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GRAFTING OF VINYL ACETATE-METHYL ACRYLATE MIXTURE ONTO CELLULOSE. EFFECT OF MONOMER CONCENTRATION AND FEED COMPOSITION

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ABSTRACT

The effects of monomer concentration and feed composition in the graft copolymerization of a mixture of vinyl acetate (VAc) and methyl acrylate (MA) onto cellulose, initiated by ceric ion, are studied. Two procedures for the reactants addition were employed and several grafting parameters were measured. MA is more reactive toward grafting than VAc, and the VAc-MA mixture shows an intermediate behavior. Minor amounts of MA favor VAc grafting, and minor amounts of VAc disfavor MA grafting. VAc is oxidated more easily by ceric ion than is MA. An explanation of the results is presented.

INTRODUCTION

Modification of natural and synthetic polymers by the graft copolymerization technique has been extensively studied. A variety of vinyl monomers has been successfully grafted onto cellulose [1-4] by using different types of initiators.

A limited number of reports on the effect of mixing unsaturated monomers in binary mixtures on the graft copolymerization of monomers onto cellulose have been published [2]. The results reported reveal that grafting yields for monomer mixtures are between the yields obtained with the monomers individually, and the actual composition of the resultant copolymer is dependent upon the monomer ratios employed. Also, synergistic behavior has been observed for the grafting of some binary monomer mixtures [3].

In this report the graft copolymerization of the binary mixture of vinyl acetate (VAc) and methyl acrylate (MA) onto cotton cellulose using ceric ammonium nitrate (CAN) as initiator is studied. The effects of monomer concentration and the composition of the binary mixture are explored.

EXPERIMENTAL

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

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 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 through the system. Then the required amount of monomers, with adequate feed composition, 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 was attained.

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 through the system. Then CAN was added (0.1100 g to generate a 5×10^{-3} N solution) and the reaction was allowed to proceed for 15 min at 30°C with an agitation speed of 80 rpm. After that cellulose-ceric ion contact time, the ceric solution was removed. Then 35 mL dilute nitric acid (2.5×10^{-3} *N*) was added, followed immediately by the appropriate monomer mixture. Stirring was adjusted to 110 rpm. At the end of the reaction period (6 h) the polymerization was stopped and the sample was purified by following the procedure described in Method A.

Other Procedures

The cellulose of the graft copolymers was hydrolyzed according to the method proposed by us [6].

A previous paper [5] describes the experimental procedures used to determine the following reaction parameters: ceric ion consumption, homocopolymer extraction, molecular weights of cellulose and grafted polymer, composition of the true graft copolymers (by extraction of nongrafted cellulose), and the average compositions of grafted and nongrafted poly(vinyl acetate-*co*-methyl acrylate).

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

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

Feed composition, f_v, is the fraction of VAc in the VAc–MA mixture.

RESULTS AND DISCUSSION

Effect of Monomer Concentration

Addition Procedure M-Ce. Vinyl Acetate–Methyl Acrylate Mixture

The effect of the concentration of the VAc–MA mixture (using f_v = 0.847) on the graft copolymerization parameters is shown in Figs. 1 and 2 and Tables 1–3.

