Grafting Acrylonitrile onto Wood Pulp:
Influence of Process Variables

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Synopsis

Graft polymerization of acrylonitrile onto a never-dried bleached kraft pulp by the ceric ion process was not affected by the presence of air, nor by the use of technical-grade ceric salt and unpurified monomer. The initial polymerization rate and final degree of conversion to grafted polymer increased with monomer and pulp concentration. An increase in the catalyst concentration also increased the initial rate and final conversion up to a maximum value, after which they leveled off. The amount of catalyst required for a given degree of conversion was minimized when operating at high concentration of pulp and monomer and when the catalyst was added last. Attainable graft level decreased when the pulp was dried but could be brought back to its normal level after the dried pulp was beaten. The molecular weight of the polymer increased with monomer concentration but was independent of ceric salt concentration when the latter was low. The number of grafted sites increased with ceric salt concentration.

INTRODUCTION

Graft polymerization of acrylonitrile onto wood pulp followed by alkaline hydrolysis of the grafted polyacrylonitrile (PAN) into a copolymer of sodium polyacrylate and polyacrylamide has been shown to result in the formation of modified fibers with outstanding water absorbency.[1] Because of the possible industrial application of these modified fibers as absorbent sanitary products, work was carried out in our laboratories with a view to optimizing grafting conditions. Among the various redox systems used in earlier work[1] for initiating the polymerization, the cellulose–ceric ion system seemed the most promising with respect to monomer conversion and grafting efficiency and was chosen for this study.

The mechanism by which ceric ion reacts with cellulosic materials in the presence of vinyl monomers to produce graft copolymers has been studied by various authors[2-9] and will not be dealt with here in any detail. The Mino and Kaiserman[2] mechanism, which involves initiation of free radicals directly on the cellulose backbone, thus favoring grafting over homopolymer formation, is generally accepted; on the other hand, Gaylord[10] has suggested that, in the particular case of acrylonitrile grafting, there is formation of an acrylonitrile–ceric ion–cellulose complex leading to spontaneous polymerization with termination on the aldehyde groups of cellulose.

The influence of some grafting variables on grafting efficiency has been studied by Kulkarni and Mehta,[8] Hebeish and Mehta,[9] and Mansour and Schurz[11] in the

case of cotton linters, but no extensive data have been published on acrylonitrile grafting of wood pulp.

This paper reports experimental data on the influence on the graft polymerization of acrylonitrile onto softwood bleached kraft pulps of such variables as monomer and ceric ion concentration; pulp concentration; pulp type and drying history; of grafting conditions such as pH, purity of reactants, atmosphere, and reactant addition procedure.

EXPERIMENTAL

Unless otherwise specified, graft polymerization was carried out by using reagent-grade ceric ammonium nitrate, undistilled reagent-grade acrylonitrile, and a never-dried softwood pulp.

In a typical experiment, 30 g never-dried pulp (10 g dry basis) is placed in a 2-liter Erlenmeyer flask containing 180 g 0.1% HNO_3 and 10 g acrylonitrile. The flask is shaken to ensure good dispersion; 0.274 g ceric ammonium nitrate is dissolved in 30 g 0.1% HNO_3 and added immediately. The flask is then stoppered and shaken continuously for 5 min and, at 10-min intervals, for about 15 sec, during 1 hr.

Reproducibility was good, and for this reason no effort was made to operate at a constant temperature. Shaking was used rather than stirring because, except at low pulp consistencies, stirring was inefficient.

After 60 min (polymerization was usually complete in a few minutes) the pulp was washed, filtered, and dried. The weight increase, expressed in per cent, corresponds to the usual graft level (G.L.). From the weight increase, the percentage conversion of monomer to polymer was calculated and thus included graft as well as homopolymer. Previous work[1] had shown that, under normal conditions, only 5% to 7% of the polymer formed could be removed by DMF extraction. Only when using very low pulp concentration (1%) and high monomer concentration (4% or more) and high catalyst concentration (5 mmole/l. or more) was there any evidence of homopolymer formation in the aqueous phase.

RESULTS AND DISCUSSION

Influence of Grafting Conditions

pH

The pH of a 2.0 mmole/l. solution of ceric ammonium nitrate in distilled water is 2.9. While polymerization can be carried out in the absence of HNO_3, the degree of conversion, as estimated by the weight of polymer added on, increases by about 20% when 0.1% HNO_3 is used to bring the pH down to 2.2. Further decrease of the pH leads to a decrease in conversion as shown in Table I.

