Grafting of Acrylonitrile and Methyl Methacrylate from Their Binary Mixtures on Cellulose Using Ceric Ions

K. C. GUPTA, SUJATA SAHOO

Polymer Research Laboratory, Department of Chemistry, University of Roorkee-247667, U.P. India

ABSTRACT: Ceric ion-initiated grafting on cellulose from a binary mixture of acrylonitrile and methyl methacrylate was carried out in heterogeneous and acidic conditions at $30 \pm 0.1°C$ in a nitrogen atmosphere. To avoid the complexation of water molecules with Ce(IV) ions, the concentration of the nitric acid was taken to be more than the concentration of ceric ions. The effect of the feed concentration, reaction time, and ceric ions concentration on grafting were investigated at a fixed composition. To investigate the effect of monomer–monomer interactions on grafting, the graft copolymerization was also studied, using different feed compositions (f_{AN}) ranging from 0.25 to 0.80. In this range of feed composition, the synergistic effect of methyl methacrylate molecules has shown an important effect on acrylonitrile monomer and facilitate the incorporation of the acrylonitrile monomer into the grafted chains. The reactivity ratios of acrylonitrile and methyl methacrylate were calculated using the Mayo and Lewis method and were found to be 0.74 and 1.03, respectively. The average sequence lengths of the monomers ($\bar{m}M$) were found to be dependent on the feed compositions and found to be arranged in alternate fashion in the grafted chains. The probability of the addition of a monomer ($P_{1,1}$) to the growing radicals on cellulose ended with its own type of monomer was found to be dependent on the feed composition. The composition of the grafted copolymers, homocopolymers, was determined by IR and elemental analysis for nitrogen. None of the grafted chain on cellulose was found to be made of a single type of monomer. The ceric ion consumption during grafting was found to be independent of the molarity of the feed but shown an appreciable change in the initial few hours of grafting. The variation in the values of the grafting parameters as a function of the reaction conditions is suitably explained. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 767–778, 2001

Key words: cellulose; acrylonitrite; methyl methacrylate; graft copolymerization; ceric ions

INTRODUCTION

Modification of the cellulose properties by grafting of various vinyl monomers has been investigated extensively in the presence of different initiators, but grafting of vinyl monomers from their mixtures on synthetic and natural polymers has rarely been studied.[1,2] The grafting of selected comonomers from their mixtures introduces dual properties in the polymer structure for their versatile applications,[3] such as immobilization of the enzymes, improving dyeing and ion-exchange properties, and production of reverse-osmosis grade polymers. During graft copolymerization of a single monomer, either some inherent properties of the cellulose are destroyed or the extent of grafting of the pure monomer is smaller than that with comonomers. A few studies of grafting of various vinyl monomers on films/fibers[4–7] and rayon[8] with a radiation-induced technique were

reported. The effect of different solvents during radiation-induced grafting from an acrylamide and styrene mixtures onto polypropylene was also studied,[9] but it is interesting to note that few reports are available for the graft copolymerization of the vinyl monomer from their mixtures onto cellulose. Matveeva et al.[1] synthesized graft copolymers of cellulose using binary mixtures of the vinyl tetrazole monomer using an $Fe^{2\pm}H_2O_2$–hydrazene redox system. Recently, Okieman and Ogebifun[10] reported the graft copolymerization of acrylonitrile and methyl methacrylate onto carboxymethyl cellulose (CMC), showing a decreasing trend in the grafting yield on increasing acrylonitrile (f_{AN}) in the feed, but the observed composition of the grafted chains is different, as expected from the reported value of the reactivity ratios of the studied monomers.

In the grafting of vinyl monomers from their mixtures, the identification of the grafted fractions of each monomer in the grafted chain is of special importance to understand the synergistic effect of the added comonomers in the feed. The fraction of vinyl monomers are determined by the spectroscopic, elemental analysis, or reactivity ratio method. Recently, the dyeing method was also applied[11] to estimate the different fractions of the monomers in the resulting graft copolymers onto textile fibers. Grafting onto cellulose is preferably carried out with an initiator which is capable of creating active sites on the cellulose; otherwise, the formation of homocopolymers and homopolymers is predominate on the overall graft copolymerization. Among the various metal ions, the ceric ions are capable of forming radicals easily at the backbone of the cellulose.[12] However, the initiation of graft copolymerization in the presence of ceric ions depends upon the pH of the medium[13] and the type of the acids used during graft copolymerization. Grafting of vinyl monomers from a binary mixtures of monomers onto cellulose was carried out in heterogeneous conditions due to the lack of relevant solvents. In the present work, an attempt was made to investigate the graft copolymerization of acrylonitrile and methyl methacrylate from their binary mixtures onto cellulose in the presence of ceric ions in an acidic medium. Various grafting parameters were evaluated as a function of the feed composition, molarity, ceric ions concentration, and reaction time. The composition of the grafted chains is verified with elemental analysis and the reactivity ratios of the monomers.

EXPERIMENTAL

Chemicals

Acrylonitrile (AN) and methyl methacrylate (MMA) (E. Merck, Bombay, India) were purified by extraction with an aqueous sodium chloride–sodium hydroxide solution and dried over sodium sulfate. The stabilizer-free monomers thus obtained were vacuum-distilled and stored below 5°C. The ceric ammonium nitrate (CAN; 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 finally vacuum-dried at room temperature on phosphorus pentaoxide. The nitrogen gas was passed through alkaline pyragallol and a concentrated sulfuric acid solution before using it in the reaction mixture.

Graft Copolymerization

A 1.0 g purified cellulose sample ($\bar{M}_n = 2.5 \times 10^5$) was added to 50 mL of an 8.0×10^{-2} mol dm^{-3} solution of nitric acid placed in a three-necked round-bottom flask fitted with an electrically operated stirrer and maintained at 30 ± 0.1°C. A known amount of CAN was added to the flask to obtain an 8.0×10^{-3} mol dm^{-3} concentration of CAN in the reaction mixture. The solution was deaerated with nitrogen for about 15 min and ceric ions were allowed to interact with the cellulose to create sufficient active sites on the cellulose. Finally, the monomer mixture (4.90 g AN and 7.34 g MMA) was added dropwise to maintain an overall molarity of 1.6 mol dm^{-3} with an AN mol fraction (f_{AN}) of 0.4. The reaction mixture was purged with nitrogen until the grafting reaction was studied. Finally, the reaction was stopped by adding a 5.0% solution (w/v) of hydroquinone and poured into excess methanol to separate the polymerization products from the remaining unpolymerized monomers. The precipitated crude product was filtered, washed repeatedly with hot and cold water to remove the residual adsorbed copolymerized monomers, and, finally, vacuum-dried and weighed.

