Grafting of Vinyl Acetate–Methyl Acrylate Mixture onto Cellulose. Effect of Ceric Ion and Nitric Acid Concentrations

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Synopsis

The effect of ceric ion and nitric acid concentrations on the graft copolymerization of a mixture of vinyl acetate and methyl acrylate onto cellulose was studied. Two procedures for the reactants addition were employed. Several grafting parameters were determined. Both ceric ion and nitric acid concentrations have a strong effect on the graft copolymerization and they affect similarly some of the polymerization parameters. A variety in the nature of the graft copolymers obtained has been reached. The general behavior of reaction parameters is discussed.

INTRODUCTION

Grafting reactions provide the potential for significantly altering the physical and mechanical properties of a substrate material. The natural abundance and a number of attractive properties of cellulose appear to make it an ideal grafting substrate.

Numerous methods have been developed for the grafting of vinyl monomers to cellulose.[1-4] Among the most promising and practical of these is the ceric ion technique. The influence of initiator concentration on grafting parameters has been examined by a number of authors, and the trends observed were dependent on the substrate, monomer, reaction conditions, and the kind of ceric salt used.[2,4]

On the other hand, the initiation of the graft copolymerization with ceric ion depends very much on the pH of the system.[1-4] The effect is not only dependent on the acid concentration but also on the nature of the acid used.

In the present study, the effect of initiator and nitric acid concentrations on the graft copolymerization of a mixture of vinyl acetate (VAc) and methyl acrylate (MA) onto cellulose by using ceric ammonium nitrate (CAN) in aqueous nitric acid is examined. Some reaction parameters could be obtained for this polymerizing system, particularly those ascertained after extraction of the nongrafted cellulose and cellulose hydrolysis of the graft copolymer.

EXPERIMENTAL

Purification of cellulosic fibers, monomers and the chemicals employed were the same as in a previous report.[5]

Graft Copolymerization

Typical examples for the graft copolymerization are as follows:

Method A. Addition Procedure M–Ce. Cellulose (1 g) ($\bar{M}_w$ = 428,302, $\bar{M}_n$ = 226,136) was immersed in 40 mL of dilute nitric acid (2.5×10^{-3} N) under stirring for 30 min at the reaction temperature (30°C) in a constant-temperature bath. Purified nitrogen was continuously bubbled throughout the system. Then, the required amount of monomers (VAc: 7.92 g; MA: 1.43 g) was added and after 15 min the initiator (CAN: 0.1100 g to generate a 5×10^{-3} N solution) was also added. Stirring was adjusted to 110 rpm. A continuous supply of purified nitrogen was maintained throughout the reaction period. After 6 h the polymerization was stopped by adding hydroquinone and the mixture was filtered on a sintered glass crucible. The solid residue was washed with water and acetone, dried in an oven at 60°C under reduced pressure and then placed in a desiccator containing phosphorous pentoxide until constant weight.

Method B. Addition procedure (Ce–M)$_r$. A cellulose sample (1 g) was immersed in 40 mL dilute nitric acid (2.5×10^{-3} N) under stirring for 30 min at the reaction temperature (30°C). Purified nitrogen was continuously bubbled throughout the system. Then CAN (0.1100 g to generate a 5×10^{-3} N solution) was added and the reaction was allowed to proceed for 15 min at 30°C using the agitation speed of 80 rpm. After that cellulose–ceric ion contact time, the ceric solution was removed. In the following second stage, 35 mL of dilute nitric acid (2.5×10^{-3} N) were added, followed immediately by the monomer mixture (VAc: 7.92 g; MA: 1.43 g). Stirring was adjusted to 110 rpm. At the end of the reaction period (6 h) the polymerization was stopped and the sample was purified following the procedure described in Method A.

Ceric Ion Consumption

The estimation of ceric ion consumption during the grafting and cellulose oxidation reactions was carried out by pipetting out 5–10 mL of the ceric solution, adding an excess of ferrous ammonium sulfate and backtitrating the excess ferrous salt with ceric sulfate using o-phenanthroline as indicator.

Homocopolymer Extraction

The crude graft copolymer samples were extracted with acetone in a Soxhlet apparatus until constant weight (50 h). The acetone was evaporated to recover the homocopolymer.

Ungrafted Cellulose Extraction

A sample of graft copolymer was immersed in a cuoxam solution containing 1.2% NaHSO$_3$ (cellulose : cuoxam ratio 1 : 125). The mixture was stirred with a magnetic stirrer in a nitrogen atmosphere at room temperature for 3 h, and then the fibers were collected and extracted twice in a similar manner until constant weight (2 h each time). The remaining residue was obtained by filtration, washed with distilled water, with dilute acetic acid (10%), again with water, and finally with acetone. The true graft copolymer was dried at 60°C under reduced pressure and then in a desiccator over phosphorous pentoxide.

Hydrolysis of Cellulose from Its Graft Copolymers

The cellulose of the graft copolymers was hydrolyzed leaving free the synthetic polymer, by a modified 72% H_2SO_4 method.[6]

Molecular Weight of Cellulose and Synthetic Polymer

The molecular weight of cellulose was obtained by measuring the intrinsic viscosity in cadoxen in a Cannon-Ubbelohde dilution viscometer.

A solution of cellulose (1.6 g/dL) was prepared by dissolving the required amount of cotton in cadoxen (containing 0.5% Cd and being 0.5 M in NaOH). The solution was diluted with water (solution to water ratio 1 : 1) to reduce the high original viscosity and to prevent cellulose precipitation. The flow time of the solvent, cadoxen : H_2O (1 : 1), was measured as well as that of six cellulosic solutions of different concentrations at 25°C. The reduced viscosity at the six concentrations was determined at 25°C. The intrinsic viscosity $[\eta]$ in deciliters per gram was obtained by extrapolation of a plot of η_{sp}/c versus c to infinite dilution.