Controlled Atmosphere and Purity of Reactants

In the early laboratory work, care was taken to remove oxygen from the pulp dispersion and to flush it with nitrogen. Also, acrylonitrile was freshly distilled before use. It was found out later that when the degassing and flushing step was omitted, conversion was unchanged. Furthermore, conversion was also unchanged when undistilled monomer and technical-grade ceric ammonium nitrate were used.

TABLE I
Influence of pH on Grafting[a]

HNO₃ Concn, %	pH after addition of ceric salt	Conversion, %
0	2.9	58
0.009	2.7	59.5
0.076	2.3	65
0.095	2.2	70
0.475	1.7	65
0.95	1.5	60

[a] Conditions: pulp concentration, 4% w/w; monomer concentration, 4% w/w; ceric salt, 2 mmole/l.

Thus, the cellulose–ceric ion system appears particularly well suited for graft polymerization of acrylonitrile onto cellulose in a commercial process.

Order of Addition of Reactants

The order of addition of the reactants is very important and has not been given much attention until recently when Mansour and Schurz,[11] working with cotton linters, obtained higher graft level and efficiency when the monomer was added last.

The data presented here distinctly show that, at least in the case of never-dried wood pulp, the opposite is true. Figure 1 shows the results of a series of experiments where the addition of monomer was delayed. The values at time zero really correspond to the case where the monomer was added immediately before the ceric ion. It can be seen that, at low ceric ion concentration, the degree of
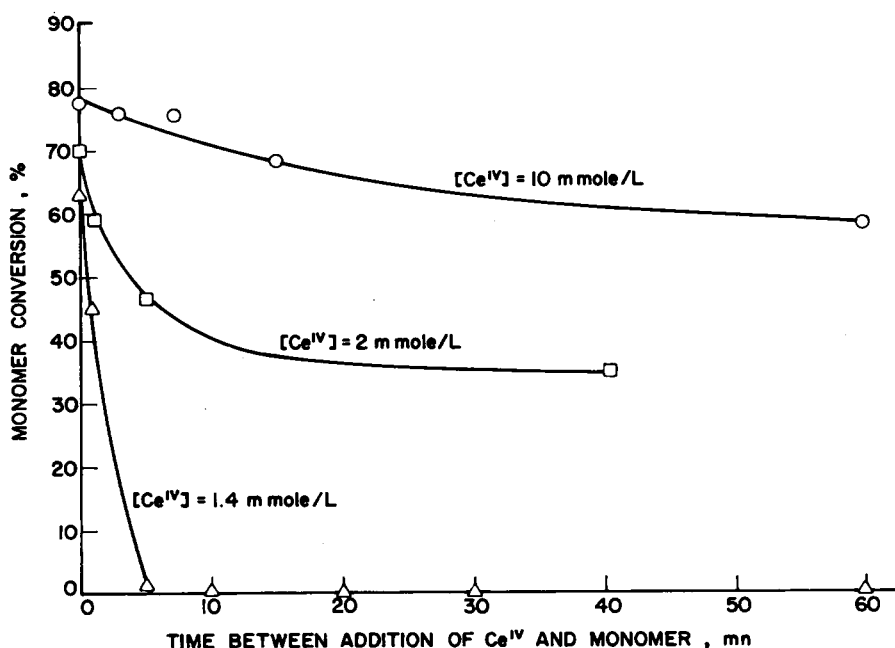

Fig. 1. Influence of delayed addition of monomer on final degree of conversion. [Pulp] = 4%, [M] = 4%.

conversion declines very quickly as the addition of monomer is delayed. At high catalyst concentrations, however, this effect is much smaller.

Ogiwara et al.,[6] in their study of the consumption of ceric ion by cellulosic materials, found that there was a very rapid initial stage, probably corresponding to the reaction of Ce(IV) with the easily reacting (or accessible) portion of the cellulose, followed by a much slower reaction, both reactions being capable of initiating graft polymerization. Approximately 50% of the total ceric ion consumed had disappeared in the first few minutes. In interpreting the results of Figure 1, it may be assumed that, at low concentration of ceric ion (1.4 mmole/l.), most of the ceric ion is reduced in the first few minutes, so that by the time the monomer is added (5 min after the ceric ion), the free radicals formed have had time to disappear by recombination or otherwise, and insufficient Ce(IV) remains to initiate polymerization.

