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GRAFTING OF VINYL ACETATE–METHYL ACRYLATE MIXTURE ONTO CELLULOSE. EFFECT OF AGITATION

M. J. FERNANDEZ, I. CASINOS, and G. M. GUZMAN

Departamento de Ciencia y Tecnología de Polímeros
Facultad de Químicas
Universidad del País Vasco
P.O. Box 1072, 20080 San Sebastián, Spain

ABSTRACT

The agitation effect on the heterogeneous graft copolymerization of a mixture of vinyl acetate and methyl acrylate onto cellulose was studied. Two procedures for the addition of the reactants were employed. Stirring speed, agitation time, and magnetic as well as mechanical stirring were tested. This polymerization system undergoes significant changes in the reaction parameters under low and high stirring speeds as well as under short agitation times. An explanation of the results is given.

INTRODUCTION

The use of ceric salts for initiating graft copolymerization of vinyl monomers on cellulosic materials has been extensively investigated [1–4]. Since grafting in an aqueous medium is a heterogeneous reaction, it is reasonable to expect that agitation should play an important role. Recent papers by Graczyk and Hornof [5–12] have shown that this is indeed so, although some other factors, such as monomer solubility, type of initiation system, and reactor geometry, are also important. They also noted

[11, 12] that the effect of stirring was strongly dependent on whether the reaction was conducted in the presence or absence of oxygen.

Except for the studies carried out by these authors with different monomers and initiators, there is almost no mention in the literature of agitation effects [13, 14].

In the present work the effect of agitation, under a purified nitrogen atmosphere on the heterogeneous graft copolymerization of a mixture of vinyl acetate (VAc) and methyl acrylate (MA) onto cellulose initiated by ceric ammonium nitrate (CAN) is studied.

EXPERIMENTAL

The purification methods of cellulosic fibers, monomers, and the chemicals employed were the same as in a previous report [15].

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 ($2.5 \times 10^{-3} N$) under stirring for 30 min at the reaction temperature ($30^\circ C$) in a constant-temperature bath. Purified nitrogen was continuously bubbled through the system. Then the required amounts of monomers (VAc, 7.92 g; MA, 1.43 g) were 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 the chosen speed. A continuous supply of purified nitrogen was maintained throughout the reaction period. After 6 h the polymerization was stopped by the addition of 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 $60^\circ C$ under reduced pressure, and then placed in a desiccator containing phosphorus pentoxide until constant weight was attained.

Method B. Addition Procedure (Ce-M),

A cellulose sample (1 g) was immersed in 40 mL dilute nitric acid ($2.5 \times 10^{-3} N$) under stirring for 30 min at the reaction temperature ($30^\circ C$). Purified nitrogen was continuously bubbled through the system.

Then CAN was added (0.1100 g to generate a $5 \times 10^{-3} N$ solution), and the reaction was allowed to proceed for 15 min at 30°C at an agitation speed of 80 rpm. After the cellulose-ceric ion contact time, the ceric solution was removed. Then 35 mL dilute nitric acid ($2.5 \times 10^{-3} N$) was added, followed immediately by the monomer mixture (VAc, 7.92 g; MA, 1.43 g). Stirring was adjusted to the chosen speed. 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.

Homocopolymerization

$2.5 \times 10^{-3} N$ Nitric acid (40 mL) was poured into a flask and then the required amounts of monomers (VAc, 7.92 g; MA, 1.43 g) were added. Purified nitrogen was bubbled through the system for 15 min. The system was stirred at the reaction temperature (30°C). Then the initiator (CAN: 0.1100 g to generate a $5 \times 10^{-3} N$ solution) was added. Agitation was adjusted to the chosen speed. A continuous supply of nitrogen was maintained throughout the reaction period. After the desired reaction period (6 h), the polymerization was stopped by the addition of 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 was attained.

Other Procedures

The cellulose of the graft copolymers was hydrolyzed according to the method proposed by us [16].

In a previous paper [15] the experimental procedures used to determine the following reaction parameters are described: ceric ion consumption, homocopolymer extraction, molecular weights of cellulose and grafted polymer, composition of true graft copolymers (by extraction of non-grafted cellulose), and average compositions of grafted and nongrafted poly(vinyl acetate-*co*-methyl acrylate).

Grafting Parameters

The grafting parameters were calculated as indicated in the following paper.

