

## The Xanthate Method of Grafting. IV. Grafting of Acrylonitrile onto High-Yield Pulp

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### Synopsis

A series of pulps with different lignin content was prepared from a softwood sodium bisulfite high-yield pulp. Sodium chlorite at pH 4 served as the delignification agent. The resulting pulps were subjected to grafting with acrylonitrile using the cellulose xanthate-hydrogen peroxide redox system to initiate the copolymerization reaction. The resulting products were isolated and analyzed for homopolymer content by dimethylformamide extraction. The results indicate that the presence of larger amounts of lignin in pulp may have a favorable effect on grafting. The plots of total conversion as well as of polymer loading show a minimum centered around approximately 15% of lignin. This minimum is observed invariably at five different reaction times and it coincides with the maximum concentration of reductive groups in the pulps as well as with the maximum cation exchange capacity. The parameter of grafting efficiency has a tendency to increase with rising lignin content, reflecting the lower relative yields of homopolymer obtained with high-lignin pulps. This observation is discussed in relation to possible chain transfer reactions by lignin.

### INTRODUCTION

It is a well-known fact that the presence of residual lignin in cellulose has an important effect on its reactivity and that this effect occurs already at very low levels of lignin content. It is therefore not surprising that the aptitude of pulp or cellulose toward chemical modification by grafting should depend on the degree of removal of lignin. Given the fact that lignin is easily oxidized by most conventional oxidants which are in turn often used to initiate graft copolymerization, one expects that its presence will retard, if not inhibit, the reaction simply because the initiator will be used up preferentially in the reaction with lignin. Moreover, the reaction of lignin with oxidants gives rise to the formation of quinonoid structures which have pronounced retarding and/or inhibiting properties.

Several articles have been published in the recent years examining in more or less detail the effects mentioned above. Perhaps the most complete study was undertaken by Straforelli<sup>1</sup> who investigated the effect of lignin as well as of several phenylpropane-based model compounds on the graft copolymerization of methyl methacrylate initiated by azobisisobutyronitrile. Another study by Kubota and Ogiwara<sup>2</sup> examines the effect of lignin in a ceric ion-initiated graft copolymerization of methyl methacrylate on high-yield pulp delignified to different lignin levels. Erdelyi<sup>3</sup> prepared a series of pulps by the

sulfate cooking process and subsequent hypochlorite bleaching, and determined their graftability in a system using ceric ammonium sulfate as initiator and acrylonitrile as monomer. As a result of the three studies cited above, it was established that (a) a higher concentration of catalyst is required if copolymerization is to be carried out in the presence of lignin; (b) the presence of lignin generally reduces polymerization rate and gives rise to prolonged inhibition periods at higher lignin levels.

The xanthate grafting method<sup>4</sup> appears to have some distinct advantages over other grafting processes. Its pilot-plant exploitation to impart fire retardancy to cellulosic fabrics has been recently announced by Brickman.<sup>5</sup> Recent investigations carried out by the present authors<sup>6</sup> show that the xanthate method is capable of producing grafts containing negligible amount of homopolymers. In yet another article,<sup>7</sup> pulps of different chemical origin and degree of bleaching were subjected to copolymerization with acrylonitrile. Although some interference of the lignin with the grafting reaction was observed, satisfactory levels of grafting could be obtained with any of the pulps used having lignin content as high as 23%. Furthermore, it became evident that in sulfite pulps, the presence of lignin even seemed to improve their graftability. The present paper is hoped to shed more light on the graft copolymerization behavior of lignin in the particular case of high-yield pulps.

## EXPERIMENTAL

### Materials

High-yield sodium bisulfite softwood pulp was supplied by the Consolidated-Bathurst Research Centre, Grand-Mère, Québec. The pulp was disintegrated and washed before the delignification procedure was applied. (The authors prefer the term "delignification" over the usual technical term "bleaching" as the primary goal of the process is to remove lignin rather than change the color of the pulp.)

Acrylonitrile (Eastman Chemicals) was purified by distillation; the central cut was collected and stored in a refrigerator in dark bottles. All the other chemicals employed in this work were used such as supplied by the manufacturers.

### Delignification

The delignification procedure has been described in detail previously.<sup>7</sup> Let it only be noted that in this case, owing to the high lignin content in the original pulp, it was not practical to remove all the lignin in one single step for samples with higher degree of delignification. The procedure was therefore carried out in two or three steps in order that excessive concentrations of sodium chlorite need not be used (over 10% per weight of pulp). Higher concentrations of the oxidant could provoke degradation of the carbohydrate moiety.

