6 h, the increase in graft yield and other grafting parameters was slow, which was due to the decrease in rate of diffusion of comonomers complex from reaction mixture to active sites on cellulose backbone and, also due to the steric hindrances offered by polymer chains, which were already grown to their full size on cellulose backbone. The steric hindrance of grafted chains after 6 h was assumed to be high because grafted chains onto cellulose were grown fully within this time period and were more effective in preventing the diffusion of comonomers for the growth of polymer chains on cellulose back bone. The molecular

Table 4. Effect of reaction time on grafting parameters

Time (min)	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
30	280	15.4	7.84	50.0	51.20	1.67
60	324	20.6	10.80	53.0	52.90	2.09
90	382	27.8	14.80	56.0	53.40	2.57
120	420	34.0	18.40	60.0	54.40	2.86
180	528	47.2	26.80	65.0	56.80	3.59
240	562	53.5	30.50	68.0	57.50	3.70
360	621	61.0	35.30	70.0	58.10	4.00
480	636	64.0	37.50	72.0	58.80	4.06
600	642	65.5	28.50	73.0	59.00	4.07
1440	643	66.4	39.20	74.0	59.10	4.08

[AN-EA] $= 1.5 \times 10^{-2}$ mol dm^{-3}, [Ce (IV)] $= 10.0 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, $f_{AN} = 0.6$, Temp. $= 35°C$, [Cell] $= 1$ wt%.

weight of grafted chains has shown a continuous increasing trend with reaction time. However, the increasing trend in the molecular weight of grafted chains was slowed after a period of 6 h. These investigations on variation in reaction time have clearly suggested that the optimum rate of grafting could be maintained by a constant supply of comonomers in the reaction mixture so that molecular weight and molecular weight heterogeneity in grafted chains is avoided. To insure that ceric (IV) ions were consumed exclusively in the formation of active sites on cellulose backbone, the ceric (IV) ions consumption at different time intervals was estimated by back titration method. The ceric (IV) ions consumption was initially very fast within 3 to 4 h of graft copolymerization and after that, the ceric (IV) ions consumption became almost negligible (Figure 12), which gave an indication that ceric (IV) ions consumed exclusively in the formation of active sites on cellulose backbone and after formation of a reasonable number of active sites, the consumption of ceric (IV) ions was reduced. The retardation in ceric (IV) ions consumption after 3 to 4 h may also be attributed to the decrease in rate of ceric (IV) ions diffusion from solution phase to cellulose backbone due to steric hindrances created by polymer chains already grafted and grown on the surface of cellulose. The increasing trend in molecular weight of grafted chains with reaction time has discarded the participation of ceric (IV) ions in termination of growing chains on cellulose backbone.

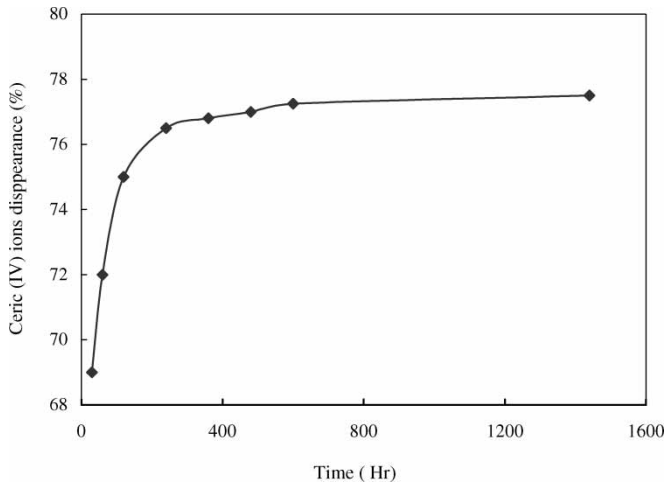


Fig. 12. Effect of reaction time on ceric (IV) ions disappearance, [AN-EA] $= 1.5 \times 10^{-3}$ mol dm^{-3}, $f_{AN} = 0.6$, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Temp.$= 35°C$, [Cell] $= 1$ wt%.

