CERIC ION INITIATED GRAFTING ON CELLULOSE FROM BINARY MIXTURE OF ACRYLONITRILE AND METHYLACRYLATE

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ABSTRACT

The Ce(IV)-ion induced grafting on cellulose from the binary mixture of acrylonitrile-methylacrylate has been investigated in heterogeneous and acidic conditions at $25 \pm 0.1°C$. Various grafting parameters were evaluated as a function of molarity, feed composition, reaction time, and concentration of ceric ion at constant concentration of nitric acid in the feed. The higher fraction of acrylonitrile in the grafted chains than the feed has indicated the synergistic effect of methylacrylate taken in the feed along with acrylonitrile. IR and elemental analysis for nitrogen contents in the synthesized copolymers were used to determine the composition of the grafted copolymers. The reactivity ratios of acrylonitrile and methylacrylate have been determined by the Mayo and Lewis method and are found to be 1.45 and 0.9, respectively. The grafting parameters have shown increasing trends on varying feed composition (f_{AN}) from 0.25 to 0.80 and varying monomer concentration from 0.6 to 5 4 mol dm^{-3}. The number of grafted moles of synthetic polymer (N_g) on cellulose were found to be dependent on molarity, feed composition,

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and ceric ion concentration. The experimental results have clearly indicated that maximum fraction of the feed was consumed in the formation of grafted copolymer chains in comparison to the homocopolymers and homopolymers. Estimation of ceric ion disappearance as a function of reaction time has clearly suggested that grafting on cellulose is initiated by the reactive sites generated through hydrogen ion abstraction by single electron transfer process.

INTRODUCTION

Cellulose is a naturally occurring polysaccharide and the properties of cellulose may be modified suitably through graft copolymerization of different vinyl monomers. A considerable number of studies on grafting of individual vinyl monomers on cellulose are available [1, 2], but very few reports are available on grafting on cellulose from a binary mixture of monomers. The technique of grafting from the binary mixtures of vinyl monomers of different functionalities facilitates the formation of graft copolymers with tailor made properties for specific applications. The synergistic effect of the comonomer in the binary mixture also plays an important role in controlling the composition of the grafted chains on the cellulose, and evaluation of this effect as a function of feed composition and other grafting conditions would be of immense importance. Recently, Okieman *et al.* [3] have reported the heterogeneous grafting of acrylonitrile and methyl methacrylate on carboxymethyl cellulose in which the grafting yield has shown a decreasing trend on increasing the acrylonitrile content in the feed, but the calculated reactivity ratios for the monomers are an inadequate explanation for the compositions of the polymers grafted on the carboxymethyl cellulose El-Salmawi *et al.* [4], have reported grafting from a binary mixture of acrylic acid and styrene onto polypropylene and the composition of grafted polymers estimated by reactivity ratios and the IR technique was found to be in order. The synergism during graft copolymerization of vinyl monomers from binary mixtures as a function of solvent composition, feed composition, and irradiation dose has been reported recently [5], and the dyeing method has been used to estimate the composition of the synthesized graft copolymers. The grafting onto cellulose is possible by growing polymer chains on the cellulose backbone using a suitable initiator, and the initiators capable of creating active sites on the back bone of the cellulose are preferred. Among the redox systems, the ceric ion intiation offers advantages as it forms free radicals easily on the backbone of the

cellulose through a single electron process [6]. However, the initiation of graft copolymerization with ceric ion depends upon the pH of the medium [7] and the type of the acids used during graft copolymerization. The investigation of pure graft copolymers is difficult since it is usually associated with homopolymers and ungrafted cellulose. Therefore, to obtain the true grafting parameters, the extraction of homopolymers and ungrafted cellulose is fundamentally required using suitable extractants without degrading the grafted chains and the backbone of the cellulose. The graft copolymerization of vinyl monomers onto cellulose is usually carried out in heterogeneous conditions due to a lack of relevant solvents for cellulose, hence, the number of grafts per cellulose chains seldom exceeds more than 10 units. Although few studies on homogeneous graft copolymerization of vinyl monomers on cellulose in organic solvents are reported [8] but no details on the effect of feed composition and ungrafted cellulose are discussed. To get the cellulose with tailor made hydrophilicity, the grafting from binary mixture of hydrophobic and hydrophilic monomers offers an effective way to obtain cellulose with desired hydrophilicity. In the present studies, the grafting on cellulose from the binary mixture of acrylonitrilemethylacrylate has been carried out using ceric ammonium nitrate as an initiator in acidic medium. The graft copolymers thus obtained were characterized for various grafting parameters and results are suitably explained.

EXPERIMENTAL

Chemicals

Acrylonitrile and methylacrylate (E. Merck, India) were purified by vacuum distillation and stored below 5°C. The ceric ammonium nitrate (E. Merck, India) and nitric acid were of reagent grade, and used without further purification. The cellulose powder (E. Merck, India) was washed with methanol deionized distilled water and vacuum dried at room temperature on phosphorous pentaoxide. The nitrogen used for purging reaction mixture was purified by passing it through an alkaline pyragallol solution and concentrated sulfuric acid.

Graft Copolymerization

1.0 g purified cellulose sample ($\overline{M}_n = 2.35 \times 10^5$) was added to a 50 ml solution of 2.0 x 10^{-3} mol dm^{-3} nitric acid placed in a three-necked round bottom flask fitted with an electrically operated stirrer, and thermostated to 25 ± 0.1°C.

A calculated amount of ceric ammonium nitrate (CAN) was added to the flask before the addition of the monomer mixture, so that the final concentration of the CAN became 6.0×10^{-3} mol dm^{-3}. The solution was deaerated with nitrogen for about 15 minutes. Finally, the calculated amount of monomers mixture (3.33 g acrylonitrile and 5.0 g methylacrylate) was added dropwise to the reaction flask and bubbling of nitrogen through reaction mixture was continued till the graft copolymerization was carried out. At the end of the experiment, the reaction was stopped by adding a 5.0% solution (WN) of the hydroquinone and the reaction mixture was poured into excess methanol. The precipitated crude graft was washed with hot water to remove the unpolymerized monomers and finally dried in a vacuum desiccator.