A total of nine pulps have been prepared (including the original material). The pulps were characterized by standard methods of the Canadian Pulp and Paper Association. The results are summarized in Table I.

TABLE I  
Properties of Pulps Prepared by Chlorite Delignification

Pulp	Kappaa	Lignin, %	Copper index <sup>b</sup>	Carboxyl index <sup>c</sup>
BB-0	134	23.0	3.4	22
BB-1	114	19.5	3.5	29
BB-2	101	17.4	3.7	32
BB-3	90	15.5	4.0	32
BB-4	76	13.0	3.5	32
BB-5	65	11.1	3.5	30
BB-6	49	8.4	3.3	25
BB-7	35	6.1	2.4	22
BB-8	21	3.7	1.8	18

<sup>a</sup> CPPA Standard G.18.

<sup>b</sup> CPPA Standard G.22.

<sup>c</sup> TAPPI Standard T237 su-63.

### Copolymerization

The descriptions of pulp pretreatment, xanthation, as well as copolymerization procedures have been given in an earlier article.<sup>8</sup> The experimental conditions were as follows: pulp, 4.50 g  $\pm$  0.01 g (oven-dry weight); acrylonitrile, 9.00 g; surfactant, Tween-40, 0.9 g; water, 425 ml; mercerization, 45 min in 150 ml 0.75*N* NaOH (room temperature); xanthation, 2 hr (room temperature); ion exchange, 2 min in 150 ml 0.004% solution of (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>; H<sub>2</sub>O<sub>2</sub>, 1.5 g (diluted to 25 ml before adding); initial pH, 5.0  $\pm$  0.1 (adjusted with 0.1*N* H<sub>2</sub>SO<sub>4</sub>); temperature, 25°C.

### Analysis of Products

The evaluation of results has proved to be more complex in the present case than in the two previous studies.<sup>6,7</sup> Depending on their degree of delignification, the individual pulps either lost or gained weight during the pretreatment and copolymerization processes. It was therefore impossible to apply simple corrections for pulp solubility in NaOH during mercerization.

TABLE II  
Blank Experiments<sup>a</sup>

Pulp	Weight after treatment, g	Loss or gain, %	Loss on extraction, <sup>b</sup> %
BB-0	4.58	1.8	3.5
BB-1	4.70	4.4	6.6
BB-2	4.50	0.0	6.8
BB-3	4.43	-1.6	7.7
BB-4	4.34	-3.6	5.0
BB-5	4.39	-2.4	4.1
BB-6	4.18	-7.1	2.6
BB-7	4.36	-3.1	5.1
BB-8	4.40	-2.20	5.9

<sup>a</sup> Weight of dry pulp charged, 4.50 g.

<sup>b</sup> Extraction with DMF during 12 hr under vacuum.

Instead, blank experiments were carried out in each case whereby a pulp sample was subjected to the complete procedure except for the absence of monomer. The resulting weights of blank remaining after the treatment were than considered equal to the parameter  $B$ , i.e., the weight of pulp present in the copolymerization product.

Further complications resulted from the fact that the pulps themselves undergo a slight weight loss on extraction with dimethylformamide. As a consequence, once again, blank experiments had to be carried out for each particular pulp and appropriate corrections had to be applied when calculating the copolymerization parameters. The results of the blank experiments referring to both weight changes due to the chemical treatment as well as due to extraction are summarized in Table II. Taking due account of the aforementioned corrections, the copolymerization parameters were calculated according to the following equations:

$$\text{total conversion, \%} = [(D - B)/C] \times 100 \quad (3)$$

$$\text{polymer loading, \%} = [(A - B)/B] \times 100 \quad (4)$$

$$\text{grafting efficiency, \%} = [(A - B)/(D - B)] \times 100 \quad (5)$$

where  $A$  is weight of products after copolymerization and extraction,  $B$  is weight of pulp substrate in the copolymerized products,  $C$  is weight of monomer charged, and  $D$  is total weight of products after copolymerization.