Extraction of Homopolymers (H_p)

The homopolymers formed during grafting were extracted with dimethylformamide (DMF) and acetonitrile in a Soxhlet apparatus for about 60 h to extract the polyacrylonitrile (PAN) and poly-

methyl methacrylate (PMMA) from the grafted crudes. The homopolymers were precipitated with a water/methanol mixture (1:1, v/v) and dried to a constant weight in a vacuum oven maintained at 50°C.

Extraction of Homocopolymers (H_{cp})

The homocopolymers were extracted from the homopolymer-extracted crude polymer with tetrahydrofuran (THF) in a Soxhlet apparatus for 60 h until a constant weight. Finally, the extracted homocopolymers were precipitated with a water/methanol mixture (1:1, v/v), washed repeatedly with deionized water, and dried to constant weight in a vacuum oven at 50°C.

Extraction of Ungrafted Cellulose

To obtain a true grafting parameter, the ungrafted cellulose was extracted from the homopolymer and the homcopolymer-extracted crude polymer by immersing the samples in a cuoxam[13] solution containing 1.2% $NaHSO_3$ under vigorous stirring. At the end of 6 h, the residue was filtered, washed with dilute acetic acid and deionized water, and dried to constant weight in a vacuum oven at 50°C.

Extraction of Grafted Copolymers (G_p)

The grafted polymer chains were isolated from the backbone of the cellulose by hydrolyzing the cellulose-extracted sample in 72% sulfuric acid[14] at 30°C. After 6 h, the mixture was diluted with water to an acid concentration of 4% and heated under reflux for another 6 h to ensure complete hydrolysis of the grafted chains. The reaction mixture was poured into acetone with vigorous stirring and the resulting precipitate was filtered. After washing and drying the precipitate, the hydrolyzed copolymer chains were extracted with THF and recovered by precipitating the extract in methanol. The hydrolyzed and precipitated residue was also extracted with DMF and acetonitrile to obtain the grafted polymer chains which might be formed with pure monomers, but on pouring the extracts in methanol, no precipitate was obtained, which clearly confirmed that during the grafting of vinyl monomers from their mixtures grafted chains of a single monomer are hardly formed.

Ceric Ions Consumption

To calculate the ceric ions consumption during graft copolymerization, a 5.0 mL aliquot of the reaction mixture was poured into an excess ferrous ammonium sulfate solution. The back titration of the excess ferrous ammonium sulfate with ceric sulfate using o-phenanthroline gave the amount of ceric ions consumed during grafting.

Characterization

The FTIR spectra of the homopolymers, homocopolymers, and grafted copolymers were recorded on a Perkin–Elmer-1600 spectrophotometer with a KBr pallet. The IR spectra showed a strong sharp band at 2240 cm^{-1} for the nitrile group of AN and a broad band at 1740 cm^{-1} to the carbonyl group of MMA. The amount of the synthesized homopolymers was determined by recording the percent transmittance of nitrile (2240 cm^{-1}) and carbonyl (1740 cm^{-1}) groups and using the calibration curves prepared for the hompolymers. The composition of the homocopolymers and grafted copolymers was obtained with a copolymer calibration curve using an optical density ratio (ODR) as determined by the following relationship:

$$\text{ODR} = \frac{\log(\text{baseline } \% \, T_{1740}/\text{MMA } \% \, T_{1740}}{\log(\text{baseline } \% \, T_{2240}/\text{AN } \% \, T_{2240}}$$

Elemental Analysis

The composition of the grafted copolymers determined by the IR technique was verified by determining the nitrogen content in the copolymers with a Perkin–Elmer-240C elemental analyzer.

Molecular Weight of the Copolymers

The molecular weights of the grafted copolymers were determined with gel permeation chromatogrphy (Water Associates 440) using Water-μ-styragel columns of a 200-mL injection volume. THF was used as the mobile phase at a flow rate of 1 mL/min and polystyrene standards of known molecular weights were used to obtain the universal calibration curve.

RESULTS AND DISCUSSION

When ceric ions are added in the reaction mixture for grafting on cellulose, it has been reported that a ceric ion–cellulose complex is initially formed which immediately creates a free radical at the backbone of the cellulose and ceric ions are reduced to cerrous ions through an one-electron

transfer process.[15] The formation of homopolymers at an optimum concentration of CAN is attributed mainly to the chain-transfer reaction from the growing graft copolymers to the monomers in the solution. The reactivity of the ceric ions is pH-dependent[13]; hence, during grafting, the concentration of the nitric acid was maintained at 8.0×10^{-2} mol dm^{-3}. In graft copolymerization of a single monomer, the grafting yield depends mainly upon the molarity of the monomers used in the reaction mixture, but when grafting is carried out in the presence of comonomers, then grafting not only depends upon the molarity of the monomers used in the reaction mixture, but also depends mainly upon the interactions taking place between the comonomers involved in the graft copolymerization. These monomer–monomer interactions facilitate the transfer of a monomer at the grafting sites to increase the overall efficiency of grafting.[16]

The efficient grafting from a binary mixture of monomers might be assumed to be due to the high polarizability of the monomer–monomer complex with a large π-electron system which makes the monomer system more reactive to interact with propagating radicals at the cellulose backbone. The total absence of grafted chains purely made of single monomer units has clearly suggested the assumption of the existence of the monomer–monomer complex in the reaction mixture, which allows the formation of grafted chains with mixed monomers and prevents the formation of homopolymeric grafted chains. In view of the possible monomer–monomer interactions, responsible for the efficient grafting of vinyl monomers, the grafting of AN and MMA comonomers on cellulose was studied by varying the molarity, feed compositions, reaction times, and ceric ions concentration.