Ceric Ion Consumption

To calculate the ceric ion consumed during graft copolymerization, an aliquot of 5.0 mL of reaction mixture was taken out and added in excess ferrous ammonium sulfate. The back titration of the excess ferrous ammonium sulfate with ceric sulphate in the presence of O-phenanthroline gave the ceric ions consumed during polymerization reaction.

Extraction of Homopolymer

To extract homopolymers from the crude graft polymers, the samples were extracted with dimethyl formanide (DW) and acetone in a soxhlet apparatus for about 60 hours to extract polyacrylonitrile and polymethylacrylate from the grafted crudes. The extracted homopolymers were weighed and used to calculate grafting parameters.

Extraction of Homocopolymers

The homopolymer extracted crude grafts samples were extracted further with chloroform in a soxhlet apparatus until constant weight. The extracted homocopolymers were characterized for molecular weight by gel permeation chromatography (GPC).

Extraction of Ungrafted Cellulose

After extracting homopolymer and homocopolymers, the grafted cellulose sample were subjected to extract ungrafted cellulose by immersing the samples in a cuoxam solution [9] containing 1.2% $NaHSO_3$ under vigorous stirring.

At the end of 6 hours, the residue was filtered, washed with dilute acetic acid, deionized water, and vacuum dried to a constant weight.

Extraction of Synthetic Copolymers

To get the experimental data for synthetic copolymers, the cellulose extracted samples were acid hydrolyzed at 30°C in 72% sulphuric acid [10]. After 4 hours, the reaction mixture was diluted with water to an acid concentration of 4% and heated under reflux for 6 hours. The hydrolyzed copolymers were purified by dissolving in chloroform and reprecipitating with methanol. Finally, the resulting synthetic copolymers were characterized for molecular weight and nitrogen content by IR and elemental analysis.

CHARACTERIZATIONS

IR Analysis

The FTIR spectra (Perkin-Elmer, 1600) of the copolymer samples were used to determine the composition of the copolymers by recording the percent transmittance at 2240 cm^{-1} for -CN and 1750 cm^{-1} for > C = 0 (Figure 1). The mole fractions of the acrylonitrile and methylacrylate monomers in the synthesized copolymers were determined with a calibration curve using an optical density ratio (ODR) determined by following relationship.

$$ODR = \frac{\text{Log (Base line \% transmittance/MA, \% transmittance)}}{\text{Log (Base line \% transmittance /AN \% transmittance)}}$$

The infrared spectrum of pure cellulose and grafted cellulose are also recorded as shown in Figure 2. The additional absorption bands at 2240 cm^{-1} and at 1750 cm^{-1} in the grafted cellulose (Figure 2B) are attributed to the grafted methylacrylate and acrylonitrile, whereas no such bands are present in the infrared spectrum of the pure cellulose (Figure 2A).

Elemental Analysis

The composition of the copolymers determined by the IR technique was verified by determining nitrogen contents of the copolymers using a elemental analyzer (Heraeus Carlo Ebra 1108).
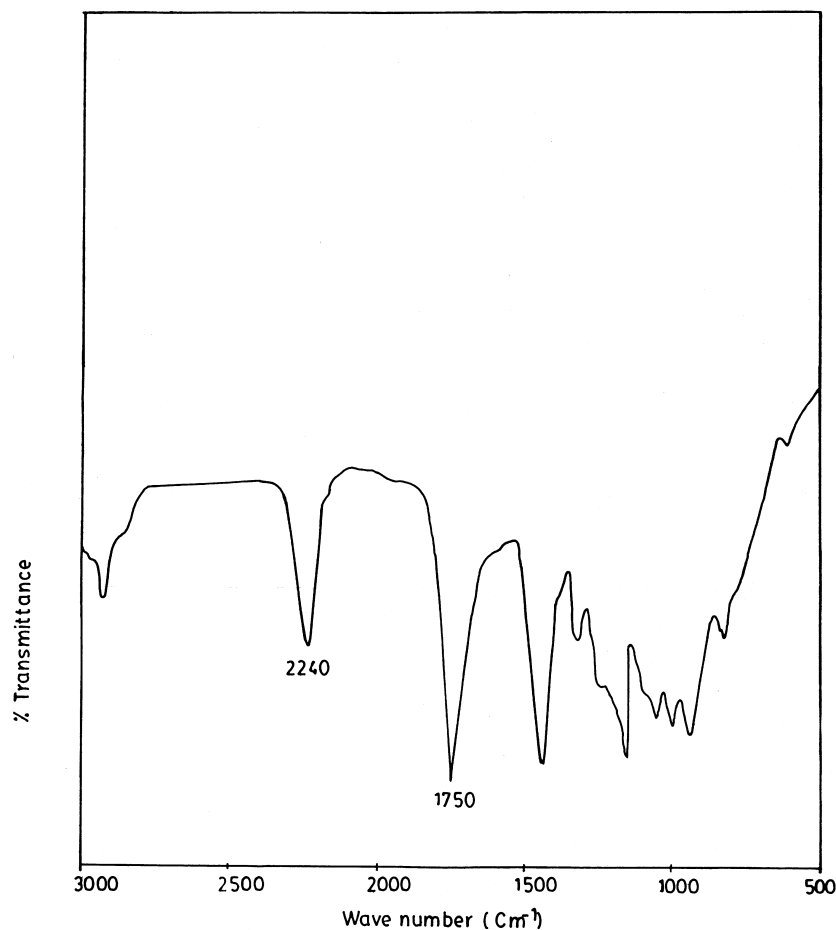
Figure 1. The IR spectrum of the grafted methylacrylate-acrylonitrile copolymer.

Molecular Weight of the Copolymers

Molecular weights of the homocopolymers (H_p) and graft copolymers (G_p) were determined by gel permeation chromatography (GPC) (water associate-440) with universal calibration curve obtained from polystyrene standard samples of known molecular weights using columns packed with linear μ-styragel. The injected copolymer solutions were eluted with tetrahydrofuran at a flow rate of 1 ml/mrnin.

Figure 2. The IR spectra of the ungrafted (A) and grafted cellulose (B) cellulose.