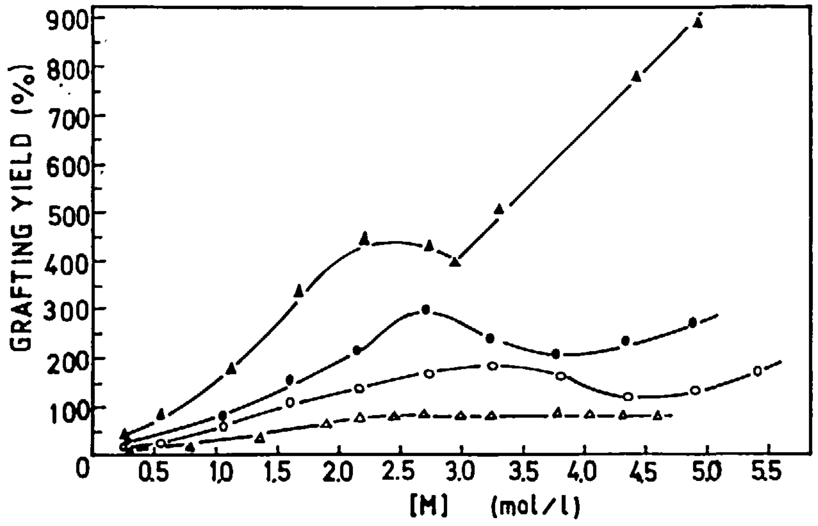

FIG. 1. Grafting yield as a function of [M]. (O) VAc—MA, addition procedure M-Ce; (●) VAc-MA, addition procedure (Ce-M)$_r$; (△) VAc, addition procedure M-Ce; (▲) MA, addition procedure M-Ce.

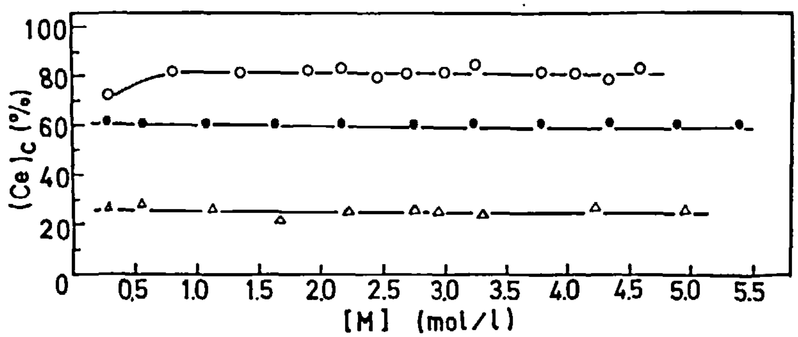

FIG. 2. Ceric ion consumption versus [M], using the addition procedure M-Ce for grafting. (O) VAc-MA; (●) VAc; (△) MA.

TABLE 1. Effect of [M] on Grafting a VAc-MA Mixture (f_v = 0.847). Part I

Exp.	[M] mol/L	G_T, %	C_t, %	C_g, %	C_h, %	C_c, %	GE, %
			Addition Procedure M-Ce				
1	0.28	70	37	22	15	30	6
3	1.08	176	61	17	44	37	28
7	3.25	465	63	17	46	40	26
11	5.42	583	35	9	26	30	27
			Addition Procedure $(Ce\text{-}M)_r$				
1	0.28	88	28	12	16	26	43
3	1.62	540	64	29	35	30	45
7	3.80	703	40	16	24	30	40
9	4.90	856	37	16	21	32	44

TABLE 2. Effect of [M] on Grafting a VAc–MA Mixture (f_v = 0.847). Part II

Exp.	[M], 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	0.28	—	—	1.0	—	—
7	3.25	2.4	4.2	7.4	72	77
11	5.42	2.7	3.6	6.9	59	54
			Addition Procedure (Ce-M)$_r$			
1	0.28	1.8	2.1	0.5	44	51
3	1.62	1.4	1.9	1.9	73	80
7	3.80	4.3	5.7	4.1	54	68
9	4.90	2.7	3.8	1.6	46	66

Grafting yield increases with increasing [M] (Fig. 1). An inflection at about [M] = 4.35 *M* is apparent. Grafting efficiency decreases rapidly at low [M] and remains almost constant at higher concentrations (Table 1). Ceric ion consumption is not affected by the amount of monomer used (Fig. 2). Cellulose conversion and grafting frequency are approximately constant with increasing [M] (Tables 1 and 2). The molecular weight of branches increases with increasing [M], showing an inflection about [M] = 4.35 *M* (Table 3). The percentage of cellulose in the true graft copolymer decreases as [M] increases (Table 3). The composition $\bar{F}_v$ of branches and homocopolymer is almost constant as [M] increases (Table 2). The number of branches is almost constant as [M] increases, but the number of homocopolymer chains increases with increasing [M] and almost becomes constant (Table 2).