The viscosity-average molecular weight $\bar{M}_v$ was calculated using the equation[1]

$$[\eta] = 1.8 \times 10^{-2} \times \bar{X}_v^{0.77}$$

where $\bar{X}_v$ is the viscosity-average degree of polymerization of cellulose

$$\bar{X}_v = \bar{M}_v/162$$

The number-average molecular weight was calculated using the equation[1]

$$\bar{M}_v = \bar{M}_n \times (1.894)$$

The molecular weight distributions of the grafted branches and homocopolymers were obtained by size exclusion chromatography (SEC).

The weight-average and number-average molecular weights $(\bar{M}_w, \bar{M}_n)$ were calculated from the chromatograms by using the universal calibration curve. A column of linear μStyragel was used. Tetrahydrofuran freshly distilled and dried was used as the elution solvent. The temperature was kept at 25°C. The calibration of the column was carried out by using 14 standard samples of polystyrene obtained from Waters Associates. The polystyrene molecular weights were between 1.8×10^3 and 2×10^7. A 0.005% polymer solution (100 μL) was injected and the flow rate was maintained at 1 mL/min. The molecular weight was calculated using the Mark-Houwink equation $[\eta] = K\bar{M}_n^a$, taking the following values for polystyrene and poly(vinyl acetate) in THF at 25°C[7,8]:

	K (cm³/g)	a
Polystyrene	1.6×10^{-4}	0.706
Poly (vinyl acetate)	3.5×10^{-4}	0.630

Synthetic Copolymer Composition

The composition of the true graft copolymers was calculated after extracting the homocopolymer and ungrafted cellulose from the apparent graft copolymer.

The average composition of the copolymer poly(vinyl acetate-co-methyl acrylate) [P(VAc-co-MA)], arising from graft copolymer and homocopolymer, was calculated from the ^{1}H-NMR spectra carried out in chloroform. Signals at $\delta5.08$ ($\begin{smallmatrix} -C-H \\ | \\ OAc \end{smallmatrix}$ of VAc) and $\delta3.88$ ($-O-CH_3$ of MA) were integrated.

Analytical Techniques

The ^{1}H-NMR spectra of the synthetic copolymer P(VAc-co-MA) were run on a Varian EM360-spectrometer of 60 MHz. A Waters ALC/GPC Model 150C instrument equipped with a differential refractometer was used for the size exclusion chromatography.

Grafting Parameters

The following grafting parameters were calculated as described previously[5]:

Apparent grafting yield G is the ratio of grafted polymer to original cellulose.

True grafting yield G_T is the ratio of grafted polymer to true-grafted cellulose.

Grafting efficiency GE is the ratio of grafted polymer to total synthetic polymer.

Total conversion of monomer to polymer C_t is the monomer fraction that polymerizes.

Graft conversion C_g is the monomer fraction that affords grafted polymer.

Homopolymer conversion C_h is the monomer fraction that affords homopolymer.

Cellulose conversion C_c is the cellulose fraction actually grafted.

True grafting frequency GF is the average-number of grafted polymer chains per true-grafted cellulose chain.

Number of grafted chains or branches, N_g, is the number of moles of synthetic polymer chains grafted to cellulose.

Number of homopolymer chains, N_h, is the number of moles of homopolymer.

Synthetic-copolymer composition, $\bar{F}_v$, is the average value of the VAc structural unit in poly(vinyl acetate-co-methyl acrylate).

Ceric ion consumption $(Ce)_c$ is the fraction of ceric ion reduced to cerous ion during the polymerization reaction.

RESULTS

Effect of the Ceric Ion Concentration

Addition Procedure M-Ce. The effect of [Ce(IV)] on the graft copolymerization parameters is shown in Figure 1 and Tables I–IV. Grafting yield reaches a maximum in the 2×10^{-3}–5×10^{-3} N [Ce(IV)] range. Grafting
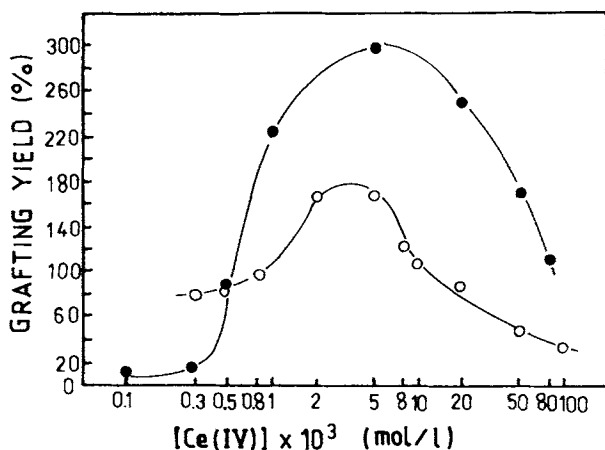
Fig. 1.   Grafting yield as a function of [Ce(IV)]: (○) addition procedure M–Ce; (●) addition procedure (Ce–M), with $(t_c)_r$ = 15 min.

efficiency decreases slightly as [Ce(IV)] increases (Table I). As far as the ceric ion consumption is concerned, the consumption is complete when [Ce(IV)] is between 3×10^{-4} N and 2×10^{-3} N. However, when [Ce(IV)] is in the range of 5×10^{-3}–2×10^{-2} N, the ceric ion consumption is somewhat below complete

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

Expt	$[Ce(IV)] \times 10^3$ (mol/L)	G (%)	G_T (%)	C_t (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)	GF
			Addition procedure M–Ce						
1	0.3	81	231	22	9	13	35	39	1.0
2	0.5	90	225	29	10	19	40	33	—
3	0.8	99	247	32	11	22	40	33	—
4	2	170	548	49	18	31	31	37	2.3
5	5	168	454	57	18	39	37	32	2.5
6	8	122	—	49	13	36	—	27	—
7	10	110	—	42	12	30	—	28	—
8	20	90	—	44	10	34	—	22	—
9	50	49	—	44	5	39	—	12	—
10	100	37	185	38	4	34	20	11	5.8
			Addition procedure (Ce–M)$_r$, contact time 15 min						
1	0.1	5	—	5	1	4	—	12	—
2	0.3	9	—	3	1	2	—	39	—
3	0.5	90	300	28	10	18	30	35	1.0
4	1	225	625	48	24	24	36	50	1.9
5	5	300	833	64	32	32	36	50	2.7
6	20	252	1008	69	27	42	25	39	4.8
7	50	173	910	74	19	55	19	25	5.3
8	80	111	1233	62	12	50	9	19	8.0