RESULTS AND DISCUSSION

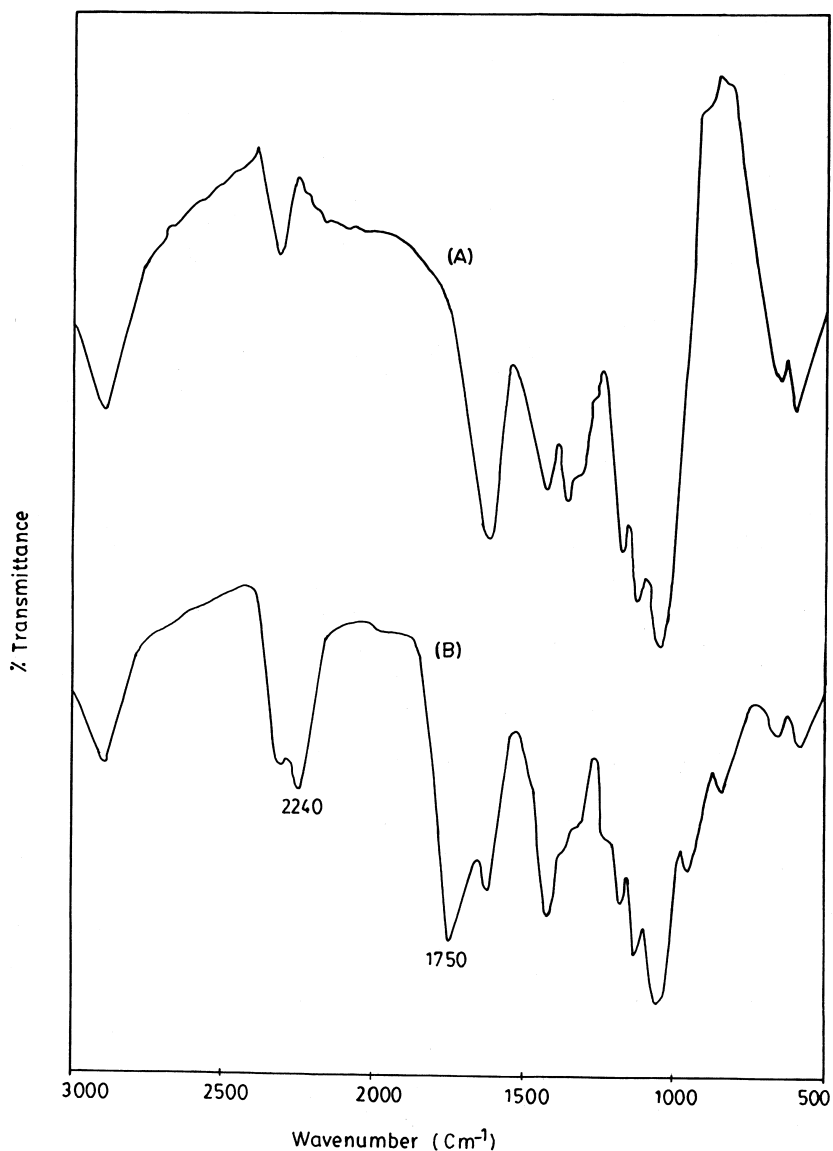The tetravalent cerium is an efficient initiator for graft copolymerization of vinyl monomers onto cellulose. The prompt radical forming tendency of Ce(IV) ions at the backbone through hydrogen ion abstraction [6] facilitates the participation of vinyl monomers more effectively in grafting process than to the formation of homopolymers. As the reactivity of ceric ions in the solution is dependent on the concentration of acid [7], all the grafting experiments were carried out at 2.0×10^{-3} mol dm^{-3} concentration of the nitric acid in the reaction mixture. The reported studies on grafting of vinyl monomers have clearly revealed that the efficiency of grafting is increased if a small amount of comonomer is added in the reaction mixture [11]. Brockway [12] has observed that methylacrylic acid and its esters are effective in increasing the overall grafting of vinyl acetate. Although the effect of the addition of monomer during grafting is not properly explained in the literature, it has certainly created an interest to study the grafting on cellulose from the binary mixture of the monomers. The higher efficiency of grafting from the binary mixture of monomers might be due to the existence of the monomer-monomer donor complex which adds to the propagating chain as a single unit in either direction. The high polymerizability of monomer-monomer complex, due to large π electrons system, makes the complex more active to interact with the propagating radicals. In view of the reported synergistic effect of the comonomers [13], the grafting studies on cellulose from binary mixture of acrylonitrile and methylacrylate have been carried out taking different concentrations and compositions of the feed at constant temperature. The effects of reaction time and ceric ion concentration on grafting parameters have been studied at a fixed composition and molarity of the binary mixtures of the monomers.

Effect of Monomer Concentration

The grafting of acrylonitrile and methylacrylate comonomers on cellulose from their binary mixture was carried out at a fixed mole fraction of the acrylonitrile ($f_{AN} = 0.4$) and varying the comonomers concentration from 0.6 mol dm^{-3} to 5.4 mol dm^{-3}. The grafting yield (% G) and other parameters are shown in Figure 3 and Table 1. The grafting yield (% G) has shown an increasing trend (Figure 3) on increasing the comonomers concentration up to 3.0 mol dm^{-3} and shows a substantial decreasing trend on further increasing the concentration beyond 3.0 mol dm^{-3}. The observed decreasing trend at a higher concentration of
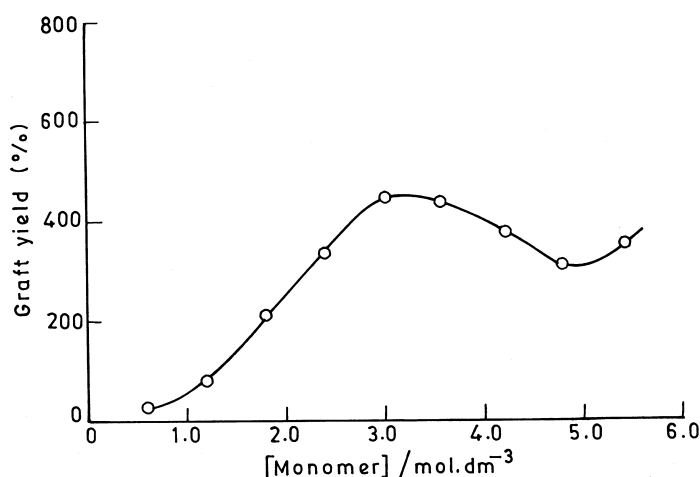
Figure 3.   Percent grafting yield (%G) as a function of [AN-MA]. [Ce(IV)]= 6.0 x 10^{-3} mol dm^{-3}, [HNO$_3$]= 2.0 $\times$ 10^{-2} mol dm^{-3}, f$_{AN}$ = 0.4,   [Cell] =1.0 g., Time = 30 minutes, Temp. = 25°C.