3.5 Effect of Temperature

To determine the effect of temperature on grafting of acrylonitrile and ethyl acrylate comonomers on cellulose, the graft copolymerization was studied by varying the temperature from 15°C to 60°C at constant feed composition (f_{AN}, 0.6), feed molarity (15×10^{-1} mol dm^{-3}) and concentration of ceric (IV) ions (10×10^{-3} mol dm^{-3}). The graft yield has increased from 145 to 237% on increasing the reaction temperature from 15°C to 40°C, but has shown a decreasing trend on further increasing the temperature beyond 40°C. The graft conversion, true grafting and efficiency of grafting have also shown a similar trend as shown by graft yield on varying the reaction temperature (Table 5). The increasing trend in graft yield and other grafting parameters was due to the increase in rate of formation of active sites on cellulose backbone and due to the increased rate of diffusion of comonomers on active sites for inception and growth of polymer chains on cellulose backbone. The increased rate of diffusion of comonomers from solution phase to active sites on cellulose backbone was also attributed to the increase in degree of swelling of cellulose at high temperature, which increased the rate of comonomers diffusion in cellulose matrices. The increase in number of active sites on cellulose at high temperature was evident from the frequency of grafted chains (G_F) on cellulose determined at different temperatures. The increasing trend in cellulose conversion with reaction temperature is another proof to assume that the increase in reaction temperature has increased the number of active sites on cellulose backbone (Table 5). On increasing the temperature, the molecular weight of grafted chains has decreased continuously, which was due to the increased rate

Table 5. Effect of temperature on grafting parameters

Temp (°C)	$\%G_T$	$\%C_T$	$\%C_G$	$\%C_C$	$\%G_E$	G_F
15	371	25.2	12.6	52	50.2	2.02
20	382	28.0	14.3	55	51.2	2.24
30	407	32.0	16.9	58	53.0	2.62
35	420	34.0	18.4	60	54.4	2.86
40	435	37.5	20.6	63	55.2	3.18
45	392	37.2	19.1	65	51.5	2.97
50	340	33.2	16.6	66	50.2	2.63
60	238	26.4	11.3	68	43.0	1.77

[AN-EA] $= 15 \times 10^{-1}$ mol dm^{-3}, [Ce (IV)] $= 10.0 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, $f_{AN} = 0.6$, Time = 120 min, [Cell] = 1 wt%.

Table 6. Effect of temperature on grafting parameters

Temp (°C)	F_{AN}	$\bar{m}M_1$	$\bar{m}M_2$	r_1	r_2	$P_{AN\text{-}AN}$	R
20	0.38	1.61	2.67	0.41	2.54	0.38	46.73
30	0.45	1.85	2.26	0.57	1.92	0.46	48.66
35	0.49	1.97	2.01	0.65	1.54	0.49	50.25
40	0.53	2.05	1.96	0.70	1.46	0.51	49.87
45	0.47	1.85	2.09	0.57	1.65	0.46	50.76
50	0.40	1.54	2.33	0.36	2.02	0.35	51.68
60	0.31	1.31	3.02	0.21	3.07	0.24	46.19

[AN-EA] $= 15 \times 10^{-1}$ mol dm^{-3}, [Ce (IV)] $= 10.0 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, $f_{AN} = 0.6$, Time = 120 min, [Cell] = 1 wt%.

of chain transfer process to monomers, hence the amount of ungrafted polymers was more at high temperature particularly above 40°C because the chain transfer rate was predominantly high above 40°C. The increasing trend in cellulose conversion beyond 40°C was attributed to oxidative degradation by ceric (IV) ions. The reaction temperature has also shown a significant effect on reactivity ratio of comonomers, which resulted in composition variation of grafted chains obtained at different temperatures as verified from elemental and IR analysis.

The reaction temperature has also influenced the sequence length of acrylonitrile ($\bar{m}M_1$) and ethyl acrylate ($\bar{m}M_2$) comonomers due to the variation in activity of growing chains. The variation in activity of growing chain with reaction temperature was evident from the observed variations in probability ($P_{AN\text{-}AN}$) of addition of acrylonitrile monomer to the growing chains ended with acrylonitrile monomer. The variation in activity of growing chains on cellulose has also influenced the run number (R) of acrylonitrile and ethyl acrylate monomers in grafted chains as determined at different reaction temperatures (Table 6).

The rate constant of grafting determined at different temperatures has been used to determine the energy of activation by drawing a plot (Figure 13) between log k vs. inverse of reaction temperature, which has been found to be 16.0 kJ mol^{-1} for graft copolymerization of comonomers on cellulose.

Thus on the basis of experimental observations, the following reaction steps have been proposed for graft copolymerization of acrylonitrile and ethyl acrylate on cellulose.

