Grafting of Vinyl Acetate–Methyl Acrylate Mixture onto Cellulose. Effect of Inorganic Salts

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SYNOPSIS

The effect of the addition of $NaNO_3$ and NaCl on the graft copolymerization of a mixture of vinyl acetate–methyl acrylate onto cellulose, using ceric ion as initiator, is examined. Several grafting parameters were measured. Presence of $NaNO_3$ affects the graft copolymerization by enhancing the cellulose oxidation, but it leaves almost unaffected the homopolymerization reaction. NaCl works similarly to $NaNO_3$. As a consequence of salt presence, ligand changes in the ceric ion complexes, as well increase in the ionic strength of the medium, are expected.

INTRODUCTION

Cotton cellulose is a natural polymer with many good textile properties; however, it lacks some of the desirable properties of synthetic polymers. Within recent years there has been considerable interest in altering the properties of natural polymers, such as cotton, by graft polymerization with vinyl monomers. The copolymers produced could possess new and interesting properties representing a combination of the properties of the two polymers used. Numerous reports are now in the literature[1-4] on the many vinyl monomers which can be graft-polymerized onto cellulose by using several types of initiators. The use of tetravalent cerium as an initiator of the graft polymerization of vinyl monomers on cellulosics has gained considerable importance on account of its high grafting efficiency.[5,6] Even though the conditions of the grafting reactions have been rather extensively studied, the role of inorganic salts in the grafting of monomers to cellulose have not been so thoroughly investigated.

In the present work, the effect of addition of inorganic salts, such as sodium nitrate and sodium chloride, on the graft copolymerization of a binary mixture of vinyl acetate (VAc) and methyl acrylate (MA) onto cellulose by using ceric ammonium nitrate (CAN) as initiator has been studied.

EXPERIMENTAL

Purification of cellulosic fibers, monomers, and the chemicals employed were the same as in a previous report.[7]

Graft Copolymerization

Method A. Addition Procedure M–Ce

Cellulose (1 g) ($\bar{M}_w = 428,000$; $\bar{M}_n = 226,000$) 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. Then the chosen amount of $NaNO_3$ was added. 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 $\times 10^{-3}$ 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),

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 being 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. Suitable amounts of $NaNO_3$ are added at the beginning of either the first stage or the second stage.

Homocopolymerization

Nitric acid (2.5×10^{-3} N, 40 mL) and the chosen amount of $NaNO_3$ were poured into a flask and, then, the required amount of monomers (VAc: 7.92 g; MA: 1.43 g). Purified nitrogen was bubbled throughout the system during 15 min. The system was stirred at the reaction temperature (30°C). Then, the initiator (CAN: 0.1100 g to generate a 5×10^{-3} N solution) was added. Agitation was adjusted to 110 rpm. A continuous supply of purified nitrogen was maintained throughout the reaction period. After the desired reaction period, the polymerization was stopped by adding hydroquinone and the mixture was filtered. The solid residue was washed with water, dried in an oven at 60°C under reduced pressure, and then placed in a desiccator containing phosphorous pentoxide until constant weight.

Oxidation Reaction

The cellulose fibers were oxidized with CAN under identical conditions as those of the graft copoly-

merization above described as Method A, except that the monomers were not added.

Other Procedures

The cellulose of the graft copolymers was hydrolyzed according to our method.[8]

In a previous paper[7] are described the experimental procedures used to determine the following reaction parameters: ceric ion consumption, homocopolymer extraction, molecular weights of cellulose and grafted polymer, composition of true graft copolymers (by extraction of nongrafted cellulose), and average compositions of grafted and nongrafted poly(vinyl acetate-co-methyl acrylate).