the comonomers may be assumed due to the increase in the viscosity of the medium which retards the rate of diffusion of the monomers to the primary methylol free radicals [7] available at the cellulose backbone. The increasing trends in the true grafting (% G$_T$) and grafting efficiency (% G$_E$) have clearly indicated that the maximum fraction of the monomers is consumed in the formation of the grafted chains in comparision to the formation of homopolymers which is further clear from the increasing trend in percent graft conversion (% C$_g$) (Table 1 (a)). The increasing trend in cellulose conversion (% C$_c$), graft-

TABLE 1 (a).   Effect of [Monomer] on Grafting Parameters at 25°C

[AN/MA] mol. dm^{-3}	% G$_T$	% C$_T$	% C$_g$	% C$_{hc}$	% C$_c$	% G$_E$
0.6	333	11	8.4	1.54	30	66
1.2	468	13	10.0	2.28	32	76
1.8	800	22	17.0	4.00	35	78
2.4	1057	25	20.0	4.50	38	50
3.0	1209	26	21.0	4.90	42	81

[Ce(IV)] = 6.0 x 10^{-3} mol. dm^{-3}, f$_{AN}$= 0.4, [HNO$_3$] = 2.0 x 10^{-3} mol. dm^{-3}

TABLE 1 (b).   Effect of [Monomer] on Grafting Parameters at 25°C

[AN-MA] mol. dm^{-3}	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (H_P)	$\overline{M}_n \times 10^{-3}$ (G_P)
0.6	0.70	0.89	1.2	50	335
1.2	1.56	2.12	3.2	59	385
1.8	3.07	4.58	6.5	90	469
2.4	3.75	6.07	7.1	105	560
3.0	4.09	7.31	8.65	120	615

[Ce(IV)] = 6.0 x 10^{-3} mol. dm^{-3}, f_{AN} = 0.4 , [HNO$_3$] = 2.0 x 10^{-3} mol. dm^{-3}

ing frequency (G_F) and number of grafted chains (N_g), on increasing the comonomers concentration have provided a reasonable explanation for the increasing trends in grafting yield and true grafting. On increasing the comonomers concentration, the molecular weights of the grafted chains have also increased (Table 1 (b)). From the data shown in Table 1 (a), it is clear that the extent of formation of the homocopolymer (% C_{hc}) is much less in comparision to the formation of graft copolymers (% C_g) which has clearly indicated that grafting predominates over the formation of homocopolymers and homopolymers in the reaction mixture.The high efficiency of grafting may be assumed to be due to a negligible rate of termination of the propagating chains anchored to insoluble cellulose in aqueous system in comparision to the mobile, tumbling homopolymer and homocopolymer chains which easily gets terminated through a mutual combination of the propagating chains or by the chain transfer reactions with solvent or monomers. The ceric ions consumption has shown an increasing trend on increasing the comonomers concentration in the feed (Figure 8) which might be due to the formation of the more reactive centers at cellulose backbone to enhance the grafting frequency (G_F) as is clear from the data shown in Table 1 (b). The low increase in percent consumption of ceric ions (Figure 8) has clearly indicated that ceric ions participation in oxidative termination of the growing chains is negligible at 6.0×10^{-1} mol dm^{-3} concentration of the ceric ions.

Effect of Feed Composition

In order to find out the effect of mole fractions of the monomers on grafting, the composition of the feed was varied by changing the mole fraction of acrylonitrile f_{AN} from 0.25 to 0.8. To compare the effect of comonomers on grafting, the percent grafting data with single monomer were also collected under identical
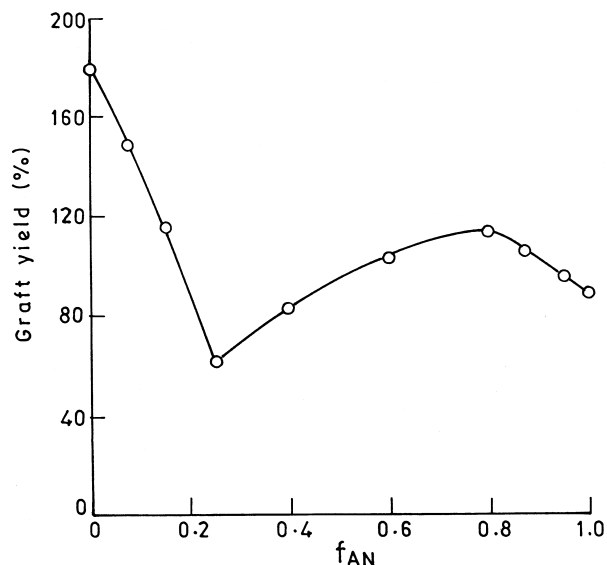
Figure 4. Percent graft yield (%G) as a function of feed composition (f_{AN}). [AN-MA] = 1.2 mol. dm^{-3}, [Ce(IV)] = 6.0 × 10^{-3} mol.dm^{-3}, [HNO_3] = 2.0 × 10^{-2} mol.dm^{-3}, [Cell] = 1.0 g, Time = 30 min., Temp. = 25°C.

experimental conditions. The data shown in Figure 4 and Table 2 collected at a constant concentration of the monomers (1.2 mol dm^{-3}) have clearly indicated that the percent graft yield (% G) and the true grafting (% G_T) have shown an increasing trend up to a certain composition of the feed (f_{AN}) = 0.8) and beyond this com-

TABLE 2 (a).   Effect of Feed Composition (f_{AN}) on Grafting Parameters at 25°C

f_{AN}	% G_T	% C_T	% C_g	% C_{hc}	% C_c	% G_E
0.00	600	26	21	3.5	40	82
0.25	433	10	7	2.8	30	75
0.40	468	13	10	2.28	32	76
0.60	480	15	12	3.0	35	78
0.80	494	17	13	3.2	36	80
1.00	469	14	11	2.9	33	75