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TABLE II

Effect of [Ce(IV)] on Grafting Parameters (Part II)

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Expt	[Ce(IV)] × 10³ (mol/L)	(Ce)ᶜ (%)	(Ce)ᶜ (meq)
	Addition procedure M–Ce		
1	0.3	100	0.01
2	0.5	100	0.02
3	0.8	100	0.03
4	2	100	0.08
5	5	60	0.12
6	8	53	0.17
7	10	36	0.14
8	20	58	0.46
9	50	85	1.70
10	100	94	3.76
	Addition procedure (Ce–M)$_r$, contact time 15 min		
1	0.1	100	0.040
2	0.3	60	0.072
3	0.5	60	0.012
4	1	60	0.024
5	5	25	0.050
6	20	13	0.100
7	50	7	0.140
8	80	≈ 2	—

consumption, but at high [Ce(IV)], 5×10^{-2} and $0.1N$, the ceric ion consumption is almost complete (Table II). If the ceric ion consumption is given in meq, it is observed that the consumption increases with [Ce(IV)].

Cellulose conversion decreases slightly as [Ce(IV)] increases (Table I). Grafting frequency increases with [Ce(IV)] (Table I). The percentage of cellulose in the true graft copolymer attains a minimum at [Ce(IV)] = 2×10^{-3} N (Table III).

The molecular weights of branches and homocopolymer decrease as [Ce(IV)] increases from 5×10^{-3} to $0.1N$, and remain constant in the range of 2×10^{-3}–3×10^{-4} N (Table III).

The compositions $\bar{F}_v$ of the grafted branches and homocopolymers increase as [Ce(IV)] increases from 3×10^{-4} to 5×10^{-4} N and they decrease with a further increase in the initiator concentration (Table IV). The number of branches and homocopolymer chains decreases with [Ce(IV)] (Table IV).

Addition Procedure (Ce–M)$_r$. In Figures 1 and 2 and Tables I–V are shown the results obtained by varying [Ce(IV)]. The addition procedure (Ce–M)$_r$ was employed for several contact times $(t_c)_r$ between cellulose and ceric ion before removing the ceric ion solution and adding monomer. Contact times of 5, 15, and 30 min were tested.

Grafting yield follows the same general behavior for the three contact times used (Fig. 2 and Tables I and V). Grafting yield increases with [Ce(IV)] to reach a maximum value and then decreases with larger initiator concentrations.

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

Expt	$[Ce(IV)] \times 10^3$ (mol/L)	Composition of true graft copolymer		Branches			Homopolymer		
		Cell. (%)	Branches (%)	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D
Addition procedure M–Ce									
1	0.3	38	62	520	2430	4.7	410	1730	4.2
2	0.5	35	65	—	—	—	140	500	3.6
3	0.8	29	71	—	—	—	130	530	4.1
4	2	15	85	550	2540	4.6	80	450	5.6
5	5	18	82	420	2270	5.4	50	230	4.6
7	10	—	—	—	—	—	35	170	4.9
9	50	—	—	—	—	—	11	80	7.3
10	100	35	65	70	370	5.3	6	90	15.0
Addition procedure (Ce–M), contact time 15 min									
1	0.1	—	—	—	—	—	480	2240	4.7
2	0.3	—	—	—	—	—	—	—	—
3	0.5	25	75	700	4690	6.7	260	740	2.8
4	1	20	80	750	4520	6.0	180	1285	7.1
5	5	11	89	700	3850	5.5	110	620	5.6
6	20	9	91	490	2440	5.0	100	350	3.5
7	50	10	90	380	1640	4.3	30	150	5.0
8	80	7	93	370	1780	4.8	25	120	4.8

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

Expt	$[Ce(IV)] \times 10^3$ (mol/L)	$N_g \times 10^6$	$N_h \times 10^5$	$\bar{F}_v$ (%)	
				Branches	Homocopolymer
Addition procedure M–Ce					
1	0.3	1.6	0.3	43	41
2	0.5	—	1.3	—	51
3	0.8	—	1.6	—	59
4	2	3.1	3.6	70	68
5	5	4.0	7.3	74	72
7	10	—	8.1	—	70
9	50	—	32.8	—	66
10	100	5.3	52.7	60	64
Addition procedure $(Ce–M)_r$, contact time 15 min					
1	0.1	—	0.1	—	28
2	0.3	—	—	—	33
3	0.5	1.3	0.6	45	54
4	1	3.0	1.2	64	77
5	5	4.3	2.5	80	83
6	20	5.1	3.9	76	79
7	50	4.6	17.2	72	79
8	80	3.0	18.8	81	751

The maximum G value is attained at lower $[Ce(IV)]$ in case $(t_c)_r = 15$ min. The highest G value is attained with a contact time of 5 min.

Grafting efficiency follows the same behavior for the three contact times employed (Tables I and V). $[Ce(IV)]$ at which the maximum value is reached
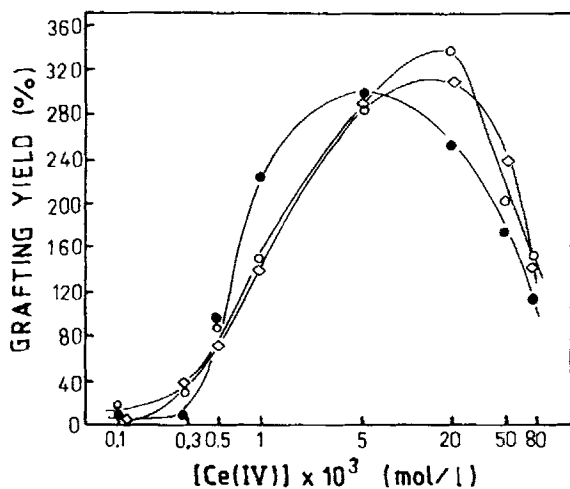

Fig. 2.   Grafting yield as a function of $[Ce(IV)]$ using the addition procedure $(Ce–M)_r$: (○) $(t_c)_r = 5$ min; (●) $(t_c)_r = 15$ min; (◇) $(t_c)_r = 30$ min.