Grafting Parameters

The following grafting parameters were calculated as described previously[7]:

Apparent grafting yield G-ratio of grafted polymer to original cellulose

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

Grafting efficiency GE-ratio of grafted polymer to total synthetic polymer

Total conversion of monomer to polymer, C_t-monomer fraction that polymerizes

Graft conversion C_g is the monomer fraction that affords grafted polymer

Homopolymer conversion C_h-monomer fraction that affords homopolymer

Cellulose conversion C_c-cellulose fraction actually grafted

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

Number of grafted chains or branches, N_g-number of moles of synthetic polymer chains grafted to cellulose

Number of homopolymer chains, N_h-number of moles of homopolymer

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

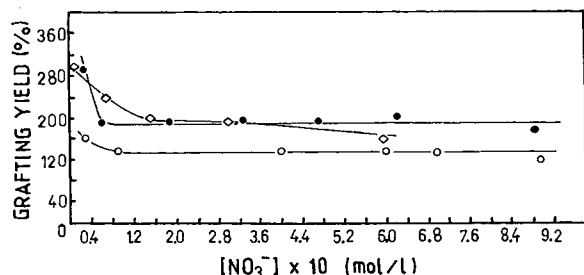Ceric ion consumption $(Ce)_c$-fraction of ceric ion reduced to cerous ion during the polymerization reaction

Figure 1 Grafting yield as a function of [NO₃⁻]: (○) addition procedure M–Ce; (●) addition procedure (Ce–M)$_r$, varying [NO₃⁻] at the stage previous to polymerization; (◇) addition procedure (Ce–M)$_r$, varying [NO₃⁻] at the stage of polymerization.

RESULTS

Effect of Nitrate Ion Concentration

Addition Procedure M–Ce

The results obtained when sodium nitrate was added to the reaction medium in order to vary the total [NO₃⁻] are shown in Figures 1 and 2 and Tables I–III. Grafting yield decreases slightly {see support in Figure 3 at [Ce(IV)] = 5 × 10⁻³ N} at low [NO₃⁻] and remains almost constant at higher concentrations (Fig. 1 and Table I). Grafting efficiency is independent of [NO₃⁻] (Table I).

On the other hand, the ceric ion consumption increases gradually with the nitrate ion concentration, reaching a complete consumption (Fig. 2). Cellulose conversion decreases at low [NO₃⁻] and increases slightly at higher concentrations (Table I).

Grafting frequency, percentage of cellulose in the true graft copolymer, compositions $\bar{F}_v$ of grafted chains and homocopolymer and molecular weight of branches and homocopolymer are practically independent of [NO₃⁻] (Tables II and III). The number of branches decreases at low [NO₃⁻] and keeps constant at higher concentrations (Table II).

Addition Procedure (Ce–M)$_r$. Effect of [NO₃⁻] at the Stage Previous to Polymerization

Grafting yield decreases quickly when [NO₃⁻] is slightly increased, remaining constant at larger concentrations (Fig. 1 and Table I). Grafting efficiency decreases slightly with [NO₃⁻] (Table I).

The ceric ion consumption during the stage previous to polymerization increases remarkably at low [NO₃⁻] and increases very slightly with higher

[NO₃⁻] (Fig. 2). Cellulose conversion increases with [NO₃⁻] (Table I). Grafting frequency decreases at low [NO₃⁻] and remains approximately constant with higher concentrations (Table II).

Percentage of cellulose in the true graft copolymer increases with [NO₃⁻] (Table III). The molecular weight of branches remains constant with [NO₃⁻] (Table III). The composition $\bar{F}_v$ of branches decreases with [NO₃⁻], whereas that of homocopolymer keeps almost constant (Table II). The number of branches and homocopolymer chains decreases slightly at low [NO₃⁻] and keeps constant at higher concentrations (Table II).

Addition Procedure (Ce–M)$_r$. Effect of [NO₃⁻] at the Stage of Polymerization

Grafting yield decreases at low [NO₃⁻] and keeps constant at higher concentrations (Fig. 1 and Table I). Grafting efficiency is independent of [NO₃⁻] (Table I). Cellulose conversion increases slightly at low [NO₃⁻] and decreases with higher concentrations (Table I). Grafting frequency decreases with [NO₃⁻] (Table II).

Percentage of cellulose in the true graft copolymer increases slightly at low [NO₃⁻] and keeps constant at higher concentrations (Table III). The molecular weights of branches and homocopolymer keep almost constant with [NO₃⁻] (Table III). The composition $\bar{F}_v$ of grafted polymer decreases at low [NO₃⁻], remaining constant with larger concentrations (Table II). The number of branches and homocopolymer chains decreases with [NO₃⁻] (Table II).