Only when the initial concentration of Ce(IV) is high enough, does there remain ceric ions available for the second slower reaction.

Influence of Concentration of Reactants

Final Conversion

Figures 2 and 3 show some results relating to the effect of pulp concentration, monomer concentration, and Ce(IV) concentration on monomer conversion.
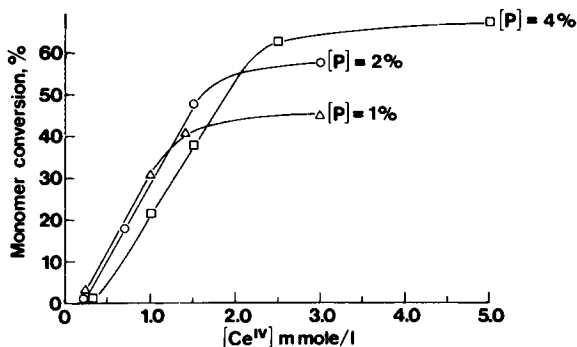

Fig. 2. Degree of monomer conversion vs. ceric salt concentration at 1% monomer concentration.
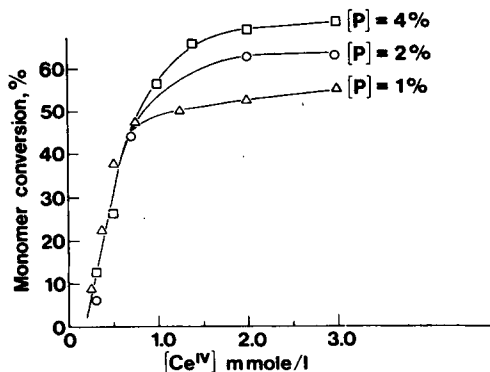

Fig. 3. Degree of monomer conversion vs. ceric salt concentration at 4% monomer concentration.

TABLE II
Percentage Conversion When Pulp and Monomer Concentration are at or Above 4% Level

[P], % w/w	[M], % w/w	[Ce(IV)], mmole/l.	Conversion, %	Graft level, %
4	4	0.3	12.5	12.5
		0.5	26	26
		1.0	56	56
		2.0	68	68
		3.0	70	70
4	8	0.3	13	26
		0.7	34	68
		2.5	69	138
		5.0	72.5	145
4	16	2	60.5	242
5	10	0.5	25	50
		1.0	31	62
		1.5	68	136
		2.0	70	140
		5.0	75	150

The per cent monomer conversion multiplied by the weight of monomer present initially and divided by the weight of pulp would give the "graft level" or "polymer add-on" usually reported in the literature.

In general, for any pulp–monomer concentration combination, no polymerization takes place until a minimum catalyst concentration is reached. The degree of conversion then increases more or less linearly with catalyst and finally tends to level off. These results agree generally with those reported by Ogiwara et al.[5] in their study of methylmethacrylate grafting on wood pulp.

Examination of Figures 2 and 3 leads to the following observations: (i) The slope of the linear portion of the curves was relatively independent of pulp concentration but increased with monomer concentration. (ii) The level-off value of the conversion increased with pulp or monomer concentration when either concentration was lower than 4%.

However, when both pulp and monomer concentrations were 4% or more, the degree of conversion became a function only of catalyst concentration, as can be seen in Table II. As a result, above 4% pulp and monomer concentration, graft level was linear with monomer concentration at any given catalyst concentration.

In their attempt to elucidate the mechanism of the reaction of ceric ion with cellulose, Ogiwara and Kubota[6] have shown that the amount of ceric ion absorbed by cellulose first increases linearly with bulk Ce(IV) concentration and then levels off. In order to see whether the leveling-off of the curve of percentage conversion versus [Ce(IV)] coincided with a leveling-off in the Ce(IV) adsorption curve, the Ce(IV) adsorption was determined using these authors' procedure for analysing for cerium; this is shown in Figure 4. The curve does indeed level off but at 25–30 mmole/l. ceric ion concentration, far in excess of 2 mmole/l., the value corresponding to level-off conversion.