[AN-MA] = 1.2 mol.dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol.dm^{-3}, [HNO_3] = 2.0 x 10^{-3} mol. dm^{-3}

TABLE 2 (b).   Effect of Feed Composition (f_{AN}) on Grafting Parameters at 25°C

f_{AN}	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (H_P)	$\overline{M}_n \times 10^{-3}$ (G_P)
0.00	2.51	4.27	4.40*	65	421
0.25	1.24	1.58	2.80	52	379
0.40	1.56	2.12	3.20	59	385
0.60	1.77	2.64	3.90	63	390
0.80	1.85	2.82	4.10	64	403
1.00	1.57	2.20	4.16*	58	400

[AN-MA] = 1.2 mol.dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol.dm^{-3}, [HNO$_3$] = 2.0 x 10^{-3} mol.dm^{-3} , * = N_{hp}.

position of the feed, the percent graft yield and other grafting parameters have shown an appreciable decreasing trend. The extent of percent grafting (% G) and true grafting (G_T) were found to be more when grafting was carried out when placing a methylacrylate monomer in the mixture, but found to be low with pure acrylonitrile. This has clearly indicated that a synergistic effect of methylacrylate is responsible for the increasing trend in grafting on varying the acrylonitrile mole fraction (f_{AN}) from 0.25-0.80. As the percent grafting of pure methylacrylate increases (Figure 4). Hence, it may be assumed that methylacrylate might have grafted initially to the active sites at the cellulose and subsequently, acrylonitrile has joined the graft copolymerization. The composition analysis of the grafted chains (F_{AN}) has further supported the existence of synergistic effect of the methylacrylate for the high mole fraction of the acrylonitrile in the grafted chains (Table 2 (c)). The effect of feed composition variation on other grafting parame-

TABLE 2 (c).   Composition of the Grafted Polymer Chains on Cellulose at 25°C

Sample No.	f_{AN}	F_{AN}	%N$_2$ in G_P	$\overline{m}M_1$	$\overline{m}M_2$
1	0.25	0.28	5.22	1.48	3.7
2.	0.40	0.45	8.96	1.96	2.35
3	0.60	0.67	14.55	3.17	1.59
4	0.80	0.89	20.44	6.82	1.22

[AN-MA] = 1.2 mol.dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol.dm^{-3}, [HNO$_3$] = 2.0 x 10^{-3} mol.dm^{-3}

$\overline{m}M_1$ and $\overline{m}M_2$ are the average sequence length of AN and MA in grafted polymer (G_P)

ters is shown in Table 2 (a and b). The initial decreasing trend in the percent graft yield (Figure 4) at low mole fraction of acrylonitrile (f_{AN}) < 0.25) is assumed to result from an increase in acrylonitrile molecules in termination of methylacrylate enriched grafted chains by chain transfer process and formation of homopolymer, hence, the fraction of acrylonitrile (F_{AN}) in the branches was found to be lower than the feed. The feed with high mole fraction of acrylonitrile (f_{AN}) > 0. 8) has shown a substantial decrease in the graft yield (Figure 4) which can be assumed to be due to the formation of more polyacrylonitrile than the graft copolymers. Thus, it is observed that an optimum range of feed composition (f_{AN}) ranging from 0.2-0.8 is useful to obtain the grafted chains with a higher mole fraction of the acrylonitfile (F_{AN}) than the feed composition. To obtain grafted chains with a higher mole fraction of methylacrylate (F_{MA}), the fraction of acrylonitrile in the feed (f_{AN}) should be less than 0.25. The compositional data of the feed (f_{AN}) and the grafted chains (F_{AN}) during feed variation (f_{AN}) from 0.2- 0.8 are shown in Table 2 (c), and used to calculate the reactivity ratios of acrylonitrile and methylacrylate with the Mayo and Lewis method [14] (Figure 5). The reactivity ratios for the acrylonitrile and methylacrylate were found to be 1.45 and 0.9, respec-
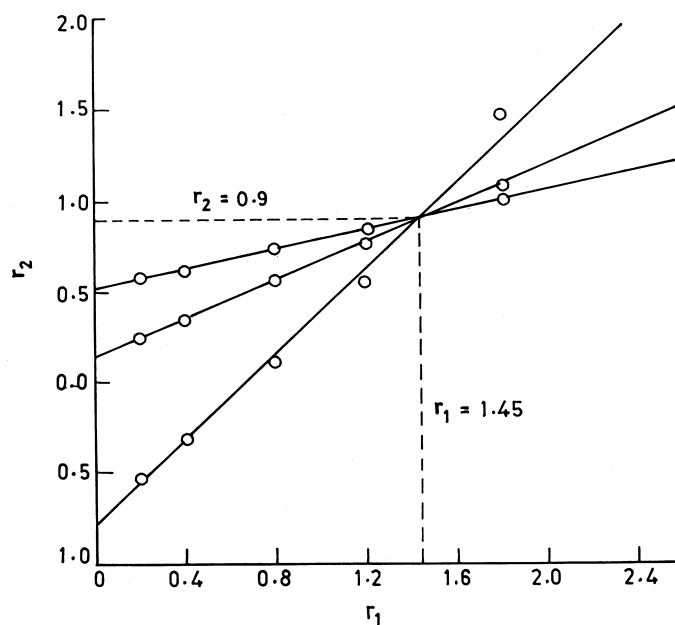

Figure 5. Mayo and Lewis plot for reactivity ratios. [AN-MA] = 1.2 mol dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol dm^{-3}, [HNO$_3$] = 2.0 x 10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 30 minutes, Temp. = 25°C, (A) f_{AN} = 0.25, (B) f_{AN} = 0.4, (C) f_{AN} = 0.6.

tively. This has clearly indicated that acrylonitrile has more affinity to combine with a growing end of the radicals associated with its own monomer than the methylacrylate. The product of r_1r_2 is 1.31, therefore, the formation of the blocks in the grafted chains is presumed. The average sequences of the monomers in the grafted chains ($^{\overline{m}}M_1$ and $^{\overline{m}}M_2$) are also calculated and given in Table 2 (c), which have clearly indicated that on increasing the mole fraction of the acrylonitrile in the feed $_{(fAN)}$, the average sequence length of acrylonitrile monomer ($^{\overline{m}}M_1$) in the grafted chains has also increased, whereas the reverse is true for methylacrylate. The observed percent nitrogen content in the grafted copolymers also supported the calculated average sequence length of the monomers in the grafted copolymers.