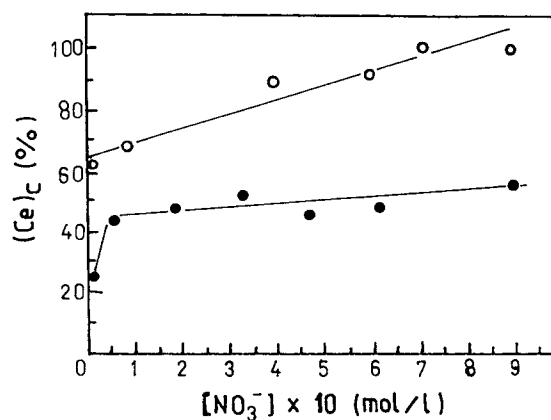**Figure 2** Ceric ion consumption vs. [NO₃⁻]: (○) addition procedure M–Ce; (●) addition procedure (Ce–M)$_r$, varying [NO₃⁻] at the stage previous to polymerization.

Table I   Effect of [NO$_3^-$] on Grafting Parameters. Part I

Exptl	[NO$_3^-$] $\times$ 10^2 (mol/L)	[NaNO$_3$] (mol/L)	G (%)	G_T (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)
			Addition Procedure M–Ce					
1	3.3	0	168	454	18	39	37	32
2	9.	0.06	140	609	15	33	23	31
3	40	0.37	140	—	15	33	—	32
4	60	0.57	143	596	15	32	24	33
5	71	0.67	136	425	15	32	32	31
6	90	0.87	122	407	13	30	30	31
			Addition Procedure (Ce–M)$_r$: NaNO$_3$ Addition at the Stage Previous to Polymerization					
1	3	0	300	833	32	32	36	50
2	6	0.03	192	480	21	25	40	45
3	19	0.16	199	433	21	24	46	47
4	33	0.30	200	—	22	26	—	45
5	47	0.44	192	—	20	28	—	42
6	62	0.59	228	475	25	32	48	43
7	89	0.86	177	334	19	27	53	41
			Addition Procedure (Ce–M)$_r$: NaNO$_3$ Addition at the Stage of Polymerization					
1	1	0	300	833	32	32	36	50
2	7	0.06	239	531	26	26	45	50
3	16	0.15	204	—	22	20	—	52
4	30	0.29	196	490	21	20	40	51
5	60	0.59	160	640	17	18	25	49

Table II   Effect of [NO$_3^-$] on Grafting Parameters. Part II

Exptl	[NO$_3^-$] $\times$ 10^2 (mol/L)	GF	$N_g \times 10^6$	$N_h \times 10^5$	$\bar{F}_v$ (%) Branches	$\bar{F}_v$ (%) Homocopolymer
			Addition Procedure M–Ce			
1	3.3	2.5	4.0	6.6	74	72
2	9	3.0	3.0	7.8	66	70
4	60	2.7	2.9	3.7	60	70
5	71	2.1	3.0	6.7	68	68
6	90	2.2	2.9	5.1	58	68
			Addition Procedure (Ce–M)$_r$: NaNO$_3$ Addition at the Stage Previous to Polymerization			
1	3	2.7	4.3	2.7	80	83
2	6	1.5	2.6	1.4	—	—
3	19	—	—	2.2	—	73
4	33	—	—	2.5	—	75
5	47	—	—	1.2	—	77
6	62	1.6	3.4	3.0	68	79
7	89	1.9	2.5	1.8	55	75
			Addition Procedure (Ce–M)$_r$: NaNO$_3$ Addition at the Stage of Polymerization			
1	1	2.7	4.3	2.7	80	83
2	7	1.8	3.2	1.5	60	77
3	16	—	—	1.3	—	70
4	30	1.2	2.1	1.4	56	69
5	60	1.1	1.2	1.5	61	61