Effect of Monomer Concentration

To study the effect of the initial concentration of the comonomers on grafting, the molarity [M] of the binary monomers (AN + MMA) was varied from 0.8 to 4.8 mol dm^{-3} at an 8.0×10^{-3} mol dm^{-3} concentration of CAN, keeping a fixed mol fraction of the AN (f_{AN} = 0.4). The percent graft yield increased on increasing the comonomer concentration to 4.0 mol dm^{-3}, and on further increasing the comonomer amount beyond this concentration (>4.0 mol dm^{-3}), an appreciable decreasing trend (Fig. 1) is set up which is assumed to be due to increase in the viscosity of the me-
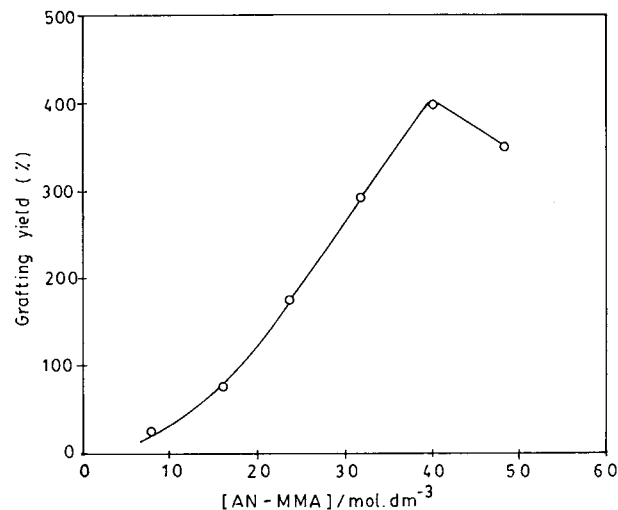

Figure 1   Percent graft yield (% G) as a function of [AN + MMA]: [Ce(IV)] = 8.0×10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0×10^{-2} mol dm^{-3}; f_{AN} = 0.4; [Cell] = 1.0 g; time = 30 min; temperature = 30°C.

dium. During molarity variation, the mol fractions of the comonomers in the binary mixture are constant (f_{AN} =0.4 and f_{MMA} =0.6); hence, the nature of the monomer–monomer interactions is assumed to be same at different molarities of the feed.

The composition analysis of the grafted chains obtained at different feed molarities at a fixed feed mol fraction (f_{AN} =0.4) showed almost a fixed mol fraction of acrylonitrite (F_{AN} = 0.37). However, the total weight of the grafted polymer increased on increasing the molarity of the feed. This constancy in the mol fraction of the monomers in the grafted chains (F_{AN} = 0.37) clearly indicated that the nature of the monomer–monomer interactions remain almost constant and do not alter on increasing the amount of the total feed at a fixed mol fraction (f_{AN} = 0.4).

The deviation in yield beyond 4.0 mol dm^{-3} is assumed to be due to the decrease in the rate of diffusion of the monomer–monomer complex at the reaction sites at the cellulose backbone. The increasing trend of true grafting (% G_T) and grafting efficiency (% G_E) clearly indicated that the percent graft conversion (% C_g) increased with increase in the molarity of the medium, which is due to increase in the rate of diffusion of the monomer–monomer complex from the solution phase to the growing end of the chains. But the rate of diffusion of the comonomer complex slowed down beyond 4.0 mol dm^{-3} of the comonomers due to an appreciable increase in the viscosity of the medium.

Table I   Effect of [Monomers] on Grafting Parameters at 30°C

(a) Effect of Monomer Concentration on Grafting Parameters at 30°C

[M] (mol dm^{-3})	% G_T	% C_t	% C_g	% C_{hc}	% C_C	% G_E
0.8	380	7.69	4.09	1.91	26.0	53.0
1.6	525	10.46	6.13	2.50	28.0	58.6
2.4	802	15.47	9.53	3.31	30.5	61.6
3.2	1051	18.06	11.44	3.86	33.0	63.3
4.0	1325	20.58	13.07	4.20	35.0	63.5
4.8	1306	17.7	9.53	4.60	32.0	53.9

(b) Effect of Monomer Concentation on Grafting Parameters at 30°C

[M] (mol dm^{-3})	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (G_p)	$\overline{M}_n \times 10^{-3}$ (H_{cp})
0.8	0.80	0.80	2.92	300	40
1.6	2.12	2.38	6.55	315	47
2.4	3.77	4.60	8.12	380	75
3.2	4.93	6.51	10.50	430	90
4.0	5.49	7.69	12.34	520	105
4.8	5.46	7.00	14.60	500	115

[Ce(IV)] = 8.0×10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0×10^{-2} mol dm^{-3}; f_{AN} = 0.4; time = 30 min.

The analysis of the homocopolymers showed a higher mol fraction of AN than that of the grafted polymer chains. This indicated that the interactions of the monomer–monomer complex with the growing radicals on the cellulose are different from those of the growing homocopolymer chains in the solution. The mol fraction of the monomers in the homocopolymer remains almost constant (f_{AN} = 0.38) during the feed concentration variation, which again supported the assumption that monomer–monomer interactions do not change with the feed concentration.

The effect of the feed concentration on the cellulose conversion (% C_c) and grafting frequency (G_F) was also studied, and from the data given in Table I(a,b), it is clear that the percent cellulose conversion (% C_c) increased on increasing the molarity of the comonomers in the reaction mixture to 4.0 mol dm^{-3}. The increasing trend in the grafting frequency (G_F) with the feed concentration suggested that a higher comonomer concentration facilitates the addition of monomer molecules to the reactive sites which were lying unused at the low concentration of the comonomers [Table I(b)]. During variation of the concentration of the comonomers, the percent ceric ions consumption was almost constant [Fig. 4(b)]; hence, it is clearly indicated that no new reactive sites

are formed during variation of the comonomer concentration but new branches start forming on unutilized initially formed reactive sites on the cellulose. The decreasing trend in cellulose conversion (% C_c) and grafting frequency (G_F) beyond 4.0 mol dm^{-3} [Table I(b)] might be due to the nonavailability of reactive sites, hindrances created by the already-grafted chains on the cellulose, and the slow rate of diffusion of the comonomers from the solution. The formation of new chains is also clear from the increasing trend in number of grafted chains (N_g) [Table I(b)]. The molecular weight of the grafted polymers, homocopolymers, and homopolymers increased on increasing the comonomer concentration in the feed [Table I(b)], which can be assumed to be due to the higher rate of copolymerization on increasing the comonomer concentration in the feed.