Effect of Ceric Ion Concentration

The effect of ceric ion concentration on grafting has been studied at a fixed feed composition ($f_{AN} = 0.4$) and fixed monomer concentration (1.2 mol. dm^{-3}) . The other experimental conditions were similar as used during a variation of monomer and feed composition. Various grafting parameters were recorded at different ceric ion concentration ranging from $2.0\text{-}15.0 \times 10^{-3}$ mol dm^{-3}. The grafting yield, true grafting. and efficiency of have shown an appreciable increasing trend up to 7.5×10^{-3} mol dm^{-3} of ceric ion but also has shown a substantial decreasing trend on further increasing the concentration of ceric ions beyond 7.5×10^{-3} mol dm^{-3} (Figure 6) (Table 3 (a)). The increasing trends of cellulose conversion (% C_c), number of grafted chains (N_g), and a percent graft conversion (% C_g) on increasing the ceric ion concentration up to 7.5×10^{-3} mol dm^{-3} have clearly indicated that within this concentration range, the ceric ions actively participate in the formation of reactive sites on the cellulose. Therefore, the graft yield (% G), percent graft conversion (% C_g) and cellulose conversion (% C_c) have shown an increasing trend up to 7.5×10^{-3} mol dm^{-3} of ceric ion (Table 3 (a and b)). The increasing trend in the grafting efficiency (%G_E) up to 7.5×10^{-3} mol dm^{-3} of the ceric ions has further supported the idea that upto this range of ceric ions, the net weight of the grafted copolymer is increased. On further increasing the concentration of ceric ions beyond 7.5×10^{-3} mol dm^{-3}, the ceric ions start participating exclusively in the termination of the growing chains of the homocopolymers and grafted copolymers. The decreasing trend in percent cellulose conversion (%C_c) beyond this concentration of ceric ion (7.5×10^{-3} mol dm^{-3}) has clearly indicated that ceric ions are not facilitating the growth of chain length of the grafted copolymers. The deviation at higher concentration of ceric ions ($> 7.5 \times 10^{-3}$ mol dm^{-3}) can be assumed to be due to the slow rate of diffu-
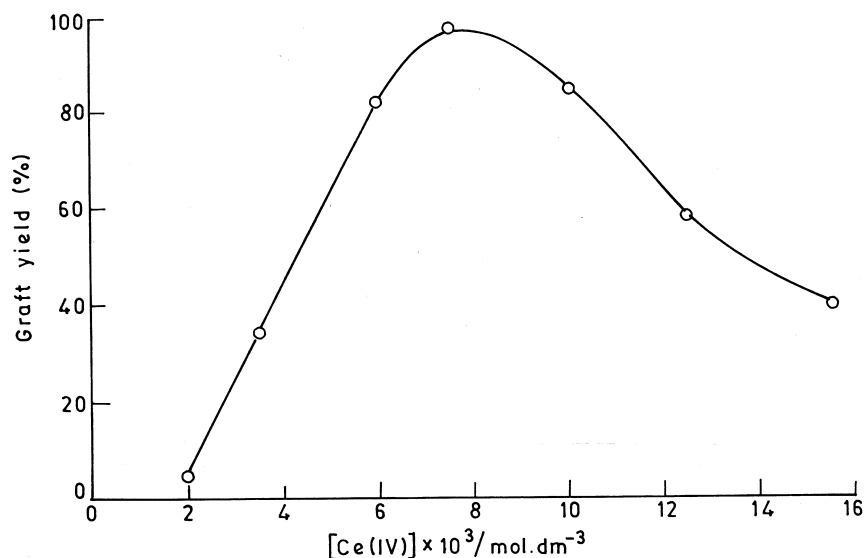
Figure 6. Percent graft yield (%G) as a function of [Ce(IV)]. [AN-MA] = 1.2 mol dm^{-3}, f$_{AN}$ = 0.4, [HNO$_3$] = 2.0 × 10^{-2} mol dm^{-3}, [Cell] = 1.0 g, Time = 30 minutes, Temp. = 25°C.

sion of ceric ions to the surface of the cellulose (Table 3 (a)). The molecular weights of graft copolymers, homocopolymers have shown a decreasing trend on increasing the ceric on concentration, hence, it is further clear that on placing high ceric ions in the reaction mixture, the ceric ions start participating in the ter-

TABLE 3 (a). Effect of [Ce(IV)] on Grafting Parameter at 25°C
[AN-MA] = 1.2 mol. dm^{-3}, f$_{AN}$ = 0.4, [HNO$_3$] = 2.0 x 10^{-2} mol dm^{-3}

Ce(IV) x 10^3 mol. dm^{-3}	% G$_T$	%C$_t$	% C$_g$	% C$_{hc}$	% C$_c$	% G$_E$
2.0	275	2.0	0.6	1.00	28	29
3.5	347	6.0	4.0	1.50	30	68
6.0	468	13.0	10.0	2.28	32	76
7.5	500	15.5	11.8	3.50	33	77
10.0	478	13.5	10.2	3.00	32	75
12.5	409	9.8	6.9	2.60	31	70
15.5	382	7.2	4.8	2.00	29	66

[AN-MA] = 1.2 mol. dm^{-3}, f$_{AN}$ = 0.4, [HNO$_3$] = 2.0 x 10^{-3} mol.dm^{-3}.