Table III   Effect of [NO₃⁻] on Grafting Parameters. Part III

Exptl	$[NO_3^-] \times 10^2$ (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	3.3	18	82	420	2270	5.4	55	230	4.2
2	9	14	86	460	2670	5.8	40	200	5.0
4	60	14	86	500	2702	5.4	80	410	5.1
5	71	19	81	460	2760	6.0	45	210	4.7
6	90	20	80	420	2750	6.6	55	250	4.5
		Addition Procedure $(Ce-M)_r$: NaNO₃ Addition at the Stage Previous to Polymerization							
1	3	11	89	700	3850	5.5	110	630	5.7
2	6	17	83	730	4370	7.9	165	620	3.8
3	19	19	81	—	—	—	105	390	3.7
4	33	—	—	—	—	—	100	360	3.6
5	47	—	—	—	—	—	220	880	4.0
6	62	17	83	680	3230	4.7	100	450	4.5
7	89	23	77	710	3450	4.9	140	680	4.9
		Addition Procedure $(Ce-M)_r$: NaNO₃ Addition at the Stage of Polymerization							
1	1	11	89	700	3850	5.5	110	630	5.7
2	7	18	82	740	4440	6.0	160	680	4.3
3	16	—	—	—	—	—	135	590	4.4
4	30	17	83	930	6500	6.9	135	550	4.1
5	60	20	80	1300	8500	6.5	125	1050	8.4

Effect of [Ce(IV)] When [NO₃⁻] Is Kept Constant

In Figure 3 and Tables IV–VII are shown the results obtained varying [Ce(IV)], using the addition pro-

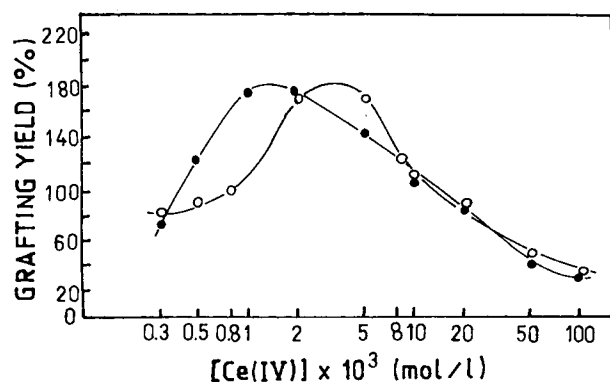**Figure 3**   Grafting yield as a function of [Ce(IV)] using the addition procedure M–Ce; (O) [NO₃⁻] variable; (●) [NO₃⁻] = 0.602 N.

cedure M–Ce, when [NO₃⁻] is variable and when it is kept constant at 0.602 N.

Grafting yield follows the same general behavior in both cases, but the maximum value of G is reached at lower [Ce(IV)] when NaNO₃ is added (Fig. 3 and Table IV). The effect of the addition of sodium nitrate on grafting yield is dependent on the ceric ion concentration employed. At [Ce(IV)] higher than 8×10^{-3} N, the values obtained in both cases are practically equal.

Grafting efficiency follows similar behavior in both cases (Table IV). The ceric ion consumption is higher when NaNO₃ is added, except when ceric ion is depleted in both cases (Table V). Cellulose conversion as well as grafting frequency are quite similar in both cases (Table IV). The molecular weights of branches and homocopolymer are similar in both cases (Table VI).

The composition $\bar{F}_v$ of branches and homocopolymer is practically equal in both cases (Table

Table IV Effect of [Ce(IV)] on Grafting Parameters When [NO$_3^-$] Is (a) Constant and (b) Varied. Part I

Exptl	[Ce(IV)] × 10³ (mol/L)	G (%)	G_T (%)	C_g (%)	C_h (%)	C_c (%)	GE (%)	GF
			(a) [NO$_3^-$] = 0.602 M					
1	0.3	72	240	8	14	30	39	1.0
2	0.5	122	305	13	21	40	35	1.6
3	1	174	497	19	27	35	38	—
4	2	170	—	18	33	—	36	—
5	5	143	596	15	32	24	23	2.6
6	10	106	—	11	38	—	23	—
7	20	86	—	9	36	—	21	—
8	50	45	—	5	33	—	13	—
9	100	37	185	4	34	20	11	5.8
			(b) [NO$_3^-$] Is Variable					
1	0.3	81	231	9	13	35	39	1.0
2	0.5	90	225	10	19	40	33	—
3	0.8	99	247	11	22	40	33	—
4	2	170	548	18	31	31	37	2.3
5	5	168	454	18	39	37	32	2.5
6	8	122	—	13	36	—	27	—
7	10	110	—	12	30	—	28	—
8	20	90	—	10	34	—	22	—
9	50	49	—	5	39	—	12	—
10	100	37	185	4	34	20	11	5.8