It may be noted from Figure 4 that, up to concentrations of about 8 mmole/l., all ceric ions disappear from the surrounding solution and are present in the fibers in the absorbed or reduced form. This is presumably the reason why there is so little homopolymer formation. Also, while the data of Figure 3 were obtained after 60 min of contact time, in separate experiments no difference was found

TABLE III
Molecular Weight of PAN Versus Grafting Conditions[a]

[M], % w/w	[Ce(IV)], mmole/l.	M_ν[b]	Number of polymer chains per 1000 AGU
1	2.5	64,000	0.39
4	2.0	238,000	0.45
4	0.5	226,000	0.19
4	1.4	244,000	0.43
4	2.0	238,000	0.45
4	10.0	145,000	0.86

[a] Pulp concentration was 4% in all experiments.
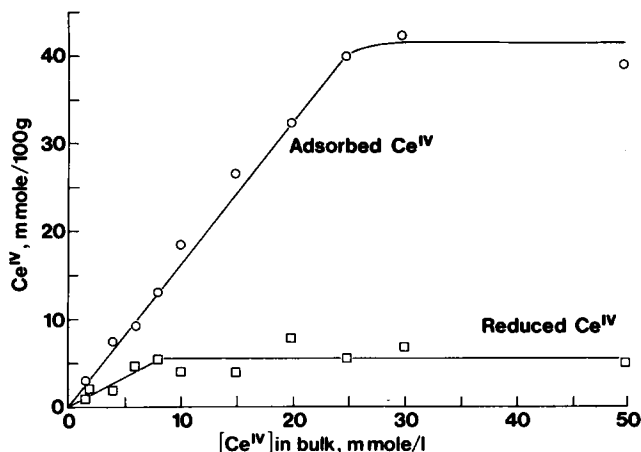[b] From $[\eta]_{DMF} = 2.43 \times 10^{-4} \bar{M}_\nu^{0.75}$.[12]

Fig. 4. Adsorption of ceric ion by pulp versus bulk ceric ion concentration. [Pulp] = 4%.

between 2 min (minimum possible time· for carrying out the titration) and 60 min. This behavior confirmed that the reaction is very fast.

In order to get a better understanding of why the final percentage conversion for a given [Ce(IV)] is independent of monomer concentration (at pulp and monomer concentrations of 4% or more), a look at molecular weights is helpful. Ogiwara et al.,[5] in an extensive study of the molecular weights of poly(methyl methacrylate) grafted onto cellulosic materials by using Ce(IV) as catalyst, found that the molecular weight increased linearly with monomer concentration and that the number of grafted chains increased with [Ce(IV)].

While only a few molecular weight determinations were made in the present work, the results indicate that the same trends appear to hold in the case of PAN grafting.

As seen in Table III, the molecular weight quadrupled when the concentration of monomer was raised from 1% to 4%, but was independent of [Ce(IV)] up to 2 mmole/l. (the value which corresponds to the level-off percentage conversion). At the same time, the number of grafted chains per anhydroglucose unit (AGU) increased with [Ce(IV)] but seemed independent of [M] in the 1% to 4% concentration range.
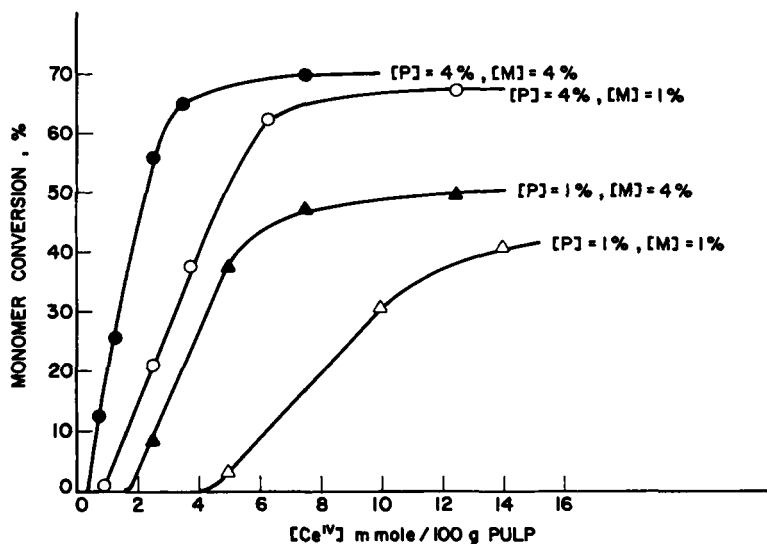
Fig. 5. Degree of conversion vs. amount of ceric salt used per 100 g pulp.