## RESULTS AND DISCUSSION

Each pulp in the series was subjected to copolymerization at five different reaction times ranging from 30 min to 18 hr. The results corresponding to the individual pulps having different lignin content are shown separately in Tables III–XI. Each table shows the following parameters: the total weight of dry products obtained, the total conversion to polymer, polymer loading, and grafting efficiency. In some cases, namely, when total conversion to polymer was near to zero, it was impossible to determine the parameter of grafting efficiency with a sufficient accuracy. In such cases, and similarly wherever total conversion is equal to zero, the grafting efficiency is not given.

It is generally agreed that in most copolymerization systems the presence of lignin causes the reaction rate to drop and brings about prolonged inhibi-

TABLE III  
Copolymerizations with Pulp BB-0

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %	Deviation from the mean, %
30	4.86	6.1	6.1	51.0	—
60	6.44	20.7	33.1	81.5	+1.9
60	6.20	18.0	28.0	79.2	-1.0
60	6.14	17.4	28.6	83.6	+4.5
60	6.35	19.6	29.1	75.6	-5.5
90	6.65	23.0	37.0	81.8	—
120	6.97	26.5	47.5	91.2	—
18 hr	11.57	80.1	127.2	75.1	—

TABLE IV  
Copolymerizations with Pulp BB-1

Time, min	Weight of products, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.70	0	0	—
60	5.63	10.4	13.4	67.3
90	5.94	13.7	24.0	91.0
120	6.68	22.0	36.3	86.0
18 hr	10.63	65.9	84.6	67.0

TABLE V  
Copolymerizations with Pulp BB-2

Time, min	Weight of products, %	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.64	1.6	1.7	53.1
60	5.39	10.0	8.3	41.5
90	5.55	11.7	12.6	54.1
120	6.58	23.2	34.9	75.2
18 hr	11.26	75.2	111.0	73.8

TABLE VI  
Copolymerizations with Pulp BB-3

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.52	0	0	—
60	4.54	0	0	—
90	5.11	7.6	14.6	94.8
120	5.80	15.3	22.5	69.4
18 hr	11.01	73.2	98.7	66.4

TABLE VII  
Copolymerizations with Pulp BB-4

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.61	3.1	0	—
60	4.93	6.6	9.2	66.8
90	5.26	10.3	16.3	76.6
120	5.59	14.0	17.9	61.8
18 hr	11.46	79.1	87.5	53.3

TABLE VIII  
Copolymerizations with Pulp BB-5

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.38	0	0	—
60	4.79	4.6	3.1	33.0
90	5.25	9.6	9.6	48.7
120	5.62	13.7	15.2	54.1
18 hr	10.74	70.6	72.8	50.2

TABLE IX  
 Copolymerizations with Pulp BB-6

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	4.37	2.1	1.9	42.4
60	5.09	10.2	8.9	40.4
90	5.53	15.0	10.2	31.4
120	7.00	31.4	40.7	60.3
18 hr	11.32	79.4	79.5	46.5

tion periods.<sup>1,2,3</sup> There are, however, some indications that higher lignin content may not always be to the detriment of pulp graftability.<sup>9</sup> A recent work<sup>7</sup> published by the present authors demonstrated that, in the case of sulfite pulp copolymerization with acrylonitrile by the xanthate method, the grafting efficiency increased with rising lignin content while the total conversion remained almost constant. Kraft pulps, on the other hand, gave a higher total conversion to polymer with rising lignin content, with a simultaneous increase in the amount of homopolymer.

It is evident from Figure 1 that the high yield bisulfite pulp shows a more complex behavior. The plots of total conversion versus lignin content at five different reaction times clearly indicate the presence of a minimum. This minimum conversion is observed at approximately 12–15% of lignin, and it occurs quite regularly and independently of the time of reaction. At the shortest reaction time used (30 min), zero formation of polymer is observed in the interval between 10% and 20% lignin. Both below and above this interval, a small but distinct conversion to polymer takes place. The reappearance of polymerization at higher lignin levels is even more evident at longer reaction times. At 60 min of copolymerization time, for example, about 15% conversion is observed when the lignin content is 3–5%. The conversion then decreases until it reaches about 5% at 15% lignin and increases thereafter to almost 20% at 23% of lignin in the pulp. A similar behavior is observed with 90 and 120 min of reaction time. In the case of 18-hr polymerizations, fairly high conversions are recorded throughout the range of lignin content employed; the presence of a minimum is nonetheless evident.