Table V Effect of [Ce(IV)] on Grafting Parameters When [NO$_3^-$] Is (a) Constant and (b) Varied. Part II

Exptl	[Ce(IV)] × 10³ (mol/L)	(Ce)$_c$ (%)	(Ce)$_c$ (meq)
	(a) [NO$_3^-$] = 0.602 N		
1	0.3	100	0.01
2	0.5	100	0.02
3	1	100	0.04
4	2	95	0.08
5	5	92	0.18
6	10	90	0.36
7	20	85	0.68
8	50	85	1.70
9	100	94	3.76
	(b) [NO$_3^-$] Is Variable		
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

VII). The number of branches is higher at low [Ce(IV)] in case of constant [NO$_3^-$], changing to the opposite at high [Ce(IV)] (Table VII). The opposite occurs for the number of homocopolymer chains.

Effect of [HNO$_3$] When [NO$_3^-$] Is Kept Constant

In Figure 4 and Tables VIII–XI are shown the results obtained varying [HNO$_3$], using the addition procedure M–Ce, when [NO$_3^-$] is variable and when it is kept constant at 0.705 N.

Grafting yield follows the same general behavior in both cases (Fig. 4 and Table VIII). The maximum value reached by G is lower in the case of NaNO$_3$ addition; but at low [HNO$_3$], higher G values are obtained in that case. Grafting efficiency is generally higher in case of addition of NaNO$_3$ (Table IX).

As far as ceric ion consumption is concerned, it is observed that at constant high [NO$_3^-$] this consumption is completely independent of [HNO$_3$]. When nitrate ion is variable the ceric ion is only completely consumed at high [HNO$_3$] (Table IX).

Grafting frequency increases with [HNO$_3$] when [NO$_3^-$] is kept constant, whereas it remains constant when [NO$_3^-$] is variable (Table IX). Percentage of cellulose in the true graft copolymer and molecular

Table VI Effect of [Ce(IV)] on Grafting Parameters When [NO$_3^-$] Is (a) Constant and (b) Varied. Part III

Exptl	[Ce(IV)] × 10³ (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
				(a) [NO$_3^-$] = 0.602 N					
1	0.3	49	51	530	3920	7.4	380	1040	2.7
2	0.5	25	75	440	2690	6.1	220	990	4.5
3	1	17	83	—	—	—	190	810	4.3
4	2	—	—	—	—	—	150	740	4.9
5	5	14	86	500	2700	5.4	80	410	5.1
7	20	—	—	—	—	—	14	90	6.4
9	100	35	65	70	380	5.4	6	90	15
				(b) [NO$_3^-$] Is Variable					
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

Table VII Effect of [Ce(IV)] on Grafting Parameters When [NO$_3^-$] Is (a) Constant and (b) Varied. Part IV

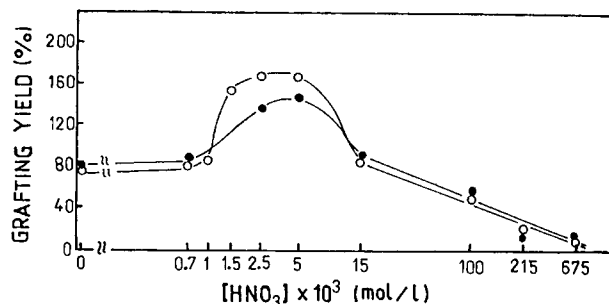| Exptl	[Ce(IV)] × 10³ (mol/L)	$N_g \times 10^6$	$N_h \times 10^5$	$\bar{F}_v$ (%)	
				Branches	Homocopolymer
			(a) [NO$_3^-$] = 0.602 N		
1	0.3	1.4	0.4	47	43
2	0.5	2.8	0.9	50	59
3	1	—	1.3	—	72
4	2	—	2.0	—	70
5	5	2.9	3.7	60	70
7	20	—	23.7	—	66
9	100	5.3	52.7	60	64
			(b) [NO$_3^-$] Is Variable		
1	0.3	1.6	0.3	43	41
2	0.5	—	1.3	—	51
3	0.8	—	1.5	—	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