TABLE 3. Effect of [M] on Grafting a VAc–MA Mixture (f_v = 0.847). Part III

		Composition of true graft copolymer		Branches			Homocopolymer		
Exp.	[M], mol/L	Cellulose, %	Branches, %	$\overline{M}_n$ × 10^{-3}	$\overline{M}_w$ × 10^{-3}	D	$\overline{M}_n$ × 10^{-3}	$\overline{M}_w$ × 10^{-3}	D
Addition Procedure M-Ce									
1	0.28	59	41	–	–	–	14	45	3.2
7	3.25	18	82	440	3500	8.0	70	300	4.3
11	5.42	15	85	480	2490	2.7	70	390	5.6
Addition Procedure (Ce-M)$_r$									
1	0.28	55	45	110	850	7.7	60	220	3.7
3	1.62	16	84	850	5600	6.6	100	470	4.7
7	3.80	12	88	370	1970	5.3	75	340	4.5
9	4.90	10	90	710	4260	6.0	215	910	4.2

Addition Procedure M-Ce. Vinyl Acetate

Figures 1 and 2 and Tables 4–6 show the results obtained when the vinyl acetate concentration is varied.

Grafting yield increases as [M] increases, reaches a maximum value, and remains constant for higher concentrations (Fig. 1). Grafting efficiency and ceric ion consumption increase slightly at low [M], and a further increase in [M] results in a constant value of those grafting parameters (Fig. 2). Cellulose conversion remains almost constant when [M] is varied (Table 4). Grafting frequency appears to show a maximum when [M] is varied (Table 5). The percentage of cellulose in the true graft copolymer decreases as [M] increases because the amount of synthetic polymer is higher than that of cellulose (Table 6). The molecular weight of branches shows a minimum, while the molecular weight of homopolymer shows a maximum as [M] varies (Table 6).

TABLE 4. Effect of [M] on Grafting Parameters. Part I

Exp.	[M], mol/L	G_T, %	C_t, %	C_g, %	C_h, %	C_c, %	GE, %
			Vinyl Acetate				
3	1.35	240	30	8	22	15	26
7	2.70	890	42	10	32	10	23
10	3.80	742	33	7	26	12	21
13	4.60	437	22	5	17	19	24
			Methyl Acrylate				
2	0.55	166	60	44	16	50	72
6	2.78	3071	94	45	48	14	48
10	4.98	5867	87	52	35	15	43

TABLE 5. Effect of [M] on Grafting Parameters. Part II

Exp.	[M], mol/L	*GF*	$N_g \times 10^6$	$N_h \times 10^5$
		Vinyl Acetate		
3	1.35	2.6	1.7	2.1
7	2.70	23	9.9	3.0
13	4.60	8	6.4	3.7
		Methyl Acrylate		
2	0.55	1.2	2.7	0.2
6	2.75	8.8	5.4	1.3
10	4.98	2.2	14.9	1.3

Addition Procedure M-Ce. Methyl Acrylate

Figures 1 and 2 and Tables 4-6 show the results obtained when the methyl acrylate concentration is varied.

Grafting yield increases with increasing [M], but an inflection is shown at about [M] = 2.95 *M* (Fig. 1). Grafting efficiency decreases at low [M] and remains nearly constant with increasing [M] (Table 4). Cellulose conversion decreases as [M] is increased, and it remains constant with a further increase of [M] (Table 4). Grafting frequency appears to show a maximum when [M] is varied (Table 5). The percentage of cellulose in the true graft copolymer decreases remarkably as [M] increases, reaching very low values when [M] is high (Table 6). The molecular weight of grafted branches seems to show a maximum as [M] increases, while the molecular weight of the homopolymer increases almost continuously (Table 6). The number of grafted branches and homopolymer chains increases as [M] increases (Table 5).