Figure 2 shows the dependence of polymer loading as a function of lignin content. According to its definition, the parameter of polymer loading expresses the ratio of the weight of polymer *truly* grafted to the weight of the pulp substrate. Once again, it is possible to observe the presence of a minimum on the polymer loading-versus-lignin curves, which is situated at ap-

 TABLE X  
 Copolymerizations with Pulp BB-7

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	5.04	7.6	9.8	62.7
60	5.44	12.1	15.9	63.7
90	7.11	30.6	36.6	58.0
120	9.05	52.2	55.4	51.4
18 hr	12.06	85.6	86.2	48.7

TABLE XI  
 Copolymerizations with Pulp BB-8

Time, min	Weight of products, g	Total conversion, %	Polymer loading, %	Grafting efficiency, %
30	5.09	7.7	12.0	76.1
60	5.99	17.7	24.9	68.7
90	8.16	41.8	38.6	45.1
120	9.28	54.2	53.0	47.8
18 hr	12.24	87.2	91.2	51.2

proximately 11–16% lignin. The upturn of the conversion curves at higher lignin levels is even more pronounced in this case—a fact which reflects the higher grafting efficiency values obtained with high-lignin pulps.

It should be noted here that the parameter of grafting efficiency itself shows a considerable scatter, in particular for the three lower reaction times (30, 60, and 90 min). This observed scatter is believed to be due mainly to low conversion levels obtained in the midrange of lignin content. Even with copolymerization times as long as 90 min, conversions lower than 10% were often obtained. If one considers an accuracy of  $\pm 3\%$  for the extraction method of determining the amount of homopolymers, the calculation of grafting efficiency will be afflicted with an error of  $\pm 10\%$  at 10% conversion and  $\pm 20\%$  at 5% conversion. These errors are further compounded by the uncertainties involved in the blank experiments. In practice, however, the grafting efficiency values found in four separate 60-min experiments (conversion level  $\sim 20\%$ ) do not deviate from the mean value by more than  $\pm 5\%$ , and this is believed to be sufficiently low to justify the present discussion.

The grafting efficiency data are plotted against lignin content in Figure 3. When one disregards the low-conversion points (compare with the corresponding points in Fig. 1), the trend of grafting efficiency to increase with rising lignin content becomes apparent. The points pertaining to the two longest copolymerization times (120 min and 18 hr) have been interconnected by means of straight lines to illustrate the above mentioned trend.

The mechanism that might lead to this type of behavior is not yet com-

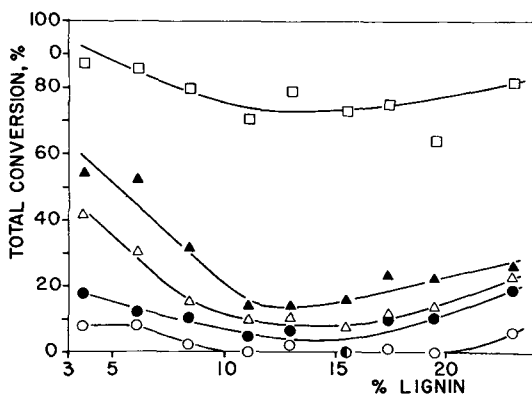


Fig. 1. Dependence of total conversion on lignin content and on reaction time: (○) 30 min; (●) 60 min; (△) 90 min; (▲) 120 min; (□) 18 hr.

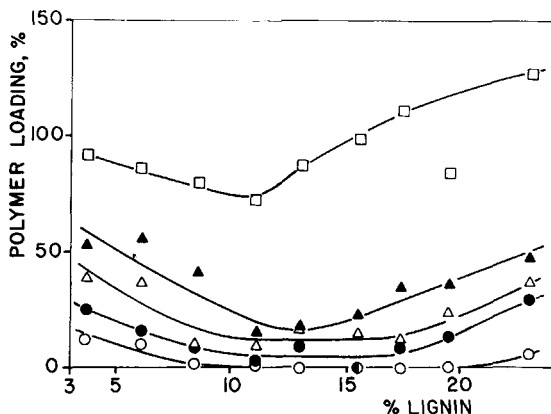


Fig. 2. Dependence of polymer loading on lignin content and on reaction time: (O) 30 min; (●) 60 min; (△) 90 min; (▲) 120 min; (□) 18 hr.

pletely clear. It is certain, however, that lignin participates actively in the copolymerization reaction. Results published by Sakata and co-workers<sup>10</sup> on the grafting of styrene onto woody fibers by radiation indicate that 40–80% of all polystyrene branches formed were grafted to lignin. Lignin also showed a much higher branching density (i.e., the number of branches per gram of substrate) than the carbohydrate component, and the molecular weight of the branches attached to lignin was two to four times lower than of those attached to carbohydrates. This last observation is in agreement with the results of Kubota and Ogiwara<sup>2</sup> obtained in a completely different system (softwood semichemical pulp, delignified to 0.2–20% lignin content; ceric ion initiator; methyl methacrylate as monomer). They found that the average molecular weight of grafts became lower in samples having a larger lignin content and that the number of grafts formed increased proportionally up to lignin content of about 2.5%. This effect, however, was accompanied by a sharp decrease in polymer loading.