Figure 4   Grafting yield as a function of [HNO₃] using the addition procedure M–Ce; (O) [NO$_3^-$] variable; (●) [NO$_3^-$] = 0.705 N.

weights of branches and homocopolymer are similar in both cases (Table X). The composition $\bar{F}_v$ of branches and homocopolymer is slightly higher when [NO$_3^-$] is variable (Table XI).

Effect of [NO$_3^-$] on the Homopolymerization Reaction

In Table XII are shown the results obtained when sodium nitrate was added to the homocopolymerization reaction medium to vary [NO$_3^-$].

Conversion of monomer to polymer as well as the ceric ion consumption remain constant with [NO$_3^-$], but molecular weight increases.

Effect of NaCl Addition

In Tables XIII and XIV are shown the results obtained when sodium chloride was added to the reaction medium, using the addition procedure M–Ce. Grafting yield remains almost constant when varying [NaCl], except at high concentrations where G decreases remarkably (Table XIII), although it is probably due to complete consumption of ceric ion during a portion of the polymerization time.

Grafting efficiency is independent of the addition of sodium chloride, whereas the ceric ion consumption increases with [NaCl] (Table XIII). The molecular weights of branches and homocopolymer increase considerably when [NaCl] is increased (Table XIV).

DISCUSSION

The most notable differences found when the ceric ion concentration is varied, either keeping constant

Table VIII   Effect of [HNO₃] on Grafting Parameters When [NO$_3^-$] Is (a) Constant and (b) Varied. Part I

Exptl	[HNO₃] × 10³ (mol/L)	[NO$_3^-$] (mol/L)	G (%)	G_T (%)	C_g (%)	C_h (%)	C_c (%)
		(a) [NO$_3^-$] Is Constant					
1	0	0.705	80	190	9	21	42
2	0.7	0.705	87	—	10	22	—
3	2.5	0.705	136	—	15	32	—
4	5	0.705	148	462	16	36	32
5	15	0.705	93	—	10	24	—
6	100	0.705	57	285	6	14	20
7	275	0.705	15	—	2	3	—
8	675	0.705	10	—	1	4	—
		(b) [NO$_3^-$] Is Variable					
1	0	0.030	75	156	8	25	48
2	0.7	0.0307	81	—	9	26	—
3	1	0.031	86	—	9	29	—
4	1.5	0.0315	156	—	17	36	—
5	2.5	0.0325	168	454	18	39	37
6	5	0.035	170	—	18	36	—
7	15	0.045	87	—	9	30	—
8	110	0.140	55	275	6	23	20
9	275	0.305	25	208	3	9	12
10	675	0.705	10	—	1	4	—

Table IX   Effect of [HNO₃] on Grafting Parameters When [NO₃⁻] Is (a) Constant and (b) Varied. Part II

Exptl	$[HNO_3] \times 10^3$ (mol/L)	$[NO_3^-]$ (mol/L)	GE (%)	$(Ce)_c$ (%)	GF
		(a) $[NO_3^-]$ Is Constant			
1	0	0.705	29	94	2.3
2	0.7	0.705	29	92	—
3	2.5	0.705	31	100	2.1
4	5	0.705	31	99	—
5	15	0.705	29	97	—
6	100	0.705	30	92	3.7
7	275	0.705	33	90	—
8	675	0.705	21	100	—
		(b) $[NO_3^-]$ Is Variable			
1	0	0.030	24	69	1.4
2	0.7	0.0307	25	60	—
3	1	0.031	24	66	—
4	1.5	0.0315	32	60	—
5	2.5	0.0325	32	61	2.5
6	5	0.035	34	72	—
7	15	0.045	24	70	—
8	110	0.140	21	99	2.0
9	275	0.305	23	100	2.2
10	675	0.705	21	100	—