Effect of Feed Composition

To determine the nature of the grafted polymers and homopolymers as a function of the feed composition and to relate the composition of the grafted polymers to the changing monomer–monomer interactions at different feed compositions, the mol fraction of the AN (f_{AN}) in the feed was varied from 0.25 to 0.80 at a constant feed

Table II Effect of Feed Composition on Grafting Parameters and Composition of Grafted Polymer Chains at 30°C

(a) Effect of Feed Composition on Grafting Parameters at 30°C[a]					
f_{AN}	$\% \; G_T$	$\% \; C_t$	$\% \; C_g$	$\% \; C_{hc}$	$\% \; C_C$	$\% \; G_E$
0.00	627	17.90	13.24	2.60	36.00	74.00
0.25	476	8.09	4.08	2.30	26.00	50.50
0.40	525	10.46	6.13	2.51	28.00	58.60
0.60	556	13.94	9.09	2.78	32.00	64.50
0.80	577	17.00	11.20	3.14	35.00	65.80
1.00	566	12.83	8.17	2.42	30.00	63.60

(b) Effect of Feed Composition on Grafting Parameters at 30°C[a]					
f_{AN}	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$
0.00	3.26	4.69	6.6	345	50
0.25	1.57	1.63	6.3	305	45
0.40	2.12	2.38	6.5	315	47
0.60	2.60	3.33	6.6	330	52
0.80	2.90	4.06	6.7	337	57
1.00	2.56	3.07	6.1	325	48

(c) Effect of Feed Composition on Composition of Grafted Polymer Chains at 30°C[b]					
f_{AN}	F_{AN}	$\% \; N$	$\bar{m}M_1$	$\bar{m}M_2$	R	$P_{AN,AN}$
0.25	0.23	3.68	1.25	4.09	37.45	0.20
0.40	0.37	6.24	1.49	2.55	49.50	0.33
0.60	0.56	10.50	2.11	1.69	52.63	0.53
0.80	0.77	16.50	3.96	1.26	38.32	0.75

[a] [M] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0 × 10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0 × 10^{-2} mol dm^{-3}; time = 30 min.
[b] [M] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0 × 10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0 × 10^{-2} mol dm^{-3}. $\bar{m}M_1$ and $\bar{m}M_2$ are the average sequence length of AN and MMA in the grafted polymer; $P_{AN,AN}$ is the probability of the AN molecule to the chains ended with AN; R is the average-number of sequence per 200 monomer units.

molarity of 1.6 mol dm^{-3}. To compare the grafting of monomers onto the cellulose from binary mixtures, the data on the percent grafting yield (% G) of pure AN and pure MMA were also collected and are given in Table II(a,b). The extent of the graft yield with pure MMA was more (61%) than with pure AN, which clearly suggested that AN has a low affinity to attach to the cellulose in comparison to the MMA. But the experimental data as shown in Figure 2(a) and Table II show the variation in their affinity in the presence of another monomer. The variation in the percent graft yield (% G) [Fig. 2(a)] and the composition of the grafted chains [Table II(c)] on varying the feed composition (f_{AN}) clearly indicated that the nature of the monomer–monomer interactions changed on changing the compositions of the feed; hence, the observed percent graft yield (% G) [Fig.

2(a)] and the composition of the grafted chains (F_{AN}) are different [Table II(c)]).

The expected percent graft yield (% G) shown by the dotted line in Figure 2(a) does not match the observed graft yield curve. At a low mol fraction of the AN (f_{AN} < 0.25), the percent grafting is more due to the high concentration of MMA in the reaction mixture, but was found to be low in comparison to the percent graft yield (% G) with pure MMA. At a low mol fraction of the AN (f_{AN} < 0.25), the monomer–monomer interactions among MMA molecules are stronger and facilitate the incorporation of the MMA molecules to the grafted chains, whereas the AN molecules exclusively participate in chain-transfer reactions, but during mol fraction (f_{AN}) variation from 0.25 to 0.8, the percent graft yield increased [Fig. 2(a)] and the fraction of AN [Table II(c)] in the grafted
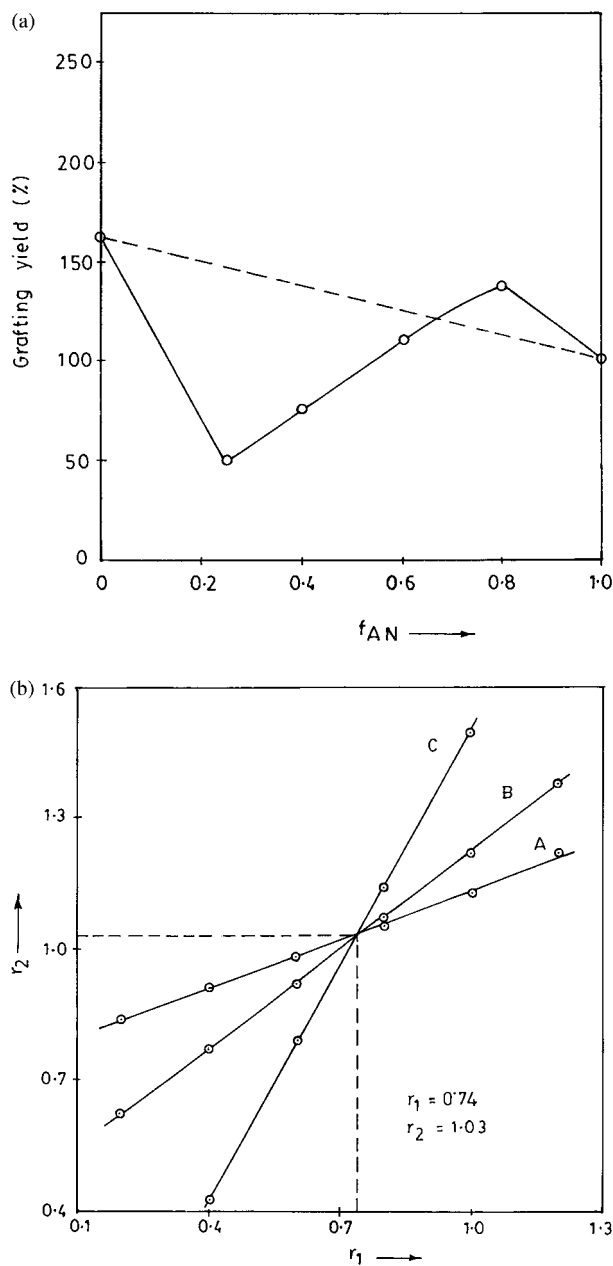
Figure 2   (a) Percent graft yield (% G) as a function of feed composition: [AN + MMA] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0×10^{-3} mol dm^{-2}; [HNO$_3$] = 8.0×10^{-2} mol dm^{-3}; [Cell] = 1.0 g; time = 30 min; temperature = 30°C. (b) Mayo and Lewis plot for reactivity ratios of the monomers: [AN + MMA] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0×10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0×10^{-2} mol dm^{-3}; [Cell] = 1.0 g; time = 30 min; temperature = 30°C. (A) f_{AN} = 0.25; (B) f_{AN} = 0.4; (C) f_{AN} = 0.6.