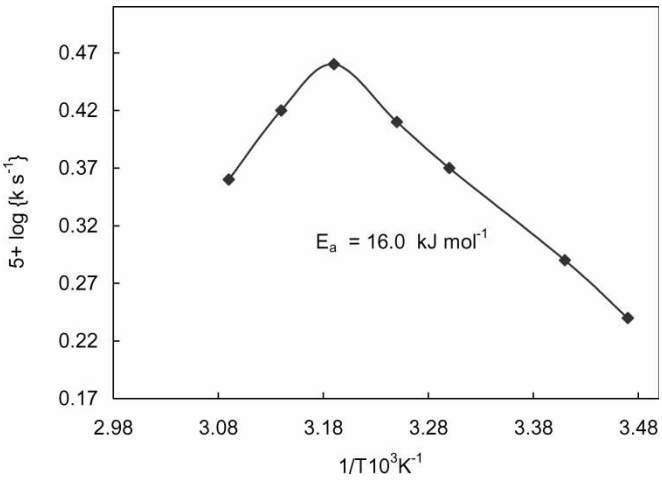


Fig. 13. Arrheneous plot between log k vs. 1/T. [AN-EA] $= 15 \times 10^{-1}$ mol dm^{-3}, $f_{AN} = 0.6$, [Ce(IV)] $= 10 \times 10^{-3}$ mol dm^{-3}, [HNO_3] $= 7.5 \times 10^{-2}$ mol dm^{-3}, Time = 120 min, [Cell] = 1 wt%.

Radical Formation:

$$\text{Cell-H} + \text{Ce(IV)} \xrightarrow{k} \underset{R}{\text{Cell}^{\cdot}} + \text{Ce(III)} + \text{H}^{+} \qquad (7)$$

Initiation:

$$\text{R}^{\cdot} + \text{AN} \xrightarrow{K_i} \text{R} - \text{AN}^{\cdot} \qquad (8)$$

$$\text{R}^{\cdot} + \text{EA} \xrightarrow{K_i} \text{R} - \text{EA}^{\cdot} \qquad (9)$$

Propagation:

$$R-(AN)^{\cdot}_{n-1}- + AN \xrightarrow{k_p} R-(AN)^{\cdot}_{n}- \quad (10)$$

$$R-(EA)^{\cdot}_{m-1}- + EA \xrightarrow{k_p} R-(EA)^{\cdot}_{m}- \quad (11)$$

$$R-(AN)^{\cdot}_{n}- + EA \xrightarrow{k_p} R-(AN)_n-EA^{\cdot}- \quad (12)$$

$$R-(EA)^{\cdot}_{m}- + AN \xrightarrow{k_p} R-(EA)_m-AN^{\cdot}- \quad (13)$$

Termination:

$$R-(AN)_n-EA^{\cdot} + {}^{\cdot}EA-(AN)_n-R \xrightarrow{k_{tc}} R-(AN)_n-(EA)_m-(AN)_n-R \quad (14)$$

$$R-(EA)_m-AN^{\cdot} + {}^{\cdot}AN-(EA)_m-R \xrightarrow{k_{tc}} R-(EA)_m-(AN)_n-(EA)_m-R \quad (15)$$

$$R-(AN)_n-EA^{\cdot} + {}^{\cdot}AN-(EA)_m-R \xrightarrow{k_{tc}} R-(AN)_n-EA-AN-(EA)_m-R \quad (16)$$

Oxidative Termination:

$$R^{\cdot} + Ce\ (IV) \xrightarrow{k_o} \text{Oxidation product} + Ce(III) + H^{+} \quad (17)$$

Where n and m are the average sequence lengths of acrylonitrile ($\bar{m}M_1$) and ethyl acrylate ($\bar{m}M_2$) blocks in grafted polymer chains, which have shown variations with feed composition and reaction temperature.

4 Conclusions

The presence of ethyl acrylate comonomer in the reaction mixture has increased the grafting of acrylonitrile on cellulose due to synergistic effect of ethyl acrylate. The graft yield ($\%G_Y$) and other grafting parameters have shown variations with feed molarity, feed composition and concentration of ceric (IV) ions at constant concentration of nitric acid. The ceric (IV) ions have substantially reduced the formation of ungrafted polymers. The variation in grafting parameters obtained at different experimental conditions has been explained successfully. The graft copolymerization of comonomers has increased thermal stability of cellulose. The energy of activation for decomposition of cellulose and grafted cellulose determined by Kissinger and Flynn and Wall method was found to be almost similar, which provided a proof for the applicability of these methods in determining the thermal stability of grafted cellulose and other polymers. The molecular weight of grafted chains has shown significant variations with concentration of ceric (IV) ions, feed molarity and feed composition. The reactivity ratios of acrylonitrile (r_1) and ethyl acrylate (r_2) have been determined and used to predict the arrangement of sequence length of acrylonitrile ($\bar{m}M_1$) and ethyl acrylate ($\bar{m}M_2$) comonomers in grafted chains.