Table X   Effect of [HNO₃] on Grafting Parameters When [NO₃⁻] Is (a) Constant and (b) Varied. Part III

Exptl	$[HNO_3] \times 10^3$ (mol/L)	Composition of True Graft Copolymer Cell (%)	Branches (%)	Branches $\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D	Homocopolymer $\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
			(a) $[NO_3^-] = 0.705$ mol/L						
1	0	34	66	190	640	3.4	45	250	5.6
2	0.7	—	—	—	—	—	40	200	5.0
3	2.5	19	81	460	3490	7.6	45	210	4.7
5	15	—	—	—	—	—	30	120	4.0
6	100	26	74	180	1340	7.4	30	410	13.7
7	275	—	—	—	—	—	10	120	12.0
8	675	—	—	—	—	—	5	60	12.0
			(b) $[NO_3^-]$ Is Variable						
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	11.0
9	275	32	68	210	700	3.3	15	130	8.7
10	675	—	—	—	—	—	6	60	10.0

Table XI **Effect of [HNO₃] on Grafting Parameters When [NO₃⁻] Is (a) Constant and (b) Varied. Part IV**

Exptl	$[HNO_3] \times 10^3$ (mol/L)	$[NO_3^-]$ (mol/L)	$N_g \times 10^6$	$N_h \times 10^5$	$\bar{F}_v$ (%) Branches	$\bar{F}_v$ (%) Homocopolymer
(a) [NO₃⁻] Is Constant						
1	0	0.705	4.2	4.4	42	56
2	0.7	0.705	—	5.3	—	52
3	2.5	0.705	3.0	6.7	32	68
5	15	0.705	—	7.5	—	55
6	100	0.705	3.2	4.4	20	37
7	275	0.705	—	3.0	—	28
8	675	0.705	—	7.4	—	31
(b) [NO₃⁻] Is Variable						
1	0	0.705	3.0	5.9	46	61
3	1	0.305	—	7.7	—	60
5	2.5	0.140	4.0	6.6	74	72
6	5	0.045	—	5.6	—	71
7	15	0.035	—	6.9	—	62
8	110	0.0325	1.7	10.7	40	48
9	275	0.031	1.2	5.5	20	30
10	675	0.030	—	6.2	—	31

[NO₃⁻] or not, seems to be on the ceric ion consumption and on the grafting yield. The increased ceric ion consumption when NaNO₃ is added is essentially due to an increased capability of ceric ion to oxidize cellulose in that medium, as shown above when NaNO₃ was added at the stage previous to polymerization. The oxidation potential of ceric ion increases when [NO₃⁻] is increased,[9] probably by affecting the nature of the ceric ion complexes. Where grafting yield is higher, it is due to higher number of branches and not to differences in molecular weight. At low [Ce(IV)], the monomer is able to trap the increased number of cellulose radicals formed in presence of NaNO₃, but at high [Ce(IV)] the ceric ion oxidation of those radicals is favored. Any salt effect by the presence of sodium nitrate should not be disregarded.

The effect of NaNO₃ addition when varying [HNO₃] is similar to that showed when varying [Ce(IV)] and so it also appears to be based on an increase in the rate of cellulose oxidation, as the ceric ion consumption approaches completion.

Increasing [NO₃⁻] produces an increase in the ceric ion consumption during grafting and in the oxidation of cellulose, but there is no effect on that consumption during the homocopolymerization reaction. Thus, it ensues that changes in the graft copolymerization parameters because of varying [NO₃⁻] are essentially due to the effect of nitrate ion favoring the cellulose oxidation, as discussed above.