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

Expt	[Ce(IV)] $\times 10^3$ (mol/L)	G (%)	C_t (%)	C_g (%)	C_h (%)	GE (%)	$(Ce)_c$ (%)	$(Ce)_c$ [$\times 10^3$ (meq)]
			Contact time = 5 min					
1	0.1	12	8	1	7	16	100	4
2	0.3	29	14	3	11	22	44	5
3	0.5	90	25	10	15	39	55	11
4	1	149	40	16	24	40	52	21
5	5	287	58	31	27	53	15	30
6	20	336	77	36	41	47	5	40
7	50	202	70	22	48	31	1	20
8	80	148	66	16	50	24	1	32
			Contact time = 30 min					
1	0.1	0	1	0	1	0	100	4
2	0.3	29	14	3	11	22	67	8
3	0.5	65	17	7	10	40	100	20
4	1	143	31	15	16	48	72	29
5	5	280	58	30	28	51	28	56
6	20	308	68	33	35	49	13	100
7	50	238	80	25	55	32	6	120
8	80	147	66	16	50	24	6	200

[a] Contact times of cellulose–ceric ion 5 and 30 min, using the addition procedure (Ce–M)$_r$.

depends on the contact time employed. More extensive work has been developed in case of $(t_c)_r$ = 15 min. Cellulose conversion increases very slightly as [Ce(IV)] increases till 2×10^{-4} N, reaches a maximum value, and decreases with higher [Ce(IV)] (Table I).
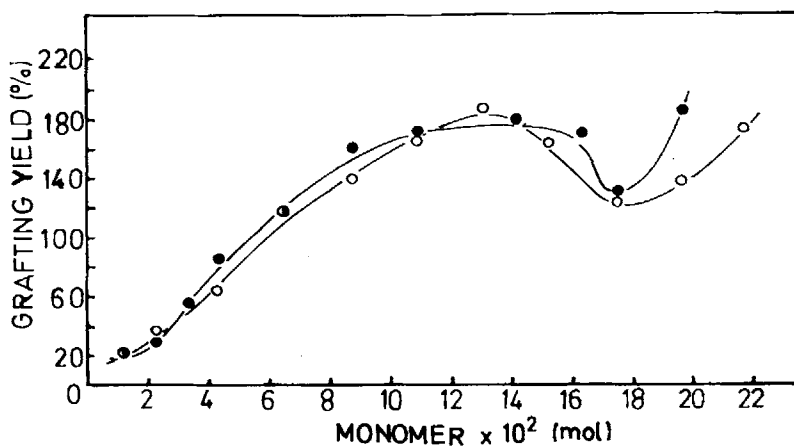

Fig. 3. Grafting yield as a function of [M] using the addition procedure M–Ce: (○) [Ce(IV)] = 5 × 10^{-3} N; (●) [Ce(IV)] = 2 × 10^{-3} N.

Grafting frequency increases gradually as the initiator concentration increases and increases abruptly at the highest concentration used (Table I). Percentage of cellulose in the true graft copolymer increases as [Ce(IV)] increases up to 5×10^{-3} N and then remains almost constant (Table III). The molecular weight of branches remains constant when [Ce(IV)] is in the 5×10^{-4}–5×10^{-3} N range and decreases with higher concentrations (Table III). However, the molecular weight of the homocopolymer decreases with increasing [Ce(IV)] in the whole range tested. The composition $\bar{F}_v$ of branches and homocopolymer increases as [Ce(IV)] increases from 5×10^{-4} to 5×10^{-3} N, remaining almost constant at higher concentrations (Table IV).

The number of grafted branches increases as [Ce(IV)] increases up to 2×10^{-2} N and then decreases with higher concentrations (Table IV). However, the number of homocopolymer chains increases with increasing [Ce(IV)] concentration. The ceric ion consumption, during the stage previous to the addition of monomer, increases as [Ce(IV)] increases, as shown in Table II.

Effect of [Ce(IV)] on the Grafting Parameters When [M] Is Varied

Addition Procedure M–Ce. In Figure 3 and Tables VI–VIII are shown the results obtained varying [M] at two different ceric ion concentrations.

TABLE VI
The Effect of [Ce(IV)] on Grafting Parameters When [M] Is Varied,
Using the Addition Procedure M–Ce (Part I)

Expt	M (mol)	G (%)	G_T (%)	C_t (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)	$(Ce)_c$ (%)
				$[Ce(IV)] = 5 \times 10^{-3}$ N					
1	0.011	21	70	37	22	15	30	60	62
2	0.022	34	—	43	18	25	—	41	62
3	0.043	65	176	61	17	44	37	28	62
4	0.065	116	—	67	21	46	—	31	62
5	0.087	140	—	64	19	45	—	29	62
6	0.109	168	454	57	18	39	37	32	61
7	0.130	186	465	63	17	46	40	26	62
8	0.152	165	—	49	13	36	—	26	62
9	0.174	124	282	39	8	31	44	21	63
10	0.196	138	—	35	8	27	—	23	62
11	0.217	175	583	35	9	26	30	27	62
				$[Ce(IV)] = 2 \times 10^{-3}$ N					
1	0.011	20	55	34	21	13	36	63	95
2	0.022	28	—	33	15	18	—	45	100
3	0.033	54	—	50	19	31	—	39	100
4	0.043	84	—	56	22	34	—	40	100
5	0.065	115	—	53	21	32	—	39	100
6	0.087	160	—	52	21	31	—	41	96
7	0.109	170	548	49	18	31	31	37	100
8	0.141	180	643	44	15	29	28	34	94
9	0.163	170	—	38	12	26	—	32	94
10	0.174	130	520	35	9	26	25	25	95
11	0.196	186	620	39	11	28	30	29	95

TABLE VII

The Effect of [Ce(IV)] on Grafting Parameters When [M] is Varied,
Using the Addition Procedure M–Ce (Part II)