When the results obtained using the VAc-MA mixture, VAc, and MA are compared, it is observed that the highest values of grafting yield are obtained when MA is used and the lowest ones when VAc is used. The values reached with the VAc-MA mixture are between those obtained

TABLE 6. Effect of [M] on Grafting Parameters. Part III

		Composition of true graft copolymer		Branches			Homocopolymer		
Exp.	[M], mol/L	Cellulose, %	Branches, %	$\overline{M}_n$ × 10^{-3}	$\overline{M}_w$ × 10^{-3}	D	$\overline{M}_n$ × 10^{-3}	$\overline{M}_w$ × 10^{-3}	D
				Vinyl Acetate					
3	1.35	29	71	210	460	2.2	50	180	3.6
7	2.70	10	90	90	110	1.2	100	360	3.6
13	4.60	18	82	130	240	1.8	73	320	4.4
				Methyl Acrylate					
2	0.55	38	62	310	2300	7.3	160	520	3.2
6	2.75	3	97	790	7330	9.3	350	2100	6.0
10	4.98	2	98	590	8740	2.2	500	3010	6.0

with pure MA and VAc, although they are nearer to the values obtained with VAc (Fig. 1 and Tables 1 and 4). The inflection in grafting yield is reached at different [M] values for the VAc–MA mixture and for MA.

The highest values of grafting efficiency are obtained with MA and the lowest ones with VAc (Tables 1 and 4). At low [M] the highest *GE* values are reached for VAc–MA and MA, and the lowest one for VAc.

The highest consumption of ceric ion is reached with VAc, followed by the mixture of VAc and MA, while the consumption reached with MA (Fig. 2) is remarkably lower.

The highest cellulose conversion is obtained with the VAc–MA mixture, followed by both MA and VAc, except for low amounts of monomer where the value obtained with MA is the highest one (Tables 1 and 4).

The highest frequency of grafting is reached with MA and VAc–MA (Tables 2 and 5). The highest molecular weights are obtained with MA and the lowest with VAc (Tables 3 and 6).

VAc and MA produce a higher number of branches than does VAc–MA. However, VAc–MA produces the largest number of homopolymer chains, followed by VAc and then MA.

Addition Procedure $(\text{Ce-M})_r$. Vinyl Acetate–Methyl Acrylate Mixture

The effect of the concentration of the VAc–MA mixture (using f_v = 0.847) on the graft copolymerization parameters is shown in Fig. 1 and Tables 1–3.

Grafting yield increases as [M] increases, reaching an inflection at about [M] $\doteq$ 3.80 *M* (Fig. 1). Grafting efficiency and cellulose conversion are approximately constant as [M] increases (Tables 1 and 2). Grafting frequency appears to show a maximum value at [M] = 3.80 *M* (Table 2). The percentage of cellulose in the true graft copolymer decreases as [M] increases (Table 3). The molecular weights of branches and homocopolymer increase as [M] increases, showing an inflection at about [M] = 1.625 *M* (Table 3). The composition $\overline{F}_v$ of branches and homocopolymer, and the number of grafted branches and homocopolymer chains, show a maximum value when [M] is varied (Table 2).

When the results obtained using both addition procedures are compared, a similar general behavior is observed. However, the grafting yield values obtained by using the addition procedure $(\text{Ce-M})_r$ are higher than those reached with the addition procedure M-Ce, and the inflection is attained at lower [M] for the addition procedure $(\text{Ce-M})_r$ (Fig. 1).

The grafting efficiency values obtained with the addition procedure

(Ce-M)$_r$ are higher than those obtained with the addition M-Ce (Table 1).

Cellulose conversion is slightly higher with the addition procedure M-Ce (Table 1).

Grafting frequency is similar in both cases. The molecular weight of branches obtained with the addition procedure (Ce-M)$_r$ is remarkably higher than that attained with the addition procedure M-Ce. The inflection is attached at a lower value of [M] for the procedure (Ce-M)$_r$.

Effect of the Feed Composition of the VAc-MA Mixture

Addition Procedure M-Ce

The effect of the feed composition of the VAc-MA mixture (using [M] = 2.74 *M*) on the grafting parameters is shown in Figs. 3 and 4 and Tables 7-9.