chains also increased. Within this range of feed composition, the monomer–monomer interactions are different from those at a low fraction of the AN ($f_{AN} < 0.25$) and facilitate the incorporation of

more AN molecules into the grafted chains along with the MMA molecules. In this range of feed composition variation ($f_{AN} = 0.25$–0.8), the cross monomer–monomer interactions show an increasing synergistic effect[11,16,17] on the AN molecules, to a maximum mol fraction (f_{AN}) of 0.8. Beyond this mol fraction ($f_{AN} > 0.8$), the nature of the monomer–monomer interactions again show variation, which results in an appreciable decrease in the graft yield [Fig. 2(a)] and mol fraction of the AN in the grafted chains has increased substantially. At a higher mol fraction of the AN ($f_{AN} > 0.8$), the cross interactions among the monomer molecules became weaker and the AN molecules started participating effectively in the formation of homopolymers rather than grafted copolymers; hence, the percent graft yield (% G) showed a decreasing trend beyond a 0.8 mol fraction of AN. From these experimental observations, it became clear that interactions among the comonomers vary with the feed compositions, which ultimately changes the composition of the grafted chains and the extent of the percent graft yield (% G). The optimum composition (f_{AN}) of AN–MMA was found to be 0.8, where the synergistic effect of MMA for acrylonitrite is maximum. The observation of grafting parameters as a function of the feed composition shown in Table II clearly indicates that the grafting frequency (G_F), number of grafted chains (N_g), cellulose conversion (% C_c), and grafting efficiency (% G_E) are consistent with the grafting yield (% G) and the true grafting (% G_T).

From the composition analysis of the grafted chains, homocopolymer chains, it has become clear that in the present system the percentage of MMA molecules in the copolymer is more in comparison to AN. This indicated that the reactivity of the MMA monomer to form the grafted polymer chains is more than that of AN. To express the relative reactivity of the MMA monomer in comparison to the AN monomer, an effort was also made to calculate the reactivity ratios of AN and MMA using the Mayo and Lewis method[18] [Fig. 2(b)]. The values of the mol fractions of the monomers in the feed (f_{AN}) and the grafted polymer chains are shown in Table II(c). The reactivity ratios for AN and MMA from the Mayo and Lewis plot [Fig. 2(b)] at a conversion of 5% were found to be 0.74 and 1.03, respectively, which clearly supports the occurrence of high mol fractions of MMA in the grafted copolymers and the homocopolymers obtained during grafting. The product of the reactivity ratios ($r_1 r_2$) was found to be less than 1;

hence, the grafted copolymers lie between the ideal and the alternating systems. The average sequence lengths of AN ($\bar{m}M_1$) and MMA ($\bar{m}M_2$) in the grafted chains showed a clear dependence on the composition of the feed (f_{AN}) [Table II(c)]. As the product of the reactivity ratio ($r_1 r_2$) is less than 1, the monomer repeat unit in the grafted chains must be arranged in an alternating fashion. In the present case, the reactivity ratio of MMA is more than the reactivity ratio of AN [Fig. 2(b)]; hence, the growing radicals ending with MMA have a greater preference to combine with MMA than with the AN molecules. Due to this reason, the alternating repeat units in the grafted polymers are the chains of the homopolymers with an average number of monomers ($\bar{m}M$) as shown in Table II(c). The average number of the monomers in the repeat unit ($\bar{m}M$) changes on changing the composition of the feed (f_{AN}), which is assumed to be due to the variation in the probability of addition (P_{11}) of the monomer to the radicals ended with its own type of monomer [Table II(c)].

The existence of alternating average sequences of the monomer units in the grafted copolymer is also proved from the observed percent of nitrogen content in the grafted chains. It is interesting to note that the run number (R) increased from 37.45 to 52.63 on increasing the mol fraction of the AN (f_{AN}) in the feed [Table II(c)], but beyond a 0.8 mol fraction of the AN (f_{AN}) in the feed, the value of the run number (R) showed a clear decreasing trend which is due to a more substantial increase in the average sequence length of the AN block ($\bar{m}M_1$) in the grafted chains than in the average sequence length of MMA ($\bar{m}M_2$). On the basis of the experimental data, the possible arrangements of the monomer sequences in the grafted chains are illustrated as given below:

$$—(AN)_{\bar{m}M_1}(MMA)_{\bar{m}M_2}—(AN)_{\bar{m}M_1}—(MMA)_{\bar{m}M_2}—$$
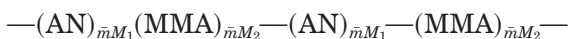
where the values of $\bar{m}M_1$ and $\bar{m}M_2$ vary with the feed composition. Thus, on the basis of the observed dependence of the monomer distribution in the grafted chains, the experimental conditions can be chosen to prepare grafted polymers of desired properties.

Effect of Ceric Ions Concentration

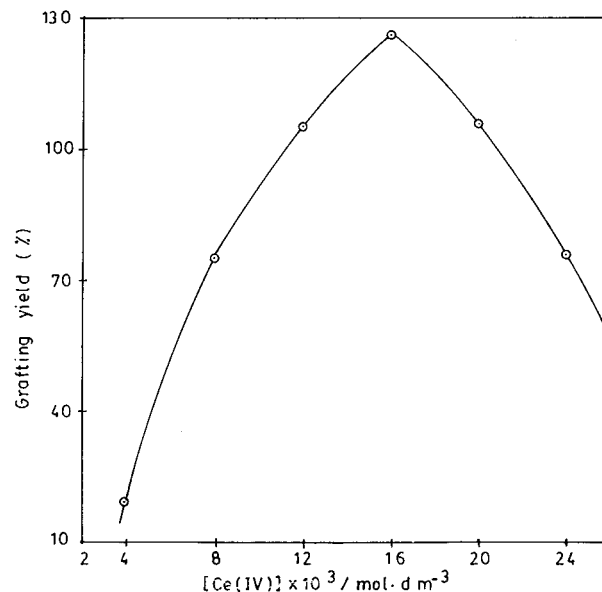The grafting parameters of AN–MMA comonomers on cellulose were determined at a fixed feed

Figure 3   Percent graft yield (% G) as a function of [Ce(IV)]: [AN + MMA] = 1.6 mol dm^{-3}; [HNO$_3$] = 8.0 $\times$ 10^{-2} mol dm^{-3}; f_{AN} = 0.4; [Cell] = 1.0 g; time = 30 min; temperature = 30°C.