Expt	M (mol)	GF	$N_g \times 10^6$	$N_h \times 10^5$
		$[Ce(IV)] = 5 \times 10^{-3} N$		
1	0.011	—	—	1.0
2	0.022	—	—	1.2
3	0.043	—	—	4.1
4	0.065	2.6	4.3	7.0
5	0.087	—	—	9.7
6	0.109	2.5	4.0	6.9
7	0.130	2.4	4.2	7.4
9	0.174	2.7	5.2	10.5
10	0.196	—	—	—
11	0.217	2.7	3.6	6.9
		$[Ce(IV)] = 2 \times 10^{-3} N$		
1	0.011	—	—	0.5
2	0.022	—	—	1.1
4	0.043	—	—	2.0
5	0.065	—	—	2.9
6	0.087	—	—	2.8
7	0.109	2.3	3.1	3.8
8	0.141	2.5	3.0	3.1
10	0.174	3.5	3.9	3.3
11	0.196	2.0	2.6	5.1

As can be observed from Figure 3 and Table VI, the same general behavior is observed in the grafting yield by changing [M] for both [Ce(IV)]. The amount of monomer for which the maximum value of G is attained depends on [Ce(IV)], while the value in the minimum is reached with the same amount of monomer in both cases.

Grafting efficiency is higher with the lowest [Ce(IV)] used and the same general behavior is observed in both cases (Table VI). The ceric ion consumption is independent of the amount of monomer employed. Ceric ion is depleted when the lowest [Ce(IV)] was tested (Table VI). Cellulose conversion is higher with the highest [Ce(IV)] (Table VI). Grafting frequency is quite similar in both cases (Table VII).

Percentage of cellulose in the true graft copolymer is higher with the highest [Ce(IV)] (Table VIII). Molecular weight of branches is slightly higher with the lowest [Ce(IV)] used (Table VIII). The composition $\bar{F}_v$ of branches and homocopolymer is quite similar with both [Ce(IV)] (Table VII). The number of grafted branches and homocopolymer chains is higher with the highest [Ce(IV)] (Table VII).

Effect of the Nitric Acid Concentration

Addition Procedure M–Ce. Grafting yield remains almost constant when the reaction was carried out either in the absence of nitric acid or in the presence

TABLE VIII

The Effect of [Ce(IV)] on Grafting Parameters When [M] Is Varied,
Using the Addition Procedure M–Ce (Part III)

Expt	M (mol)	Composition of true graft copolymer		Branches			Homopolymer		
		Cell. (%)	Branches (%)	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D
				$[Ce(IV)] = 5 \times 10^{-3} N$					
1	0.011	59	41	—	—	—	14	45	3.2
2	0.022	—	—	—	—	—	40	140	3.5
3	0.043	36	64	—	—	—	40	180	4.5
4	0.065	—	—	270	920	3.4	37	200	5.4
5	0.087	—	—	—	—	—	35	190	5.4
6	0.109	18	82	420	2270	5.4	53	230	4.3
7	0.130	18	82	440	3500	8.0	70	300	4.3
9	0.174	26	74	240	840	3.5	44	240	5.4
10	0.196	—	—	—	—	—	—	—	—
11	0.217	15	85	480	2490	5.2	70	390	5.6
				$[Ce(IV)] = 2 \times 10^{-3} N$					
1	0.011	36	64	—	—	—	22	90	4.1
2	0.022	—	—	—	—	—	32	140	4.4
4	0.043	—	—	—	—	—	63	220	3.5
5	0.065	—	—	—	—	—	62	230	3.7
6	0.087	—	—	—	—	—	84	600	7.1
7	0.109	15	85	550	2540	4.6	77	450	5.8
8	0.141	13	87	590	3140	5.3	115	630	5.5
10	0.174	16	84	330	1580	4.8	120	700	5.8
11	0.196	14	86	710	3980	5.6	90	530	5.9

of it at a low concentration ($0.7 \times 10^{-3} N$), as can be seen from Figure 4 and Table IX. Later on, G attains a maximum at [HNO$_3$] ca. $3 \times 10^{-3} N$ and successively it reaches values near zero.

Grafting efficiency behaves similarly showing a maximum at [HNO$_3$] ca. $3 \times 10^{-3} N$ (Table IX). Complete consumption of ceric ion is observed at the highest [HNO$_3$] used, but lower consumption was found at lower concentrations (Table IX). Cellulose conversion decreases with increasing [HNO$_3$] (Table IX).

Grafting frequency remains almost constant when varying [HNO$_3$] (Table X). Molecular weight of branches shows a maximum at [HNO$_3$] near $10^{-2} N$ (Table XI). The same behavior is observed for the homocopolymer. Composition $\bar{F}_v$ of grafted branches and homopolymer increases as [HNO$_3$] increases, reaching a maximum value at [HNO$_3$] ca. $3 \times 10^{-3} N$ and decreasing at higher concentrations (Table X). The number of branches increases by increasing [HNO$_3$] (Table X).

Addition Procedure (Ce–M)$_r$. Effect of [HNO$_3$] at the Stage Previous to the Polymerization. In Figure 4 and Tables IX–XI are shown the results
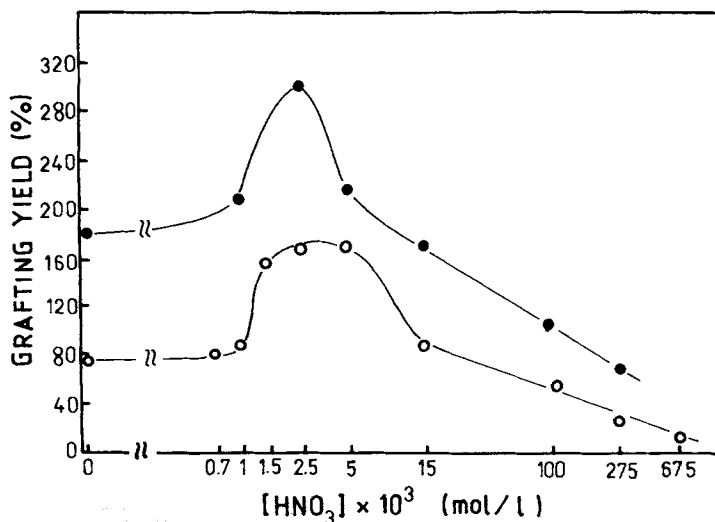
Fig. 4. Grafting yield as a function of [HNO_3]: ($\bigcirc$) addition procedure M-Ce; ($\bullet$) addition procedure (Ce-M)$_r$, varying [HNO_3] at the stage previous to polymerization.