5 Acknowledgements

Authors are thankful to C.S.I.R., New Delhi, for financial assistance. The research facilities provided by I.I.T. Roorkee is thankfully acknowledged.

6 References

1. Mahmoud, N.M. and Ahmed, H.E. (2004) *Prog. Polym. Sci.*, **29**, 499–561.
2. Roma´n-Aguirre, M., Ma´rquez-Lucero, A. and Zaragoza-Contreras, E.A. (2004) *Carbohydr. Polym.*, **55**, 201–210.
3. Okiemen, F.E. and Idehen, K.I. (1988) *Acta Polym.*, **39**, 236.
4. Deo, H.T. and Gotmare, V.D. (1999) *J. Appl. Polym. Sci.*, **72**, 887.
5. Abdel-Razek, E.A., Ali, M.M., Sarhan, A.A., Abdel-Salan, N.M., Ahmed, M. and Abdul-Bary, E.M. (1997) *Mansoura Science Bull. Chem.*, **24**, 155.
6. Okiemen, F.E. and Ogbeinfun, D.E. (1996) *Eur. Polym. J.*, **32**, 311.
7. El-Rafie, M.H., Khalil, E.M., Abdel-Hafiz, S.A. and Hebeish, A. (1985) *Acta Polym.*, **36**, 688.
8. El-Rafie, M.H., Zahran, M.K. and Hebeish, A. (1993) *Poly. Degrad. Stab.*, **42**, 233.
9. Okiemen, F.E. (1998) *Angew. Wandte, Makromol. Chem.*, **5**, 260.
10. Onishi, Y., Butler, G.B. and Hogen-Esch, T.E. (2004 J) *Appl. Polym. Sci.*, **92**, 3022–3029.
11. Zahran, M.K., Morsy, M. and Mahmoud, R.I. (2004) *J. Appl. Polym. Sci.*, **91**, 1261–1274.
12. Liu, Y., Yang, L., Shi, Z. and Li, J. (2004) *Polym. Int.*, **53**, 1561–1566.
13. Melten, C. (2004) *J. Appl. Polym. Sci.*, **94**, 1519.
14. Abu-Ilaiwi, F.A., Ahmed, M.B., Ibrahim, N.A., AbRahman, M.Z., Md Dalhan, K.Z., Zin, W.M. and Yunus, W. (2004) *Polym. Int.*, **53**, 386–391.
15. Gupta, K.C. and Sahoo, S. (2003) *Polym. Prept., Am. Chem. Soc. Polymer Chemistry Division*, **44**, 155–156.
16. El-Salwami, K., El-Naggar, A.M. and Attia, S.E. (1997) *Polym. Int.*, **44**, 181.
17. Ying, L., Kang, E.T. and Neoh, K.G. (2003) *J. Membrane Sci.*, **224**, 93.
18. Kubota, H., Fukushima, Y. and Kuwabara, S. (1997) *Euro. Polym. J.*, **33**, 67–71.
19. Kubota, H. and Shiobara, N. (1998) *React. Funct. Polym.*, **37**, 219.
20. Hebiesh, A., El-Rafie, M.H., Khalil, E.M. and Abdul Hafiz, S.A. (1986) *Cell. Chem. Technol.*, **20**, 629.
21. Gupta, K.C. and Gupta, S.K. (1987) *J. Appl. Polym. Sci.*, **33**, 2849.
22. Gupta, K.C. and Sahoo, S. (2001) *Cellulose*, **8**, 233–242.
23. Mansour, O.Y. and Nagaty, A. (1985) *Prog. Polym. Sci.*, **11**, 91–165.
24. Mino, G. and Kaizerman, S. (1960) *J. Polym. Sci.*, **31**, 242–243.
25. Gao, J., Tian, R. and Zhang, L. (1996) *Chinese. J. Polym. Sci.*, **14**, 163–171.
26. Jayame, G. and Lang, F. In *Methods in Carbohydrate Chemistry*; Whither, R.L. Ed.; Academic Press: New York, 1969, 77.
27. Wendlandt, W.W. *Thermal Methods of Analysis*, 2nd Ed.; John Wiley & Sons: New York, 1973.
28. Flynn, J.H. and Wall, L.A. (1966) *Polym. Lett.*, **4**, 323.
29. Brockway, C.E. (1968) *J. Polym. Sci. Polym. Symp.*, **24**, 139–146.
30. Mayo, F.R. and Lewis, F.M. (1944) *J. Am. Chem. Soc.*, **66**, 1594–1601.