RESULTS AND DISCUSSION

Effect of Stirring Speed

Graft Copolymerization

Addition Procedure M-Ce. As can be seen in Fig. 1, grafting yield increases slightly as the stirring speed increases from 0 to 20 rpm and remains almost constant in the 20–700 rpm range. When the agitation speed is higher than 700 rpm, a decrease in G value is observed, and it reaches a constant value in the 1300–1700 rpm range.

As far as grafting efficiency is concerned, its values are practically independent of stirring speed in the 0–1500 rpm range, as seen in Table 1.

Cellulose conversion is very low in the absence of agitation, but from a slow agitation of 8 rpm, C_c reached a higher and constant value, as shown in Table 1. C_c appears to decrease slightly after 700 rpm (Table 1).

Grafting frequency shows a smooth maximum in the 100–350 rpm range (Table 2). In the absence of agitation, the GF value is remarkably higher than those values obtained in the presence of agitation (Table 2).

Ceric ion consumption, $(Ce)_c$, is not affected by the agitation speed in the 8–700 rpm range. Above that range a strong consumption is produced up to the complete disappearance of ceric ion at 1300 rpm (Table 1).

Molecular weights of branches and homocopolymers remain almost constant when the agitation speed is in the 8–800 rpm range, decreasing

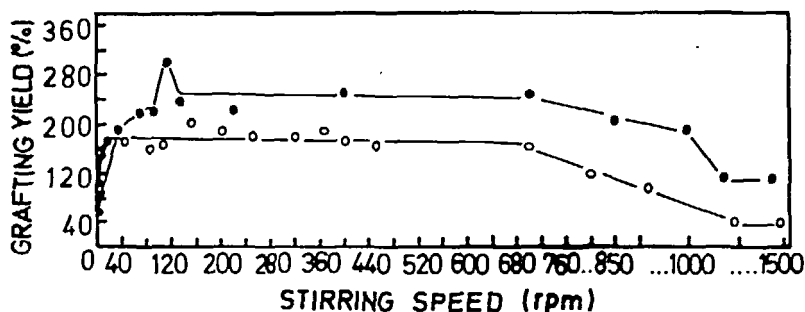


FIG. 1. Grafting yield as a function of stirring speed. (○) Addition procedure M-Ce; (●) addition procedure (Ce-M).

TABLE 1. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure M-Ce Is Used. Part I^a

Exp.	Stirring speed, rpm	G_T , %	C_t , %	C_g , %	C_h , %	C_c , %	GE , %	$(Ce)_c$, %
1B	0	1300	35	11	24	8	32	59
2	8	387	51	16	35	40	32	61
7	110	454	57	18	39	37	32	61
16	800	293	35	13	22	42	38	84
19	1500	130	12	4	8	30	34	99

^a G_T = true grafting yield.

C_t = total conversion of monomer to polymer.

C_g = graft conversion.

C_h = homopolymer conversion.

C_c = cellulose conversion.

GE = grafting efficiency.

$(Ce)_c$ = ceric ion consumption.

slightly at higher stirring speeds (Table 3). In the absence of agitation, both the molecular weight and polydispersity are higher than those obtained in the presence of agitation. Molecular weights of branches are much higher than those of homocopolymers.

The percentage of cellulose in the true graft copolymer is lower than that of the synthetic polymer, except at 1500 rpm where the values are equal. This percentage remains almost constant when the agitation speed is in the 8-700 rpm range, but increases at higher speeds (Table 3).

The composition of \bar{F}_v of the grafted branches increases as the agitation speed increases up to 110 rpm, remains constant between 110 and 700 rpm, and decreases for higher stirring speeds, as shown in Table 2. The same behavior is observed for homocopolymer composition (Table 2).

The number of branches and homocopolymer chains increases with increasing agitator speed up to 110 rpm, leveling off up to 700 rpm, and then decreases. That number is lower in the absence of agitation than in the presence of agitation, as shown in Table 2.

TABLE 2. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure M-Ce Is Used. Part II^a

Exp.	Stirring speed, rpm	GF	$N_g \times 10^6$	$N_h \times 10^5$	\bar{F}_v , %	
					Branches	Homocopolymer
1B	0	3.9	1.3	3.1	60	55
2	8	1.8	3.2	5.8	69	72
7	110	2.5	4.0	6.9	74	72
16	800	1.6	2.9	6.0	60	54
19	1500	1.0	1.3	2.4	50	44

^aGF = true grafting frequency.

N_g = number of grafted chains or branches.

N_h = number of homopolymer chains.

\bar{F}_v = synthetic-copolymer composition.