obtained when [HNO_3] was changed while a cellulose-ceric ion contact during 15 min, previous to the addition of monomer, was allowed. The grafting yield reaches a maximum where [HNO_3] takes a value of ca. 2.5×10^{-5} N (Fig. 4). Grafting efficiency also shows a maximum in the same position as G (Table IX). The ceric ion consumption prior to the monomer addition increases with [HNO_3] (Table IX). Cellulose conversion decreases as [HNO_3] increases. The highest cellulose conversion is attained in the absence of acid (Table IX).

Grafting frequency reaches a maximum where [HNO_3] takes a value of ca. 3×10^{-3} N (Table X). Molecular weights of branches and homocopolymer are independent of [HNO_3] (Table XI). The compositions $\bar{F}_v$ of grafted branches and homocopolymer are practically equal and decrease as [HNO_3] increases (Table X). The number of grafted branches decreases as [HNO_3] increases (Table X). On the other hand, the number of homocopolymer chains is almost constant (Table X).

Addition Procedure (Ce–M)$_r$. Effect of [HNO_3] at the Stage of Polymerization. In Figure 5 and Tables XII–XIV are shown the results obtained varying [HNO_3] at the stage of the polymerization reaction. Grafting yield increases rapidly with acid concentration, reaching the maximum value at pH 2 (Fig. 5 and Table XII). pH 4.75 was attained by addition of sodium hydroxide in the stage of polymerization, which inhibits polymerization, probably by inducing precipitation of ceric ion. Grafting efficiency and cellulose conversion are constant at low acid concentration and decrease at higher concentrations (Table XII). Grafting frequency increases notably as the acid concentration increases (Table XII).

Percentage of cellulose in the true graft copolymer decreases with increasing acid concentration (Table XIII). The molecular weights of branches and homocopolymer decrease in the same way (Table XIII). The composition $\bar{F}_v$ of branches shows slightly higher values than that of homocopolymer and also two respective maxima near pH 2 are shown (Table XIV). The number of

TABLE IX
Effect of [HNO$_3$] on Grafting Parameters (Part I)

Expt	[HNO$_3$] × 10^3 (mol/L)	pH	G (%)	G_T (%)	C_t (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)	(Ce)$_c$ (%)
				Addition procedure M–Ce						
1	0	2.15	75	156	33	8	25	48	24	69
2	0.7	2.1	81	—	35	9	26	—	25	60
3	1	2.1	86	—	38	9	29	—	24	66
4	1.5	2.05	156	—	53	17	36	—	32	60
5	2.5	2	168	454	57	18	39	37	32	61
6	5	1.9	170	—	54	18	36	—	34	72
7	15	1.7	87	—	39	9	30	—	24	70
8	110	1.15	55	275	29	6	23	20	21	99
9	275	0.7	25	208	11	3	9	12	23	100
10	675	0.35	10	—	5	1	4	—	21	100
				Addition procedure (Ce–M)$_r$, stage previous to polymerization						
1	0	2.15	186	423	49	20	29	44	41	25
2	1	2.1	208	—	52	22	30	—	43	25
3	2.5	2	300	833	64	32	32	36	50	25
4	5	1.8	219	730	53	23	30	30	44	37
5	15	1.7	173	—	42	19	23	—	44	44
6	100	1.15	107	—	37	11	26	—	31	46
7	275	0.7	70	350	28	8	20	20	27	53

branches shows a maximum, while the number of homocopolymer chains increases with increasing acid concentration (Table XIV).

DISCUSSION

Effect of the Ceric Ion Concentration

The results obtained varying [Ce(IV)] (Figs. 1 and 2 and Tables I–V) follow the general behavior reported in the literature.[2] When [Ce(IV)] increases, it affects the rates of the reactions in which this ion is involved, such as generation of cellulosic radicals, oxidation of cellulosic radicals, termination of growing polymer chains, and initiation of homocopolymerization. Cellulose conversion decreases at high [Ce(IV)] since the cellulosic radicals already generated are rapidly oxidized by ceric ion.

The grafting frequency increases with [Ce(IV)] because the formation of cellulosic radicals increases. On the other hand, since at high [Ce(IV)] the oxidation of cellulosic radicals can be important, there must exist a competition between ceric ion and monomer for the cellulosic radicals, so that the monomer reacts with the most accessible cellulosic radicals and the ceric ion oxidizes the most internal ones.

Molecular weight decreases because termination of the growing polymer chains by the ceric ions becomes important at high [Ce(IV)]. At low [Ce(IV)], grafting yield increases since the number of branches increases and molecular

TABLE X
Effect of [HNO₃] on Grafting Parameters (Part II)

Expt	[HNO₃] × 10³ (mol/L)	GF	$N_g \times 10^6$	$N_h \times 10^5$	$\bar{F}_v$ (%) Branches	Homocopolymer
			Addition procedure M–Ce			
1	0	1.4	3.0	5.9	46	61
3	1	—	—	7.7	—	60
5	2.5	2.5	4.0	6.6	74	72
6	5	—	—	5.6	—	71
7	15	—	—	6.9	—	62
8	110	2	1.7	10.7	40	48
9	275	2.2	1.2	5.5	20	30
10	675	—	—	6.2	—	31
			Addition procedure (Ce–M)$_r$, stage previous to polymerization			
1	0	1.4	2.7	2.4	74	73
2	1	—	—	2.4	—	—
3	2.5	2.7	4.3	2.7	80	83
4	5	2.2	3.0	2.2	67	76
5	15	—	—	2.2	—	70
6	100	—	—	2.9	—	67
7	275	1	0.9	1.3	43	44

weight keeps constant, and it decreases beyond a certain [Ce(IV)] since the molecular weight of the grafted branches decreases.