Ceric ammonium nitrate hydrolyzes extensively in dilute nitric acid to produce a whole spectrum of complex ions containing nitrate ions, hydroxyl ions,

Table XII **The Effect of [NO₃⁻] on the Homopolymerization Reaction**

Exptl	$[NaNO_3]$ (mol/L)	$[NO_3^-] \times 10^2$ (mol/L)	Conversion (%)	$(Ce)_c$ (%)	$\bar{F}_v$ (%)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D
1a	0	3.2	24	53	—	—	—	—
1b	0	3.2	28	50	48	40	300	7.5
2a	0.6	63	27	57	—	70	530	7.6
2b	0.6	63	31	53	—	100	730	7.3

Table XIII   Effect of the Addition of Sodium Chloride on Grafting Parameters. Part I

Exptl	[NaCl] (mol/L)	G (%)	C_g (%)	C_h (%)	GE (%)	$(Ce)_c$ (%)
1	0	168	18	39	32	61
2	0.40	185	20	46	30	70
3	0.60	173	19	31	37	75
4	0.70	192	21	58	31	85
5	0.90	166	18	53	30	99
6	1.00	110	12	27	31	100

and water molecules.[10–12] The concentration of each species is not known and it will depend upon [Ce(IV)], [NO$_3^-$], and [H$^+$]. Since the ceric ion consumption in the presence of cellulose is higher when [NO$_3^-$] is increased, it seems that the ceric species present under those conditions are more oxidant, either favoring formation of the cellulose–ceric ion complex or its disproportionation, or both. The addition of sodium nitrate can also produce a decrease in the monomer solubility. As the monomer solubility is reduced, the difficulty of the monomer diffusion towards the active sites on cellulose increases, decreasing the grafting frequency and the cellulose conversion.

If the results obtained with sodium nitrate and sodium chloride are compared, it is observed that the ceric ion consumption increases, in both cases, with salt concentration. Molecular weight of branches is not affected by the addition of sodium nitrate, but it increases when sodium chloride is added to the reaction medium.

The strong effects of NaNO$_3$ and NaCl on the rate of cellulose oxidation in the absence of monomer can be seen in Table XV. Both show high ceric ion consumption compared with a reference test in the absence of salts. On the other hand, in the absence of cellulose and monomer, the presence of nitrate ion does not produce any effect on the ceric ion con-

sumption; that is, no species present in the medium is oxidable in the present reaction conditions.

The effect of sodium chloride on the graft copolymerization seems to be similar to that of sodium nitrate, the cellulose oxidation capacity of ceric ion is increased, and the solubility of both the monomer and polymer in the aqueous medium is lowered as discussed above. Analogous to nitrate ion, chloride ion can also take part as a ligand in the ceric ion complexes.

CONCLUSIONS

The addition of sodium nitrate affects appreciably the ceric ion consumption and the grafting yield. These effects are due to an enhanced oxidation of cellulose. The homopolymerization reaction initiated by ceric ion is unaffected by the presence of sodium nitrate.

The effect of the addition of sodium nitrate or sodium chloride on the reaction parameters is similar, but the latter salt does affect the molecular weight of the grafted synthetic polymer.

After extraction of the nongrafted cellulose[13] and cellulose hydrolysis[14,15] of the graft copolymer the grafting parameters G_T, GF, and C_c could be determined.

Table XIV   Effect of the Addition of Sodium Chloride on Grafting Parameters. Part II

Exptl	[NaCl] (mol/L)	$\bar{F}_v$ (%) Branches	$\bar{F}_v$ (%) Homocopolymer	Branches $\bar{M}_n \times 10^{-3}$	Branches $\bar{M}_w \times 10^{-3}$	Branches D	Homocopolymer $\bar{M}_n \times 10^{-3}$	Homocopolymer $\bar{M}_w \times 10^{-3}$	Homocopolymer D
1	0	74	72	420	2450	5.8	55	230	4.2
4	0.70	78	76	1040	7680	7.4	85	460	5.4
5	0.90	70	74	1370	8140	6.0	95	530	5.6

Table XV Effect of Addition of a Salt on Ceric Ion Consumption on the Cellulose Oxidation

Exptl	Salt	[Salt] (mol/L)	$(Ce)_c$ (%)
1	—	—	42
2	$NaNO_3$	0.60	70–75
3	NaCl	0.60	77
4	NaCl	0.83	94

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