Grafting yield quickly decreases as f_v increases; after reaching a minimum, *G* increases very slightly up to f_v = 0.7 and then decreases again as f_v approaches unity (Fig. 3). The presence of minor amounts of VAc in the feed lowers *G* abruptly compared with the value obtained with pure MA. On the contrary, the presence of minor amounts of MA enhances *G* as compared with the value obtained with pure VAc. The *G* value for any

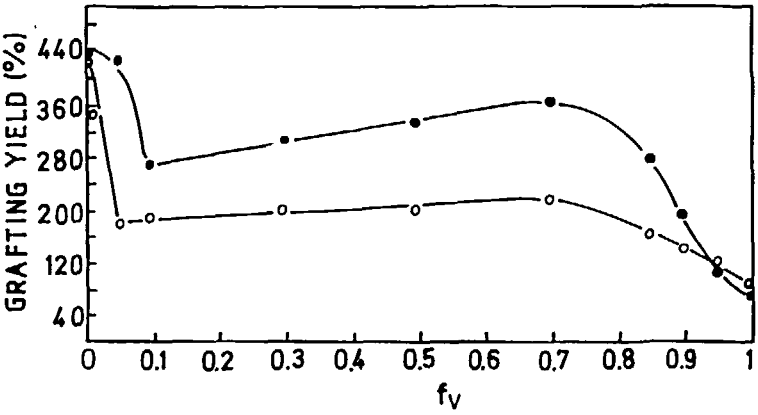

FIG. 3. Grafting yield as a function of the feed composition. (O) Addition procedure M-Ce; (●) addition procedure (Ce-M)$_r$.

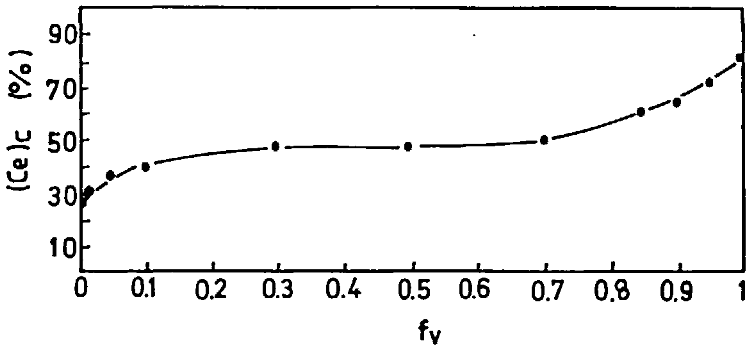

FIG. 4. Ceric ion consumption as a function of the feed composition using the addition procedure M-Ce.

TABLE 7. Effect of the Feed Composition of a VAc–MA Mixture on Grafting Parameters ([M] = 2.74 mol/L). Part I

Exp.	f_v	G_T, %	C_t, %	C_g, %	C_h, %	C_c, %	GE, %	GF
				Addition Procedure M-CE				
1	0	3071	93	45	48	14	48	8.8
3	0.049	1314	94	19	75	14	21	3.0
7	0.695	653	68	24	44	34	35	2.9
11	1	890	42	10	32	10	23	23
				Addition Procedure (Ce-M)$_r$				
1	0	1514	92	46	46	29	49	3.5
3	0.098	1528	91	29	62	18	32	4.6
7	0.847	833	64	32	32	36	50	2.7
10	1	467	29	8	21	15	26	3.7

TABLE 8. Effect of the Feed Composition of a VAc–MA Mixture on Grafting Parameters ([M] = 2.74 mol/L). Part II

		Composition of true graft copolymer		Branches			Homocopolymer		
Exp.	f_v	Cellulose, %	Branches, %	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	D	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	D
				Addition Procedure M-Ce					
1	0	3	97	790	7330	9.3	350	2100	6.0
3	0.049	7	93	930	7470	8.0	270	1420	5.3
7	0.695	13	87	510	4060	8.0	55	300	5.5
11	1	10	90	90	110	1.2	100	360	3.6
				Addition Procedure $(\text{Ce-M})_r$					
1	0	6	94	980	13410	13.7	165	1310	7.9
3	0.098	6	94	760	5190	6.8	75	460	6.1
7	0.847	11	89	700	3850	5.5	110	620	5.6
10	1	55	45	290	630	2.2	145	470	3.2