The decrease observed in grafting efficiency at high [Ce(IV)] indicates that homocopolymerization is favored over grafting. Increasing [Ce(IV)], the initiation of homocopolymerization is increased more than that of grafting, as can be realized by comparing values of the number of branches and homocopolymer chains. This effect on the initiation rates is indicated in the literature.[2,9]

The ceric ion consumption is higher at high [Ce(IV)] since this ion is involved in termination of the growing polymer chains, initiation of homocopolymerization and in oxidation of cellulose.

When the results obtained varying [Ce(IV)], using both addition procedures M–Ce and (Ce–M)$_r$, are compared, the same general behavior is observed. However, the grafting yield values obtained with the addition procedure (Ce–M)$_r$ are remarkably higher than those obtained with the addition procedure M–Ce. This results from the larger molecular weight obtained with procedure (Ce–M)$_r$, as the number of branches in both procedures is similar. This can be due to the higher amount of monomer available for grafting since a lower number of growing homocopolymer chains is initiated with the procedure (Ce–M)$_r$ because of the lower [Ce(IV)] present.

The higher values of grafting efficiency obtained with the addition procedure (Ce–M)$_r$ are due to a lowered formation of homocopolymer as discussed above. Cellulose conversion and grafting frequency are very similar with both addition procedures. Molecular weight follows the same behavior with both addition procedures, higher values being obtained with the addition procedure (Ce–M)$_r$.

TABLE XI
Effect of [HNO₃] on Grafting Parameters (Part III)

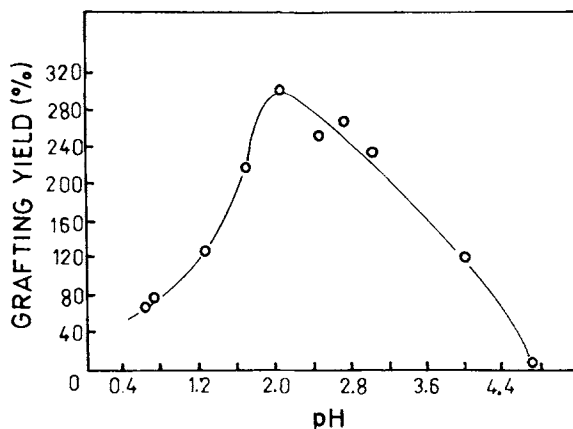| Expt	$[HNO_3] \times 10^3$ (mol/L)	Composition of true graft copolymer		Branches			Homocopolymer		
		Cell. (%)	Branches (%)	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D
Addition procedure M–Ce									
1	0	39	61	250	1060	4.2	40	230	5.8
3	1	—	—	—	—	—	35	240	6.9
5	2.5	18	82	420	2270	5.4	55	230	4.2
6	5	—	—	—	—	—	60	300	5.0
7	15	—	—	—	—	—	40	210	5.3
8	110	27	73	320	1500	4.7	20	220	11
9	275	32	68	210	700	3.3	15	130	8.7
10	675	—	—	—	—	—	6	60	10
Addition procedure $(Ce-M)_I$, stage previous to polymerization									
1	0	22	78	700	2810	4.0	115	490	4.3
2	1	—	—	—	—	—	115	480	4.2
3	2.5	11	89	700	3850	5.5	110	630	5.7
4	5	12	88	740	4420	6.0	125	670	5.4
5	15	—	—	—	—	—	100	390	3.9
6	100	—	—	—	—	—	85	400	4.7
7	275	35	65	800	3880	4.9	145	890	6.1

Fig. 5. Grafting yield vs. pH in the polymerization stage, using the addition procedure (Ce–M)$_r$.

This fact seems to be the result of a faster termination of the growing polymer chains by ceric ion when the addition procedure M–Ce is employed, since the [Ce(IV)] in the reaction medium is higher during polymerization.

The ceric ion concentration affects the grafting parameters when [M] is varied (Fig. 3 and Tables VI–VIII). Grafting efficiency is higher with the lowest [Ce(IV)] used since the initiation of homopolymerization, indicated by N_h, is less important with that initiator concentration. Cellulose conversion is slightly higher with the highest [Ce(IV)] since the amount of ceric ion that is present in the reaction medium is higher and a higher amount of cellulose can be oxidized. The molecular weights of branches and homocopolymer are lower with the highest [Ce(IV)] as a result of a higher termination rate of the growing polymer chains either by mutual or linear termination. The grafting yield is

TABLE XII
Effect of Changing pH in the Graft Copolymerization Stage,
Using the Addition Procedure (Ce–M)$_r$ (Part I)

Expt	pH	G (%)	G_T (%)	C_t (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)	GF
1	0.65	67	2233	34	7	27	3	21	12.6
2	0.75	77	—	34	8	26	—	24	—
3	1.25	125	781	43	13	30	16	31	3.4
4	1.65	217	—	58	23	35	—	40	—
5	2	300	833	64	32	32	36	50	2.7
6	2.35	242	—	52	26	26	—	50	—
7	2.45	242	—	48	26	22	—	54	—
8	2.55	245	—	50	26	24	—	52	—
9	2.7	260	—	51	28	23	—	55	—
10	2.75	250	—	45	27	18	—	60	—
11	3	231	679	46	25	21	34	54	1.9
12	4	123	439	29	13	16	28	45	1.0
13	4.75	0	—	1	0	1	—	0	—

TABLE XIII
Effect of Changing pH in the Graft Copolymerization Stage,
Using the Addition Procedure (Ce–M)$_r$ (Part II)

		Composition of true graft copolymer		Branches			Homopolymer		
Expt	pH	Cell. (%)	Branches (%)	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	D
1	0.65	4	96	400	1600	4	45	160	3.6
3	1.25	11	89	520	2350	4.5	65	300	4.6
4	1.65	—	—	—	—	—	85	320	3.8
5	2	11	89	700	3850	5.5	110	630	5.7
9	2.7	—	—	—	—	—	140	570	4.1
10	2.75	—	—	—	—	—	125	510	4.1
11	3	13	87	810	4480	6.0	195	870	4.5
12	4	27	73	1000	8420	8.4	580	1820	3.1

slightly higher with the lowest initiator concentration, since the molecular weight, being higher in this case, surpasses the effect of the lower number of branches.