TABLE 3 (b).   Effect of [Ce(IV)] on Grafting Parameters at 25°C

$[Ce(IV)] \times 10^3$ mol. dm^{-3}	GF	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (H_P)	$\overline{M}_n \times 10^{-3}$ (G_P)
2.0	0.09	0.11	0.9	95	425
3.5	0.64	0.82	1.9	65	410
6.0	1.56	2.12	3.2	59	385
7.5	2.05	2.88	5.5	53	340
10.0	2.13	2.90	5.6	45	293
12.5	2.22	2.92	5.7	38	198
15.5	2.40	2.96	5.8	28	135

[AN-MA] = 1.2 mol dm^{-3}, f_{AN} = 0.4, [HNO_3] = 2.0 x 10^{-3} mol.dm^{-3}

mination of the growing homocopolymer and graft copolymer chains (Table 3 (b)) through a oxidation process as reported in the literature [15, 16]. The increasing trend in the grafting frequency (G_F) and number of grafted moles (N_g) (Table 3 (b)) on increasing the ceric ions concentration, has clearly indicated that the number of grafted moles of copolymers has increased on increasing the ceric ion concentration, but the total grafted weight of the copolymer has not increased due to the substantial decrease in the molecular weight of the grafted copolymers (Table 3 (b)). These studies have clearly indicated that the optimum concentration of ceric ions for an efficient grafting of acrylonitrile-methyl acrylate comonomers is 7.5×10^{-3} mol dm^{-3} and beyond this concentration, the ceric ions start actively participating in the termination process of the growing polymeric chains on cellulose backbone.

Effect of Reaction Time

In order to find out the effect of reaction time on grafting of vinyl monomers on to cellulose, the experiments were carried out at a fixed feed composition (f_{AN} = 0.4), concentration (1.2 mol dm^{-3}), keeping other conditions constant. The percent graft yield has shown an appreciable increase up to a reaction time of 6 hours and beyond, the increase in graft yield and other grafting parameters was found to be slow (Figure 7). The leveling off of the grafting yield after 6 hours could be attributed to the decrease in the net concentration of monomers and initiator available for grafting at cellulose surface. The decrease in graft yield may also be assumed to be due to the retardation in the rate of dif-
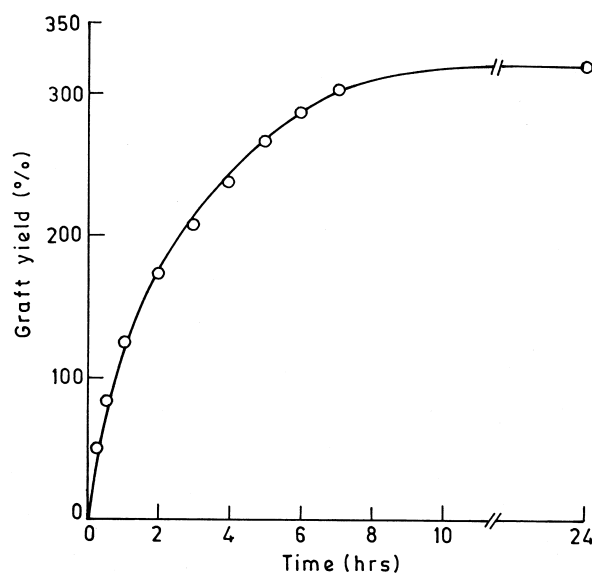
Figure 7. Percent graft yield (%G) as a function of reaction time. [AN-MA] = 1.2 mol dm^{-3},[Ce(IV)] = 6.0 x 10^{-3} mol dm^{-3}, [HNO$_3$] = 2.0 × 10^{-2} mol dm^{-3}, [Cell] = 1.0 g, f$_{AN}$ = 0.4, Temp. = 25°C.

fusion of the ceric ions at the surface of the cellulose [10]. The grafting efficiency (G$_E$) and cellulose conversion (% C$_c$) have shown an increasing trend. However, the rate of increase in these parameters beyond 6 hours has decreased appreciably (Table 4 (a and b)). The grafting frequency (G$_F$), number of grafted chains (N$_g$) and the molecular weights of the polymers have increased with the reaction times (Table 4 (b). This increasing trend in grafting parameters has clearly indicated that the radicals once formed are not easily terminated but facilitate further addition of the monomer molecules to the growing end of the chain. To have an idea about reaction time on ceric ion disappearance and to optimize the reaction time for maximum graft yield and efficiency, the percent conversion of ceric ions as a function of reaction time at fixed feed composition and concentration has also been studied (Figure 4 (b)). From the observed trend of ceric ion disappearance, it is clear that during the first initial 2 hours of grafting, the percent disappearance of ceric ion was very fast and beyond it, the rate of disappearance of ceric ion was gradual. This has indicated that ceric ions consumption is maximum in the initial two hours in formation of reactive sites [17] on cellulose through easily abstractable hydrogen ion and beyond two hours, the

TABLE 4 (a).   Effect of Reaction Time on Grafting Parameters at 25°C

Time (min)	% G_T	% C_t	% C_g	% C_{hc}	% C_c	% G_E
15	400	7.8	6	1.5	30	75
30	468	13	10	2.28	32	76
60	542	19	15	3.28	35	77
120	582	26	21	4.5	40	78
180	597	31	25	5.49	44	78
240	617	36	28	6.06	47	79
300	628	39	32	6.81	50	79.5
360	646	42	34	7.2	52	80
420	648	44	36	7.38	54	81
1440	663	47	38	7.51	55	82

[AN-MA] = 1.2 mol.dm^{-3}, f_{AN} = 0.4, [HNO$_3$] = 2.0 x 10^{-3} mol. dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol.dm^{-3}

TABLE 4 (b).   Effect of Reaction Time on Grafting Parameters at 25°C

Time (min)	G_F	N_g x 10^6	N_{hc} x 10^6	$\overline{M}_n$ x 10^{-3} (H_P)	$\overline{M}_n$ x 10^{-3} (G_P)
15	1.11	1.42	2.90	42	350
30	1.56	2.12	3.20	59	385
60	2.02	3.01	3.40	79	415
120	2.39	4.07	3.60	102	425
180	2.53	4.73	4.00	112	437
240	2.63	5.26	4.20	120	450
300	2.69	5.73	4.50	126	460
360	2.74	6.06	4.57	131	475
420	2.76	6.33	4.62	133	480
1440	2.77	6.47	4.63	135	494