If one can assume that the number of grafted sites is a function only of [Ce-(IV)] and the molecular weight a linear function of [M], then the independence of conversion on [M] would be explained. The big unknown here is the mechanism of the termination reaction.

Above 2 mmole/l. Ce(IV) concentration, the number of grafting sites continues to increase but more slowly, and the molecular weight of the chains decreases, which indicates a contribution of the excess ceric ion in the termination step, as mentioned by Ogiwara et al.[5]

The fact that the percentage conversion is not very sensitive to pulp concentration when the latter is low and becomes fully independent of it when it reaches 4% or more is very important from an economical standpoint. This can be seen in Figure 5, where the same data as in Figures 2 and 3 are plotted; but here, catalyst concentration is expressed on the basis of pulp. It is clear that the amount of costly ceric ion required to achieve a given degree of conversion, i.e., a given weight of grafted product, is minimized when both pulp and monomer concentration are high.

Kinetics

Attempts to follow the rate of conversion versus time at constant temperature led to erratic results, except when both pulp and monomer concentration were low. The reason lies in the poor heat transfer during the first phase of the polymerization where the rate is high.

Since in commercial practice one would use high pulp and monomer concentration to minimize catalyst consumption, as was just shown, it was decided to operate under adiabatic conditions, i.e., under conditions more representative of what would happen in a real process.

A polyethylene bottle well insulated with polyurethane foam and fitted with a thermometer was used in these experiments. The bottle was shaken all the time until the temperature reached its plateau value.
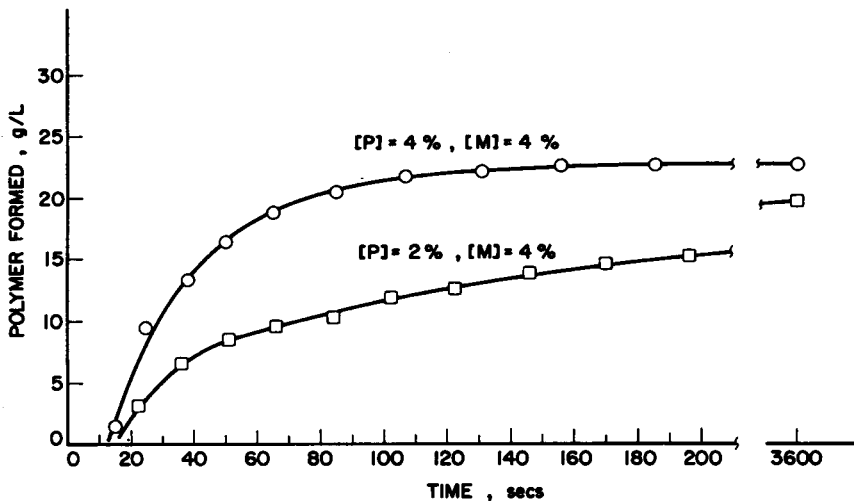
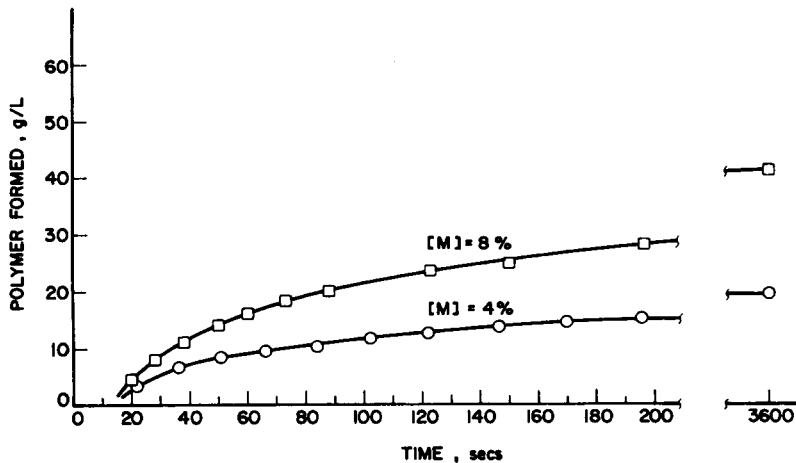Fig. 6. Influence of pulp concentration on polymerization rate. [Ce(IV)] = 2 mmole/l.; [M] = 4%.