Effect of the Nitric Acid Concentration

The behavior found when [HNO$_3$] is varied is similar (Fig. 4 and Tables IX–XI) to the general dependence reported by other authors.[2-4] It has been observed that changes in the [HNO$_3$] affect the rates of oxidation by ceric ion and polymerization.[2,10-12] The changes observed in these rates have been attributed to the formation of different complexes between ceric ion and nitrate ions, hydroxyl ions, and water molecules.[2]

An increase in [HNO$_3$] makes the rates of initiation and termination by ceric ion increase.[2,3] The increase in grafting yield with [HNO$_3$] up to a certain value can be a result of the higher increase in the rate of initiation than in the

TABLE XIV
Effect of Changing pH in the Graft Copolymerization Stage,
Using the Addition Procedure (Ce–M)$_r$ (Part III)

				$\bar{F}_v$ (%)	
Expt	pH	$N_g \times 10^6$	$N_h \times 10^6$	Branches	Homocopolymer
1	0.65	1.7	5.6	50	65
3	1.25	2.4	4.3	54	75
4	1.65	—	3.8	—	83
5	2	4.3	2.7	80	83
9	2.7	—	1.5	—	77
10	2.75	—	1.3	—	73
11	3	2.8	1.0	59	76
12	4	1.2	0.3	48	50

rate of termination. On the other hand, the decrease in grafting yield with increasing [HNO_3] beyond a certain value can be explained if the rates of termination of growing polymer chains and of cellulose radicals are predominant over the rate of initiation.

The increase in the ceric ion consumption seems to be due to the greater involvement of ceric ions in the initiation and termination reactions as a consequence of the higher oxidation capacity of the initiator at low pH.

The decrease in cellulose conversion with increasing [HNO_3] may be due to the enhancement of the oxidation capacity of ceric ion, so that this ion can oxidize the cellulose radicals already generated before being trapped by monomer. On the other hand, at high [HNO_3] a partial hydrolysis of cellulose[5] takes place and as a result some grafted polymer is extracted as homocopolymer. Reverse addition of the reactants [i.e., (Ce–M)$_r$] affects some of the grafting parameters differently (Fig. 4 and Tables IX–XI). The increase in the ceric ion consumption seems to be due to the enhancement of the oxidation capacity of ceric ion with [HNO_3].[2,3]

The grafting yield increases at low [HNO_3], because the rate of generation of cellulosic radicals increases. The further decrease of G, at high [HNO_3], is the result of a decrease in the number of cellulosic radicals which add monomer, because of their increased oxidation by Ce(IV). Both statements are supported by the behavior of the number of branches.

The cellulose conversion decreases, since not only the rate of formation of cellulosic radicals increases but also the rate of termination of those radicals by ceric ions, while the ability of the monomer to add to cellulose radicals does not increase. The same reason can explain the decrease observed in the grafting frequency. The molecular weight of branches is not affected by changing [HNO_3] prior to the monomer addition since the graft copolymerization is carried out in a second stage at the same pH.

The higher grafting yield values obtained by the procedure (Ce–M)$_r$, when compared with the procedure M–Ce, are due to the higher molecular weight reached, because the number of branches is nearly the same. High values of the rates of homocopolymerization initiation, cellulose radicals formation, cellulose radicals oxidation, and radical chain termination by ceric ion are probably the explanation of the low molecular weight, low grafting yield, low number of branches, and high number of homocopolymer chains obtained when high acid concentrations are used (Fig. 5 and Tables XII–XIV).

CONCLUSIONS

Both ceric ion and nitric acid concentrations have a strong effect on the graft copolymerization and they affect similarly some of the reaction parameters.

Some reaction parameters could be obtained for this polymerizing system, particularly those ascertained after extraction of the nongrafted cellulose and cellulose hydrolysis of the graft copolymer.

Two ways of addition of the reactants, M–Ce and (Ce–M)$_r$, have been used in this work, which affect differently the reaction parameters.

Reaction conditions have been found leading to "high" values of G, C_c, GE, GF, $\bar{M}_n$, N_g, and $\bar{F}_v$, 300, 48, 63, 12.6, 10^6, 5.3×10^{-6}, and 81, respectively; and

"low" values of them 5, 9, 0, 1, 7×10^4, 0.9×10^{-6}, and 20, respectively. Generally, a low number of grafted chains with high molecular weight is obtained.

References

1. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, New York, 1981.

2. D. J. McDowall, B. S. Gupta, and V. T. Stannett, *Prog. Polym. Sci.*, **10**, 1 (1984).

3. S. N. Battacharyya and D. Maldas, *Prog. Polym. Sci.*, **10**, 171 (1984).

4. O. Y. Mansour and A. Nagaty, *Prog. Polym. Sci.*, **11**, 91 (1985).

5. M. J. Fernández, I. Casinos, and G. M. Guzmán, *J. Polym. Sci. Polym. Chem. Ed.*, to appear.

6. M. J. Fernández, I. Casinos, and G. M. Guzmán, *Makromol. Chem. Macromol. Symp.*, **20/21**, 11 (1988).

7. W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size Exclusion Liquid Chromatography*, Wiley, New York, 1979.

8. D. Goedhart and A. Opschoor, *J. Polym. Sci.*, **8**, 1277 (1970).

9. A. Y. Kulkarni and P. C. Mehta, *J. Appl. Polym. Sci.*, **12**, 1321 (1968).

10. F. R. Duke and A. A. Forist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).

11. M. Ardon, *J. Chem. Soc.*, 1811 (1957).

12. F. R. Duke and R. F. Bremen, *J. Am. Chem. Soc.*, **73**, 5179 (1951).