Addition Procedure (Ce-M). Grafting yield increases as the agitation speed increases from 8 to 110 rpm, then remains constant when the stirring speed is in the 110–700 rpm range, and decreases for stirring speeds higher than 700 rpm, reaching a constant value from 1200 to 1400 rpm, as shown in Fig. 1.

Grafting efficiency remains almost constant between 40 and 1500 rpm. The values obtained at 8 rpm and in the absence of agitation are much lower than those obtained at other agitation speeds (Table 4).

Cellulose conversion is remarkably lower in the absence of agitation than when the reaction medium is agitated (Table 4).

The frequency of grafting increases with increasing stirring speed, being almost constant in the 110–1000 rpm range and decreasing at higher speeds (Table 4).

The molecular weights of branches and homopolymers are almost constant in the 40–700 rpm range, and decrease at higher agitation speeds (Table 5). The molecular weight is remarkably lower in the absence of agitation than when the reaction medium is agitated.

The percentage of cellulose in the true graft copolymer is almost con-

TABLE 3. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure M-Ce Is Used. Part III

Exp.	Stirring speed, rpm	Composition of true graft copolymer		Branches		Homocopolymer			
		Cellulose, %	Branches, %	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	D	
1B	0	7	93	810	8320	72	590	10.3	8.2
2	8	21	79	477	2450	56	370	5.1	6.6
7	110	18	82	420	2270	53	230	5.4	4.3
16	800	25	75	420	2610	34	170	6.2	5.0
19	1500	50	50	290	1330	31	160	4.6	5.2

TABLE 4. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure (Ce-M), Is Used. Part I

Exp.	Stirring speed, rpm	G_T , %	C_t , %	C_g , %	C_h , %	C_c , %	GE , %	GF
1B	0	337	21	6	15	16	27	1.5
3	40	533	46	21	25	36	45	1.6
6	110	833	65	32	33	36	50	2.7
14	1400	280	23	12	11	40	52	1.2

stant between 40 and 1000 rpm and increases at 1400 rpm, as can be observed in Table 5. The percentage of cellulose obtained in the absence of agitation is very low.

The composition \bar{F}_v of the grafted branches and homocopolymers increases as the stirring speed increases up to 110 rpm, remains constant between 110 and 700 rpm, and decreases at higher agitation speeds (Table 6). The percentage of VAc is equal in value for branches and homopolymers.

The number of branches and homocopolymer chains increases with increasing agitator speed up to 110 rpm, levels off up to 700 rpm, and then decreases. That number is lower in the absence of agitation than in the presence of agitation (Table 6).

When the results obtained using addition sequences M-Ce and (Ce-M), are compared, the same effect of agitation on the grafting yield is observed whatever the addition sequence of reactants employed. The G values obtained with the addition procedure (Ce-M), are higher than those reached when the addition procedure M-Ce is used. This behavior is observed for all stirring speeds studied, except for agitation speeds lower than 40 rpm and in the absence of agitation, where the G value obtained using the addition M-Ce is higher than that obtained when the addition of monomers is carried out after the removal of ceric solution.

While the grafting efficiency values obtained using the addition procedure M-Ce are not affected by changes in the agitator speed, when the

TABLE 5. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure (Ce-M), Is Used. Part II

Exp.	Stirring speed, rpm	Composition of true graft copolymer		Branches			Homocopolymer		
		Cellulose, %	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
1B	0	6	94	400	3920	9.8	150	1040	6.9
3	40	16	84	760	3710	4.9	120	600	5.0
6	110	11	89	700	3850	5.5	110	620	5.6
14	1400	26	43	520	2370	4.6	110	670	6.1

TABLE 6. Effect of Stirring Speed on Grafting Parameters When the Addition Procedure (Ce-M), Is Used. Part III

Exp.	Stirring speed, rpm	$N_g \times 10^6$	$N_h \times 10^5$	\bar{F}_v , %	
				Branches	Homocopolymer
1B	0	1.4	1.0	48	50
3	40	2.5	2.0	70	74
6	110	4.3	2.7	80	83
14	1400	2.2	0.9	43	50

addition procedure (Ce-M), is used the grafting efficiency values obtained in the absence of agitation and at low stirring speeds are lower than those obtained at the other agitation speeds. The grafting efficiency values obtained with the addition procedure (Ce-M), are higher than those obtained with the addition M-Ce, except for speeds of 0 and 8 rpm, where the higher values are obtained with the addition M-Ce (Tables 1 and 4).