Fig. 7. Influence of monomer concentration on polymerization rate. [Ce(IV)] = 2 mmole/l.; [pulp] = 2%.

The influence of pulp concentration, monomer concentration and catalyst concentration can be seen in Figures 6, 7, 8, and 9 where the quantity of polymer formed, as calculated from the temperature rise, heat capacity, and heat of polymerization (Appendix) is shown versus reaction time. Since neither the polymerization rate expression nor its temperature dependence are known, the results can be interpreted only in a qualitative way.

In Figure 6, the influence of pulp concentration is shown at one monomer level. At 4% pulp consistency, the initial rate of polymer formation is higher and its final level reached more quickly than in the 2% consistency case. The reason for the higher initial rate at 4% consistency is simply explained: Each fiber, in both the 2% and 4% cases, is surrounded at the beginning by the same catalyst and monomer concentration. Thus, even though the rate of polymerization per fiber
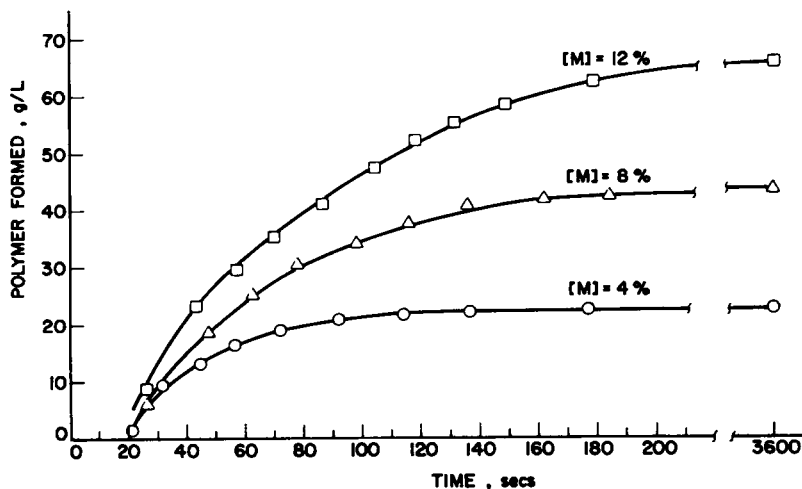
Fig. 8. Influence of monomer concentration on polymerization rate.   [Ce(IV)] = 2 mmole/l.; [pulp] = 4%.
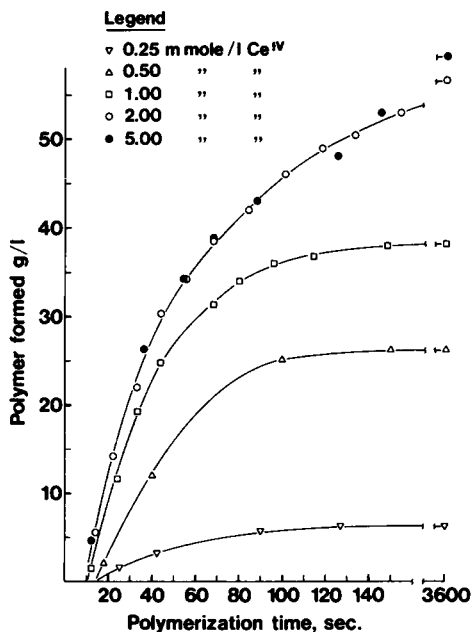

Fig. 9. Influence of ceric salt concentration on polymerization rate. [Pulp] = 4%; [M] = 8%.

is probably the same, there are twice as many fibers at 4% consistency as there are at 2%, so that the total polymer formed per unit time is greater.   As the reaction proceeds, each fiber in the 4% consistency case sees the concentration of monomer decrease much more quickly because of the competition from its neighbours; and this, coupled with the temperature dependence of the reaction rate constant, would explain why the curve levels off more quickly than in the 2% case.

In Figures 7 and 8, the influence of monomer concentration can be seen at 2% and 4% pulp consistency.   In both cases, the initial rate increases with monomer concentration, as would be expected in conventional polymerization kinetics.

Finally, the influence of ceric ion concentration is shown in Figure 9 at 4% pulp consistency and 8% monomer concentration.   One notes here that the initial rate of polymer formation increases quickly first with Ce(IV) concentration but becomes independent of it above 2 mmole/l.