(f_{AN} = 0.4) and comonomer concentration (1.6 mol dm^{-3}) in the reaction mixture. The ceric ions concentration was varied from 4.0 to 24.0 $\times$ 10^{-3} mol dm^{-3} and the observed results are given in Figure 3 and Table III. The reported studies on ceric ion-initiated polymerization clearly indicated that ceric ions in the absence of sufficient nitric acid form inactive species with water moleculers[19]; hence, great care was taken to keep sufficient nitric acid (>8.0 $\times$ 10^{-2} mol dm^{-3}) in the reaction mixture to maintain the activity of the ceric ions to create active sites at the backbone of the cellulose. The percent graft yield increased [Fig. 3] on increasing the ceric ions concentration to 16.0 $\times$ 10^{-3} mol dm^{-3}, but showed a decreasing trend on the graft yield on further increasing the ceric ions concentration beyond 16.0 $\times$ 10^{-3} mol dm^{-3} [Table III(a)]. The percent cellulose conversion (% C_c), true grafting (% G_T), and grafting efficiency (% G_E) showed increasing trends to a 16.0 $\times$ 10^{-3} mol dm^{-3} concentration of the ceric ions. These increasing trends of the grafting parameters indicated that ceric ions exclusively participate in the formation of active sites on the cellulose to a 16.0 $\times$ 10^{-3} mol dm^{-3} concentration of the ceric ions, and beyond it, no more active sites are formed on the cellulose. The decreasing trend in the graft yield and other parameters beyond a 16.0 $\times$ 10^{-3} mol dm^{-3} concentration of

Table III Effect of Ceric Ions Concentration on Grafting Parameters at 30°C

(a) Effect of Ceric Ions Concentration on Graphic Parameters at 30°C

$[Ce(IV)] \times 10^3$ (mol dm^{-3})	$\% \ G_T$	$\% \ C_t$	$\% \ C_g$	$\% \ C_{hc}$	$\% \ C_C$	$\% \ G_E$
4.0	376	2.80	1.50	0.90	25.00	54.30
8.0	525	10.46	6.13	2.50	28.00	58.60
12.0	561	13.90	8.58	3.60	31.00	61.70
16.0	565	16.59	10.30	4.60	34.00	62.00
20.0	524	16.10	8.60	5.00	33.00	59.80
24.0	486	14.39	6.21	5.50	30.00	43.28

(b) Effect of Ceric Ions Concentration on Graphic Parameters at 30°C

$[Ce(IV)] \times 10^3$ (mol dm^{-3})	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (G_p)	$\overline{M}_n \times 10^{-3}$ (H_{cp})
4.0	0.49	0.49	2.40	385	50
8.0	2.12	2.38	6.50	315	47
12.0	2.77	3.44	10.70	305	42
16.0	3.30	4.50	15.00	280	38
20.0	3.03	4.00	15.00	280	38
24.0	5.53	3.04	22.40	250	30

[M] = 1.6 mol dm^{-3}; [HNO$_3$] = 8.0 × 10^{-2} mol dm^{-3}; f_{AN} = 0.4; time = 30 min.

ceric ions may be assumed to be due to a decrease in the rate of diffusion of the ceric ions at the surface of the cellulose and due to its participation in the termination reactions with growing homocopolymer and propagating chains[20,21] on the cellulose which has decreased the molecular weights of the polymers formed beyond 16.0 × 10^{-3} mol dm^{-3} of ceric ions [Table III(b)].

This participation of ceric ions in the termination reaction is further clear from the decreasing trend in the percent cellulose conversion (% C_c) [Table III(a)] and the number of grafted moles per chain of the cellulose (G_F) [Table III(b)]. The excess ceric ions may also participate in the oxidative termination of the primary radicals formed on the cellulose surface.[22] On increasing the ceric ion concentration beyond 16.0 × 10^{-3} mol dm^{-3}, the percent homopolymer formation (% C_h) increased, which indicated that unconsumed and excess ceric ions may also cause the formation of the homocopolymers and homopolymers. From these experimental observations, it was concluded that the concentration of the ceric ions during grafting of AN and MMA from their mixture should not be more than 16.0 × 10^{-3} mol dm^{-3}; otherwise, the efficiency of grafting and the number of grafted moles per chain of the cellulose will decrease appreciably.

Effect of Reaction Time

An effort was made to study the effect of the reaction time on the percent grafting of comonomers onto cellulose at a fixed feed composition and molarity of the reaction mixture. The time variation grafting data given in Figure 4 and Table IV clearly indicate that the percent graft yield (% G) increased appreciably up to 6 h, and beyond it, the percent increase in the grafting is insignificant. The percent grafting showed a substantial increase in the initial few hours of the reaction time due to a large number of available reactive sites at the surface of the cellulose, but later on, the rate of grafting increased slowly and steadily. The decreasing trend in the graft yield beyond the initial few hours may be assumed to be due to a decrease in the rate of diffusion of the comonomer molecules from the reaction mixture, where the total number of monomer molecules has become smaller than the number of monomer molecules which were present at the initial stage of the reaction. The composition of the grafted polymers obtained at later stages of reaction times was found to be slightly different from the polymers obtained in the initial period of the reaction. This compositional heterogeneity in the grafted chains and homopolymers was assumed to be due to
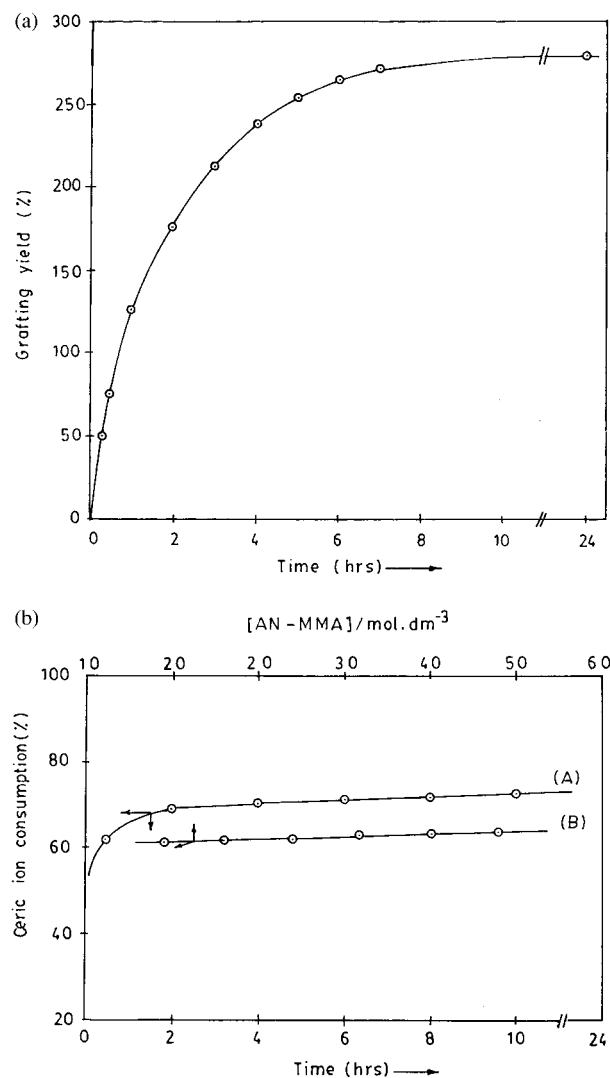
(a)