The cellulose conversion obtained using the addition M-Ce is higher than that obtained with the addition procedure (Ce-M),, except for the highest agitator speed used and in the absence of agitation, where the inverse behavior is observed (Tables 1 and 4). The molecular weight of grafted polymer is higher when the addition procedure (Ce-M), is used. The composition \bar{F}_v of branches and homopolymers seems to be independent of the addition procedure employed (Tables 2 and 6).

The lower cellulose conversion and grafting yield values obtained in the absence of agitation and at low agitation speeds may be due to the slow diffusion of ceric ion and monomer toward cellulose, with the cellulosic radicals being generated and trapped by monomer in the most accessible regions of the cellulose fibers. The decrease in grafting yield observed at high agitation speeds may be due to an enhancement in diffusion of ceric ion toward polymer radicals, thereby causing an increase in the rate of termination of polymer chains by ceric ion, because it is accompanied by decreasing molecular weight, decreasing number of grafted chains, and complete consumption of ceric ion. Enhancement in

diffusion of ceric ion toward cellulose does not appear to be relevant at this point, because N_g decreases.

Homocopolymerization

Table 7 shows the reaction parameters obtained from polymerization carried out in the absence of cellulose and with changing agitation speed.

Conversion of monomer decreases as the agitator speed increases, and in the absence of agitation the value obtained is the same as that reached at high stirring speeds. Ceric ion consumption increases slightly as the stirring speed increases, and it is slightly lower when the reaction medium is not agitated.

Molecular weight decreases slightly as the stirring speed increases. The percentage of VAc of the copolymer decreases as the agitation speed increases.

The observed decrease in molecular weight could be due, as before, to an increase in the rate of termination of the growing polymer chains by ceric ion. In the same way, the high ceric ion consumption can be attributed to the participation of this ion in the oxidative termination of the growing polymer chains. The decrease in monomer conversion is due both to a decrease in the initiation rate and to an increase in the termination rate, since both the number of polymer chains, N_n , and the molecular weight decrease (Table 7).

Effect of Agitation Time

Graft Copolymerization

The grafting procedure used was that described as Method A in the Experimental Section.

Agitation by a Magnetic Stirrer. The results obtained by changing the agitation time, t_a , during a reaction period of 6 h, when the system is agitated magnetically at about 750 rpm, are shown in Fig. 2.

Grafting yield decreases when the agitation time increases from 5 min to 1 h, and it becomes constant at longer t_a periods. The values obtained in the absence of agitation are lower than those reached at any agitation time (Fig. 2 and Table 8). The grafting efficiency and the ceric ion con-

TABLE 7. Effect of Agitation Speed on Homocopolymerization Reaction

Exp.	Stirring speed, rpm	Conversion, %	(Ce) _c , %	\bar{F}_v , %	\bar{M}_n $\times 10^{-3}$	\bar{M}_w $\times 10^{-3}$	D	N_h $\times 10^{-5}$
1	0	16	40	56	40	314	7.8	3.8
2B	110	28	50	48	38	295	7.8	6.8
3A	1300	16	56	40	30	156	5.3	5.0

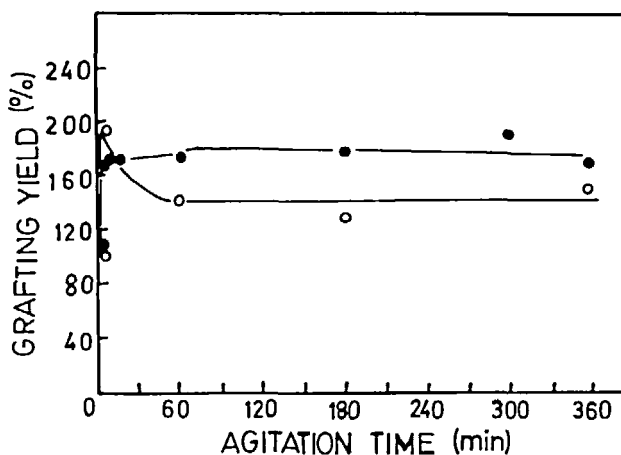


FIG. 2 Grafting yield as a function of agitation time for a reaction time of 6 h. (○) Magnetic stirrer; (●) mechanical stirrer.

sumption are independent of the agitation time and whether the system is agitated or not.

Agitation by a Mechanical Stirrer. Tables 9–11 and Fig. 2 show the results obtained when the agitation time, t_a , is changed during a reaction time of 6 h in a system that is mechanically agitated at 110 rpm.