Thus, catalyst concentration below 2 mmole/l. influences both the initial polymerization rate and the final degree of conversion, presumably by increasing the rate of production of grafting sites as well as their total number.   Above 2 mmole/l., however, the rate of production becomes independent of [Ce(IV)] but the total number of grafting sites per 1000 anhydroglucose units continues to increase, as was shown in Table II.

It is interesting to note here that the final conversion values obtained using adiabatic conditions were in good agreement with those obtained under nonadiabatic conditions.   This would indicate that the final degree of conversion is fairly independent of temperature, at least in the range of 20–40°C.   Adiabatic grafting experiments carried out at initial temperatures of 13° and 46°C, respectively, have further confirmed this temperature insensitivity of the final percentage conversion.

Influence of Pulp Drying History and Pulp Type

Drying History

As was mentioned in the experimental section, a never-dried pulp was used in most of this work.   It is now well established that graft polymerization onto cellulose is sensitive to the degree of swelling, i.e., accessibility, of the substrate. It could then be expected that grafting level would decrease once the pulp was dried, but would increase again if the dried pulp were beaten.   Indeed, this was verified experimentally, as shown in Table IV.

TABLE IV
Influence of Pulp Drying History and Type[a]

Pulp description	Graft level, %
A.　Never-dried, bleached mixed soft woods, unbeaten	70
B.　Same pulp as A but commercially dried	
unbeaten	48
beaten to 600 CSF	64
beaten to 450 CSF	68
C.　Spruce bleached kraft, commercially dried	
unbeaten	50
beaten to 700 CSF	57
beaten to 576 CSF	61
D.　Southern pine bleached kraft, commercially dried	
unbeaten	50
beaten to 585 CSF	60

[a] Grafting conditions: pulp, 4% w/w concentration; monomer, 4% w/w concentration; [Ce(IV)], 2.0 mmole/l.

Pulp Type

Two other commercial pulps, both bleached kraft, one spruce and one southern pine, were evaluated under similar conditions. There was little difference between the three commercially dried unbeaten pulps, and beating in all cases increased the graft level, although not to the same extent (Table IV).

Recycling of Monomer

In a commercial process, recycling of the unconverted monomer (30–40% of the initial charge) would be necessary for obvious economical reasons. In order to see whether recycling the monomer had any detrimental effect, a sample of pulp was grafted using 4% pulp consistency, 8% monomer concentration, and 1.5 mmole/l. Ce(IV) concentration. After the grafting reaction, the grafted pulp was filtered, and the filtrate volume was measured and brought back to its original concentration by adding an amount of fresh monomer equivalent to that consumed during the polymerization. A new batch of pulp was processed with this solution. After 10 cycles, there was no change in the percentage conversion. This is not surprising because, as indicated previously, at the concentration of ceric ion used (1.5 mmole/l.), there is no residual ceric ion in the filtrate which could accumulate and cause homopolymerization of acrylonitrile in the long run.

SUMMARY

Graft polymerization of acrylonitrile onto bleached kraft pulps by the ceric ion process can be carried out in the presence of air, using technical-grade ceric ammonium nitrate and undistilled acrylonitrile.

Optimum results are obtained by (a) using a never-dried pulp, although beating the dried pulp brings the polymer add-on substantially to the same level, and (b) adding the ceric ion catalyst to the pulp slurry after mixing the monomer with the pulp.

The amount of ceric ion required for a given degree of polymer grafting is minimized when one operates at high concentrations of pulp and monomer.

The polymerization rate increases with both monomer and ceric ion concentration, and, under normal conditions, polymerization is completed in a matter of minutes.

Appendix

The quantity of polymer formed during the adiabatic grafting experiments was calculated according to the following expression:

$$\text{polymer formed, g/l.} = \frac{\Delta\theta[BC_{pB} + SC_{pS}]}{\Delta H_p \times V}$$

where $\Delta\theta$ = temperature rise, °C; B = weight of PE bottle, g; C_{pB} = specific heat of PE, 0.475 cal/g°C(13); S = weight of slurry, g; C_{pS} = specific heat of slurry, and assumed to be 1.0 cal/g°C; ΔH_p = heat of polymerization of acrylonitrile, 326 cal/g[13]; V = volume of slurry, liters (assuming specific gravity 1.0).

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