[AN-MA] = 1.2 mol.dm^{-3}, f_{AN} = 0.4, [HNO$_3$] = 2.0 x 10^{-3} mol.dm^{-3}, [Ce(IV)] = 6.0 x 10^{-3} mol.dm^{-3} .
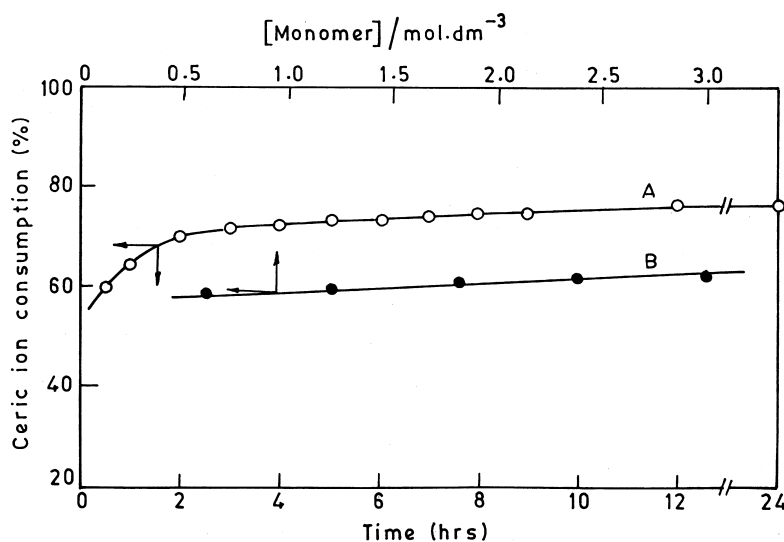
Figure 8. Ceric (IV) ion consumption as a function of reaction time (A) and monomer concentration variation (B). $f_{AN} = 0.4$, $[HNO_3] = 2.0 \times 10^{-2}$ mol dm^{-3}, [Cell] = 1.0 g, Temp. = 25°C. [AN-MA] = 1.2 mol dm^{-3} (A).

rate of consumption of ceric ion is low as it starts participating in the formation of reactive species through difficult oxidisable portions of the cellulose. The studies of ceric ion disappearance have allowed us to state that initiation of polymer chains grafted to cellulose takes place predominately during the initial first 2 hours of the reaction and beyond this reaction time, the ceric ions start participating either in oxidizing the difficult part of the cellulose or in termination of the growing radicals in the reaction mixture.

Thus, on the basis of the experimental observations, the following reactions steps are proposed to occur during grafting on cellulose from the binary mixture of acrylonitrile (AN) and methylacrylate (MA) in presence of the ceric ions.
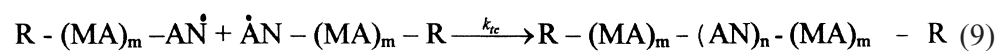
Radical Formation:

$$\text{Cell} - \text{H} + \text{Ce (IV)} \xrightarrow{k} \text{Cell}\overset{\bullet}{} + \text{Ce (III)} + \text{H}^+ \qquad (1)$$
$$(\dot{R})$$

Initiation:

$$\dot{R} + \text{AN} \xrightarrow{k_i} R - \text{AN}\overset{\bullet}{} \qquad (2)$$

$$\dot{R} + MA \xrightarrow{k_i} R - M\dot{A} \tag{3}$$

Propagation:

$$R - A\dot{N} + AN \xrightarrow{k_p} R - (A\dot{N})_n \text{----} \tag{4}$$

$$R - M\dot{A} + MA \xrightarrow{k_p} R - (M\dot{A})_m \text{----} \tag{5}$$

$$R - (A\dot{N})_n \text{--} + MA \xrightarrow{k_p} R - (AN)_n - M\dot{A} \tag{6}$$

$$R - (M\dot{A})_m \text{--} + AN \xrightarrow{k_p} R - (MA)_m - A\dot{N} \tag{7}$$

Termination:

$$R - (AN)_n - M\dot{A} + \dot{M}A - (AN)_n - R \xrightarrow{k_{tc}} R - (AN)_n - (MA)_m - (AN)_n - R \tag{8}$$

$$R - (MA)_m - A\dot{N} + \dot{A}N - (MA)_m - R \xrightarrow{k_{tc}} R - (MA)_m - (AN)_n - (MA)_m - R \tag{9}$$

$$R - (AN)_n - M\dot{A} + \dot{A}N - (MA)_m - R \xrightarrow{k_{tc}} R - (AN)_n - MA-AN - (MA)_m- \tag{10}$$

Oxidative Termination:

$$\dot{R} + Ce\,(IV) \xrightarrow{k_o} \text{oxidation product} + Ce\,(III) + H^+ \tag{11}$$
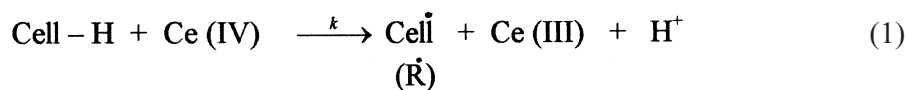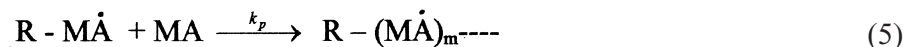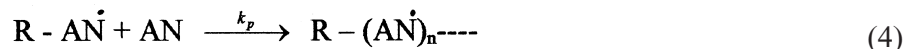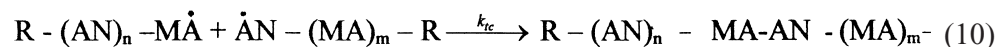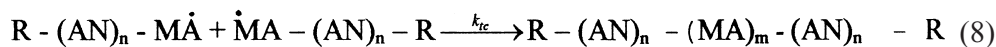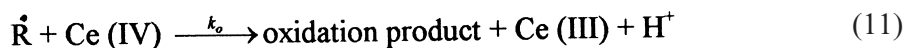
where n and m are the average sequence lengths of the acrylonitrile ($\overline{m}M_1$) and methylacrylate ($\overline{m}M_2$) blocks in the grafted chains. The values of n and m varied from 1.48 to 6.82 and 3.7 to 1.22 during grafting as given in Table 2 (c).

CONCLUSION

The grafting on cellulose from the binary mixture of acrylonitrile and methylacrylate can be carried out successfully in the presence of Ce (IV) ions and the extent of grafting changes appreciably on varying the comonomers concentration and mole fraction in the feed. Synergistic effect of the methylacrylate allows acrylonitrile monomer to participate effectively in the graft copolymerization on cellulose. Thus, the acrylonitrile-methylacrylate system has shown a

tendency to form monomer blocks with an average sequence length ranging from 1.2 to 6.8 in the grafted chains. Variation in the values of different grafting parameters as a function of experimental conditions is suitably explained.

ACKNOWLEDGEMENT

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