TABLE 9. Effect of the Feed Composition of a VAc–MA Mixture on Grafting Parameters ([M] = 2.74 mol/L). Part III

				$\bar{F}_v$, %	
Exp.	f_v	$N_g \times 10^6$	$N_h \times 10^5$	Branches	Homocopolymer
		Addition Procedure M-Ce			
1	0	5.4	1.3	0	0
3	0.049	2.0	2.6	5	5
7	0.695	4.1	7.5	55	49
11	1	10.0	3.0	100	100
		Addition Procedure $(\text{Ce-M})_r$			
1	0	4.5	2.8	0	0
3	0.098	3.6	7.8	5	11
7	0.847	4.3	2.7	80	83
10	1	2.4	1.4	100	100

composition of the binary mixture is between those attained with both pure monomers.

Grafting efficiency behaves similarly to grafting yield (Table 7).

As can be observed from Fig. 4, ceric ion consumption is affected by the composition of the binary mixture VAc–MA. It increases as VAc enriches the binary mixture. The ceric ion consumption observed with pure VAc is much higher than that observed with pure MA.

Cellulose conversion shows a maximum at about $f_v = 0.7$ (Table 7). The presence of a small amount of MA in the feed enhances cellulose conversions compared to the value obtained with pure VAc. However, the presence of a minor amount of VAc does not affect the value of cellulose conversions obtained with pure MA. The cellulose conversions obtained with pure VAc and MA are very similar.

Grafting frequency remains constant when f_v is in the 0.05–0.85 range

(Table 7). Higher values of *GF* are attained with pure VAc and MA. The presence of a minor amount of VAc or MA in the feed lowers *GF* strongly compared with the values obtained with pure MA or VAc. The percentage of cellulose in the true graft copolymer increases as f_v increases (Table 8). The amount of synthetic polymer is much higher than that of cellulose.

The molecular weight of branches decreases as f_v increases (Table 8). The molecular weight of homocopolymer decreases at low f_v values and remains constant as f_v increases up to $f_v = 1$, where it increases. The composition $\overline{F}_v$ of grafted branches and homocopolymer chains increases as f_v increases (Table 9).

The number of branches remains constant when f_v is in the 0.05–085 range (Table 9). Higher values of N_g are obtained with pure VAc and MA. The number of homocopolymer chains reaches a maximum at low f_v values.

The Addition Procedure (Ce-M)$_r$

When the addition procedure (Ce-M)$_r$ is used, the grafting parameters behave in a similar way to changing f_v, as in procedure M-Ce (Fig. 3 and Tables 7–9). However, the (Ce-M)$_r$ procedure results in: a) higher values of grafting yield, grafting efficiency, cellulose conversion, and molecular weight; b) similar values of grafting frequency and number of branches; and c) lower number of homocopolymer chains.

Minor amounts of MA favor grafting of VAc because they facilitate reaching a higher molecular weight. Minor amounts of VAc disfavor grafting of MA because they prevent the addition of MA to the cellulose radicals, thereby leading to a smaller number of branches.

On the basis of the high consumption of ceric ion in the case of pure VAc, as opposed to the case of pure MA, it is proposed that VAc is oxidized faster by ceric ion than is MA to initiate homopolymerization. Also, the oxidation of the monomeric radical by ceric ion in the aqueous medium, before it is trapped by the monomer (especially by MA, if present) and gets into the organic phase, is probably important in the case of VAc but not in the case of MA. VAc radicals should be more reactive with MA, if present, than with VAc. Termination of homopolymer radical chains by combination with cellulose radicals could be the most important source of graft copolymer in the case of pure VAc because VAc shows low reactivity toward cellulose radicals and VAc radicals are easily formed by ceric ion. These proposals lead to an understanding of some of the results reported here.

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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, *Ibid., 10*, 171 (1984).
[4] O. Y. Mansour and A. Nagaty, *Ibid., 11*, 91 (1985).
[5] M. J. Fernández, I. Casinos, and G. M. Guzmán, To Be Published.
[6] M. J. Fernández, I. Casinos, and G. M. Guzmán, *Makromol. Chem., Macromol. Symp., 20/21*, 11 (1988).

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