Grafting yield is independent of agitation time if this is more than 5 min. If the reaction is carried out in the absence of agitation, the value

TABLE 8. Effect of Agitation Time on Grafting Parameters When the System Is Agitated Magnetically at 750 rpm

Exp.	t_a , min	C_p , %	C_g , %	C_h , %	GE , %	$(Ce)_c$, %
1	0	40	12	30	27	63
3	15	62	18	44	29	57
6	360	52	16	36	31	64

TABLE 9. Effect of Agitation Time on Grafting Parameters When the System is Agitated Mechanically at 110 rpm. Part I

Exp.	t_a , min	G_T , %	C_{12} , %	C_g , %	C_h , %	C_c , %	GE , %	$(Ce)_c$, %
1B	0	1250	35	11	24	8	35	59
2	5	933	52	18	34	18	34	55
4	15	552	57	18	39	31	32	—
8	360	454	57	18	39	37	32	61

obtained is remarkably lower than that reached in the presence of agitation, as can be seen in Fig. 2.

Both grafting efficiency and ceric ion consumption are not affected by the agitation time (Table 9). Cellulose conversion increases as agitation time increases, as can be seen from Table 9.

The maximum grafting frequency is obtained in the absence of agitation and at low agitation time (Table 10). The molecular weights of branches and homocopolymer are practically independent of the agitation time (Table 11).

The percentage of reacted cellulose in the true graft copolymer in-

TABLE 10. Effect of Agitation Time on Grafting Parameters When the System is Agitated Mechanically at 110 rpm. Part II

Exp.	t_a , min	GF	$N_g \times 10^6$	$N_h \times 10^5$	\bar{F}_v , %	
					Branches	Homocopolymer
1B	0	3.9	1.2	2.6	60	55
2	5	5.6	4.3	4.1	77	68
4	15	3.1	4.3	6.0	80	68
8	360	2.5	4.0	6.9	77	72

TABLE 11. Effect of Agitation Time on Grafting Parameters When the System Is Agitated Mechanically at 110 rpm.
Part III

Exp.	t_{ag} min	Composition of true graft copolymer		Branches			Homocopolymer		
		Cellulose, %	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
1B	0	7	93	810	8330	10.3	72	590	8.2
2	5	9	91	397	2540	6.5	78	440	5.6
4	15	15	85	400	2480	6.2	60	330	5.5
8	360	18	82	420	2270	5.4	53	230	4.3

creases as the agitation time increases, and it is remarkably lower when the system is not agitated (Table 11).

The composition \bar{F}_v of both branches and homocopolymer increases as the agitation time increases up to 15 min, and it remains constant for longer periods of agitation, as shown in Table 10. The percentage of VAc in branches is slightly higher than in homocopolymer. The number of grafted chains and homocopolymer increases as the agitation time increases up to 5–15 min and then remains almost constant, as shown in Table 10.

If the results obtained using the magnetic stirrer are compared with those obtained using the mechanical stirrer, it is observed that the values of G obtained between 1 and 6 h with the mechanical stirrer are higher. The increase in grafting yield observed by applying agitation for 5 min is more noticeable with the magnetic stirrer. Grafting efficiency as well as ceric ion consumption are independent of the type of agitation employed.

Homocopolymerization

Table 12 shows the reaction parameters obtained when polymerizations were carried out in the absence of cellulose and with changing agitation time while using an agitation speed of 110 rpm for a reaction period of 6 h.

When the system is agitated mechanically, conversion of monomer and ceric ion consumption increase very slightly as the agitation time increases. In the absence of agitation the values obtained are slightly lower than those obtained in the presence of agitation. Molecular weight appears to be almost constant. The composition \bar{F}_v of the copolymer does not change with agitation time, and is slightly higher in the absence of agitation.

When the system is agitated magnetically for 6 h, the behaviors of the polymerization parameters are very similar to what is shown in the case of mechanical agitation under the same reaction conditions.

Effect of the Reaction Time

The grafting procedure used was that described as Method A in the Experimental Section.