(b)

Figure 4   (a) Percent graft yield (% G) as a function of reaction time: [AN + MMA] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0 × 10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0 × 10^{-2} mol dm^{-3}; f_{AN} = 0.4; [Cell] = 1.0 g; time = 30 min; temperature = 30°C. (b) Ceric ion consumption as a function of (A) reaction time and (B) comonomer concentration. f_{AN} = 0.4; [HNO$_3$] = 8.0 × 10^{-2} mol dm^{-3}; temperature = 30°C; [AN + MMA] = 1.6 mol dm^{-3}; time = 30 min.

the difference in the reactivity ratios of the employed comonomers and the change in the composition of the reaction mixture as the reaction proceeded. In the present case, the transfer of the mol fraction of MMA (f_{MMA}) from the feed is more than the mol fraction of the AN (f_{AN}); hence, a compositional heterogeneity is generated in the grafted chains obtained at later stages of the reaction. The monomer–monomer interactions in the feed are assumed to be different at different stages of the reaction times due to variations in

the mol fraction of the monomer (f_{AN}) as the reaction proceeded. The mol fraction of the AN (f_{AN}) in the reaction mixture is found to increase as the reaction proceeded, which ultimately promoted the formation of more PAN than of the grafted polymer and the homocopolymer.

The observation of the data shown in Table IV indicated an increasing trend for true grafting (% G_T), grafting efficiency (% G_E), cellulose conversion (% C_c), and total conversion of the monomer to the polymer (% C_t). The number of grafted chains (N_g) and homocopolymer chains (N_{hc}) also showed an increasing trend [Table IV(b)] on increasing the reaction time. The determination of the ceric ion consumption as a function of the reaction time clearly indicated that ceric ions consumption increases appreciably during the initial 2 h of the reaction time [Fig. 4(b)], but beyond 2 h, the percent increase in the ceric ions consumption is low. The high rate of ceric ions consumption in the initial period of grafting is due to the high rate of ceric ions participation in the formation of the reactive sites[23] at the cellulose backbone with the easily abstractable hydrogen ions. Although ceric ions consumption increased beyond 2 h of reaction time, the rate and extent of consumption is very low. The ceric ions after 2 h may be consumed in the formation of the reactive sites at cellulose by oxidizing a difficult portion of the cellulose or in the oxidative termination[22] reaction of the primary and secondary immature growing radicals in the reaction mixture. However, this participation of ceric ions in the termination reaction was assumed to be low because the total number of ceric ions left for termination is very low beyond 2 h of reaction time. Otherwise, the grafting parameters such as molecular weight and grafted moles must have shown a clear decreasing trend beyond 2 h.

The time-variation studies have clearly suggested that the initial 2 h of grafting reactions are very important during which the rate of formation of radicals at the cellulose surface is high; hence, the rate of monomer conversion to the grafted polymer is also high. Thus, on the basis of the experimental data obtained as a function of various reaction parameters, the following reaction steps are proposed for the grafting of comonomers on the cellulose from their binary mixtures:
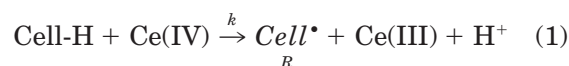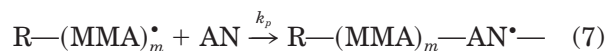
Reaction Scheme

Radical Formation:

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

Table IV   Effect of Reaction Time on Grafting Parameters at 30°C

(a) Effect of Reaction Time on Grafting Parameters at 30°C

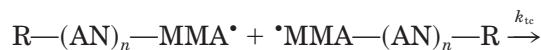| Time (min)	% G_T	% C_t	% C_g	% C_{hc}	% C_c	% G_E
15	468	6.29	3.40	1.60	25.0	54.50
30	525	10.46	6.13	2.50	28.0	58.60
60	650	16.51	10.22	3.60	30.0	61.60
120	733	23.05	14.30	5.30	33.0	62.00
180	775	27.80	17.57	6.20	36.0	63.00
240	818	30.41	19.62	6.30	37.0	64.50
300	834	31.97	20.85	6.50	38.0	65.20
360	848	33.11	21.66	6.60	38.5	65.43
420	853	34.00	22.24	6.95	39.0	65.50
1440	862	34.34	22.89	7.35	40.0	66.60

(b) Effect of Reaction Time on Grafting Parameters at 30°C

Time (min)	G_F	$N_g \times 10^6$	$N_{hc} \times 10^6$	$\overline{M}_n \times 10^{-3}$ (G_p)	$\overline{M}_n \times 10^{-3}$ (H_{cp})
15	1.40	1.40	5.60	300	35
30	2.12	2.38	6.50	315	47
60	3.02	3.62	6.56	345	67
120	3.74	4.92	8.65	355	75
180	4.01	5.77	8.80	372	80
240	4.27	6.31	9.05	380	85
300	4.30	6.53	9.10	390	90
360	4.31	6.62	9.17	400	97
420	4.33	6.71	9.18	405	98
1440	4.34	6.82	9.42	410	105

[M] = 1.6 mol dm^{-3}; [Ce(IV)] = 8.0×10^{-3} mol dm^{-3}; [HNO$_3$] = 8.0×10^{-2} mol dm^{-3}; f_{AN} = 0.4.

Initiation:

$$\text{R}^\bullet + \text{AN} \xrightarrow{K_i} \text{R—AN}^\bullet \quad (2)$$

$$\text{R}^\bullet + \text{MMA} \xrightarrow{K_i} \text{R—MMA}^\bullet \quad (3)$$

Propagation:

$$\text{R—(AN)}^\bullet_{n-1} + \text{AN} \xrightarrow{k_p} \text{R—(AN)}^\bullet_{n} \text{—} \quad (4)$$

$$\text{R—(MMA)}^\bullet_{n-1} \cdot \text{MMA} \xrightarrow{k_p} \text{R—(MMA)}^\bullet_{m} \text{—} \quad (5)$$

$$\text{R—(AN)}^\bullet_{n} + \text{MMA} \xrightarrow{k_p} \text{R—(AN)}_{n} \text{—MMA}^\bullet \text{—} \quad (6)$$

$$\text{R—(MMA)}^\bullet_{m} + \text{AN} \xrightarrow{k_p} \text{R—(MMA)}_{m} \text{—AN}^\bullet \text{—} \quad (7)$$

Termination:

$$\text{R—(AN)}_{n} \text{—MMA}^\bullet + {}^\bullet\text{MMA—(AN)}_{n} \text{—R} \xrightarrow{k_{tc}}$$

$$\text{R—(AN)}_{n} \text{—(MMA)}_{m} \text{—(AN)}_{n} \text{—R} \quad (8)$$

$$\text{R—(MMA)}_{m} \text{—AN}^\bullet + {}^\bullet\text{AN—(MMA)}_{m} \text{—R} \xrightarrow{k_{tc}}$$

$$\text{R—(MMA)}_{m} \text{—(AN)}_{n} \text{—(MMA)}_{m} \text{—R} \quad (9)$$

$$\text{R—(AN)}_{n} \text{—MMA}^\bullet + {}^\bullet\text{AN—(MMA)}_{m} \text{—R} \xrightarrow{k_{tc}}$$

$$\text{R—(AN)}_{n} \text{—MMA—AN—(MMA)}_{m} \text{—R} \quad (10)$$

Oxidative Termination:

$$R^{\bullet} + Ce(IV) \xrightarrow{k_0} \text{oxidation product}$$

$$+ Ce(III) + H^+ \quad (11)$$
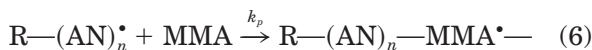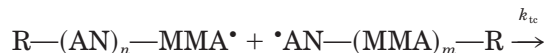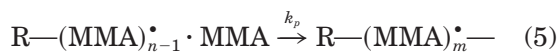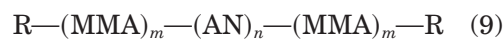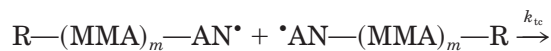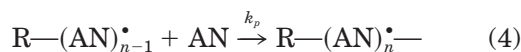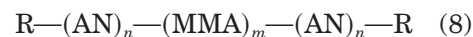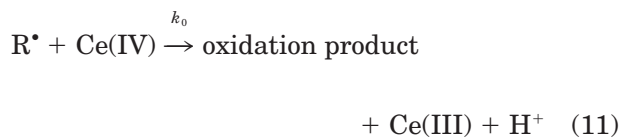
The average sequence lengths of AN units ($\bar{m}M_1$) and MMA units ($\bar{m}M_2$) in the grafted chains were found to be dependent on the feed composition (f_{AN}) and the reaction time. The arrangement of the monomer sequence lengths ($\bar{m}M_1$ and $\bar{m}M_2$) in the grafted chains was assumed to be of an alternate type because the product of the observed reactivity ratios ($r_1 r_2$) is less than unity.

CONCLUSIONS

The grafting of AN and MMA from their binary mixtures was carried out using CAN as an efficient initiator in an acidic medium. The effect of various reaction parameters, such as the feed composition, feed molarity, reaction time, and ceric ions concentration, were carefully studied and interpreted reasonably. The presence of MMA in the feed along with AN facilitates the participation of AN in the grafting through monomer–monomer interactions in the feed. The reactivity ratios and average sequence lengths of the monomers ($\bar{m}M_1$ and $\bar{m}M_2$) in the grafted chains were calculated. The composition of the grafted chains is controlled by the monomer–monomer interactions which ultimately depend upon the mol fractions of the monomers in the feed. Various other grafting parameters as a function of reaction conditions were determined and found useful to optimize the reaction parameters for efficient grafting of the studied monomers onto cellulose from their binary mixtures.

REFERENCES

1. Matveeva, D. N.; Galbraikh, L. S.; Kalmykora, T. K.; Vysatskaya, E. P. Khim Rev D 1983, 747, 1.
2. McCronic, C. L.; Park, L. S. J Appl Polym Sci 1985, 30, 45.
3. Beddows, G. G.; Gil, M. H.; Gutherie J. T. Polym Photochem 1986, 7, 213.
4. Gawish, S. M.; Kantouch, A.; El- Nagar, A. M. A.; Moslech, S. J Appl Polym Sci 1992, 44, 1671.
5. Gawish, S. M.; Kantouch, A.; El-Nagar, A. M. A.; Mosleh, S. J Appl Polym Sci 1995, 57, 45.
6. Dessarki, A. M.; Toher, N. H., El-Arnaouty; M. Polym Int 1998, 45, 67.
7. El-Salmawi, K. M.; El-Nagar, A. M.; Said, H. M.; Zahrani, A. H. Polym Int 1997, 42, 225.
8. Marga, V. Batan 1985, 18, 1.
9. Tahar, N. H.; Dessouki, A. M.; Khalil, F. H. Radiat Phys Chem 1990, 36, 785.
10. Okieman, F. E.; Ogbeifun, D. E. J Appl Polym Sci 1996, 59, 981.
11. El- Salmawi, K.; El-Nagar, A. M.; Altia, S. E. Polym Int 1997, 44, 181.
12. Mansour, O. Y.; Wagaty, A. Prog Polym Sci 1985, 11, 91.
13. Jayams, G.; Lang, F. In Methods in Carbohydrate Chemistry; Whitler, R. L., Ed.; Academic: New York, 1969; Vol. 3, pp 77–80.
14. Nishioka, N.; Matsumoto, Y.; Yumen, K.; Monmal, K.; Kosai, K. Polym J 1988, 18, 323.
15. Mino, G.; Kaizerman, S. J Polym Sci 1958, 31, 54.
16. Fanta, G. F.; Burr, R. C.; Doanne, W. M.; Russel, C. R. J Appl Polym Sci 1979, 23, 229.
17. Brockway, C. E. J Polym Sci 1968, 24, 139.
18. Mayo, F. R.; Lewis, M. J. J Am Chem Soc 1944, 66, 1594.
19. Duke, F. R.; Froist, A. A. J Am Chem Soc 1949, 71, 2790.
20. McDowell, D. J.; Gupta, B. S.; Stannett, V. T. Prog Polym Sci 1984, 10, 1.
21. Arthur, J. C.; Baugh, P. J.; Hinojosa, O. J Appl Polym Sci 1966, 10, 1561.
22. Collison, E.; Daintons, F. S.; McNaughton, G. S. Trans Faraday Soc 1957, 63, 476.
23. Ogiwara, Y.; Kubota, H. J Polym Sci 1968, 6, 1489.