Figure 3 and Tables 13–15 show the results obtained when the system is either agitated during the initial 15 min of the reaction period or during the entire reaction period, with the reaction time as the variable. No

TABLE 12. Effect of Agitation Time on Homocopolymerization Reaction

Exp.	t_a , min	Conversion, %	(Ce) _c , %	\bar{F}_v , %	\bar{M}_n $\times 10^{-3}$	\bar{M}_w $\times 10^{-3}$	D	N_h $\times 10^{-5}$
<u>Mechanical Stirrer</u>								
1	0	16	40	56	40	314	7.8	3.8
2	15	19	45	49	38	200	5.3	4.6
3B	360	28	50	48	38	295	7.8	6.8
<u>Magnetic Stirrer</u>								
4	360	22	—	44	51	300	5.9	4.0

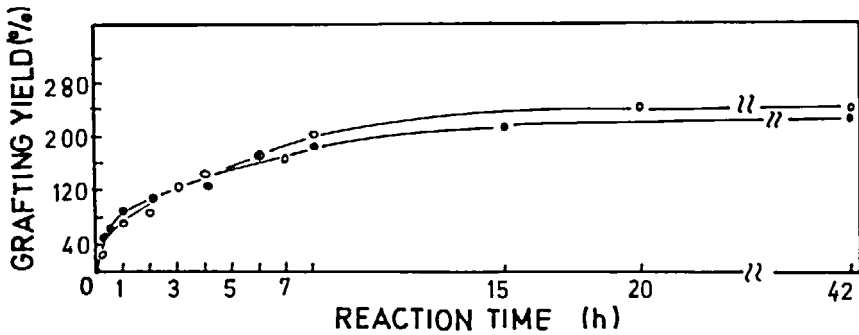


FIG. 3. Grafting yield as a function of reaction time. (O) Agitation for 15 min; (●) agitation during the entire reaction period.

TABLE 13. Effect of Reaction Time on Grafting Parameters When the System is Agitated Mechanically at 110 rpm. Part I

Exp.	t , min	G_T , %	C_i , %	C_g , %	C_h , %	C_c , %	GE , %	$(Ce)_c$, %
<u>Agitation Time: Initial 15 min</u>								
1	15	177	16	6	11	30	35	31
2	60	216	25	7	18	32	29	55
7	420	—	54	18	36	—	33	56
9	1200	787	72	27	45	31	36	77
<u>Agitation Time: Continuously during the Reaction Period</u>								
2	15	177	16	5	11	30	35	31
5	120	330	37	12	25	33	32	60
7	360	454	57	18	39	37	32	60
10	2520	572	67	25	42	40	37	84

TABLE 14. Effect of Reaction Time on Grafting Parameters When the System is Agitated Mechanically at 110 rpm. Part II

Exp.	t , min	GF	$N_g \times 10^6$	$N_h \times 10^5$	\bar{F}_v , %	
					Branches	Homocopolymer
<u>Agitation Time: Initial 15 min</u>						
1	15	1.1	1.4	2.4	40	40
2	60	1.2	1.7	3.4	52	48
9	1200	4.0	5.4	8.5	78	50
<u>Agitation Time: Continuously during the Reaction Period</u>						
2	15	1.1	1.4	2.5	40	38
5	120	2.4	3.5	5.5	58	58
7	360	2.5	4.0	6.9	75	72
10	2520	2.9	5.2	10.1	81	73

essential difference is observed in the behavior of the polymerization parameters as a consequence of applying continuous or limited agitation during the total reaction time.

The results described here allow us to state that agitation affects the reaction parameters in a general way, but a low stirring speed (8-40 rpm) and a short agitation time (5 min) are sufficient to leave any posterior behavior of the reaction parameters unaffected by agitation. Only when high agitation speeds are employed (>700 rpm) is a strong effect of agitation on the reaction parameters observed. Moreover, agitation during the initial 15 min of the total reaction time results in the same reaction parameters behavior as does continuous agitation.

It is expected that polymer systems with different diffusion characteristics for ceric ion and monomer to cellulose, as well as diffusion of ceric ion to radical chains, will show different reaction parameters behavior on agitation.

TABLE 15. Effect of Reaction Time on Grafting Parameters When the System Is Agitated Mechanically at 110 rpm.
Part III

Exp.	t , min	Composition of true graft copolymer		Branches			Homocopolymer		
		Cellulose, %	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
<u>Agitation Time: Initial 15 min</u>									
1	15	36	64	370	1200	3.2	40	370	9.3
2	60	32	68	400	1450	3.6	48	420	8.8
9	1200	11	89	450	2580	5.7	50	280	5.6
<u>Agitation Time: Continuously during the Reaction Period</u>									
2	15	36	64	370	1200	3.2	40	370	9.3
5	120	24	76	310	1880	6.1	43	250	5.8
7	360	18	82	420	2270	5.4	53	230	4.3
10	2520	15	85	440	3780	8.6	39	270	6.9

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