The molecular weight effect observed in the two studies cited above was also recorded by the present authors in previous investigations.<sup>7</sup> Copolymerizing a sulfite softwood pulp with acrylonitrile by the xanthate method, a mo-

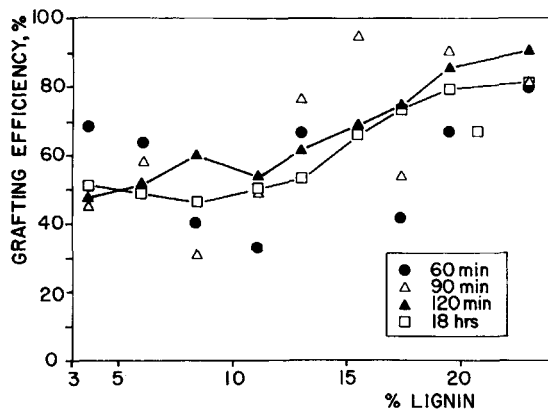


Fig. 3. Dependence of grafting efficiency on lignin content and on reaction time.



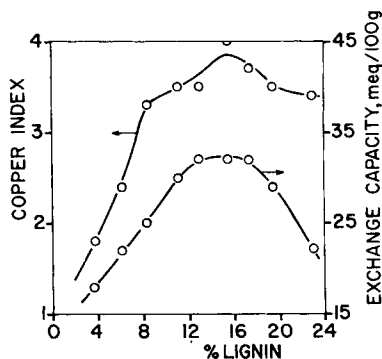
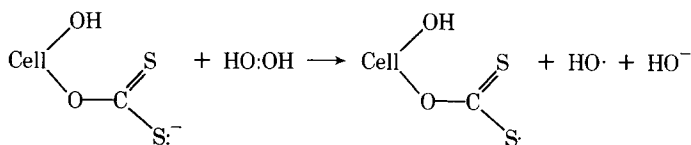


Fig. 4. Copper index and cation exchange capacity as a function of lignin content.

lecular weight decrease from 65,000 to 17,500 was observed corresponding to a lignin content increase from 1.6% to 7.0%. The total formation of polymer did not change considerably in this case. In a parallel investigation using a Kraft pulp, the graft molecular weight behaved rather erratically due to experimental difficulties and was generally quite low ( $\leq 20,000$ ). The total conversion to polymer as well as polymer loading, however, increased remarkably with rising lignin content. It is, therefore, evident that the degree to which lignin interferes with the grafting reaction varies from one type of pulp to another, depending largely on its chemical history.

A simple explanation for the effects of lignin on reaction rate and graft molecular weight may be based on a mechanism involving chain transfer by lignin. According to Kraessig<sup>11</sup> as well as to Dimov and Pavlov,<sup>12</sup> the initiation reaction in the xanthate method gives rise both to cellulose macroradicals and to hydroxyl radicals (if lignin-bound xanthates are present, then lignin macroradicals may also be formed):



The latter either recombine or bring about the formation of homopolymers. In the presence of a reactive transfer agent such as lignin, however, there is a great probability that these radicals will be scavenged by the reaction with lignin giving more stable and hence less reactive radicals. It has been demonstrated by Straforelli<sup>1</sup> that lignin does, in fact, cause inhibition and/or retardation in polymerizing systems. He does not report any data on the individual formation of homopolymers and copolymers. It appears probable, however, that the lignin present in the reaction mixture may reduce the formation of homopolymers in two ways: (a) by transforming hydroxyl radicals formed by the redox reaction into lignin radicals, thus limiting the number of homopolymer chains formed; (b) by the recombination of growing homopolymer chains with lignin radicals leading to the formation of copolymers.

Owing to the low reactivity of lignin radicals, the overall reaction rate decreases. The high frequency of transfer is further reflected in the increased

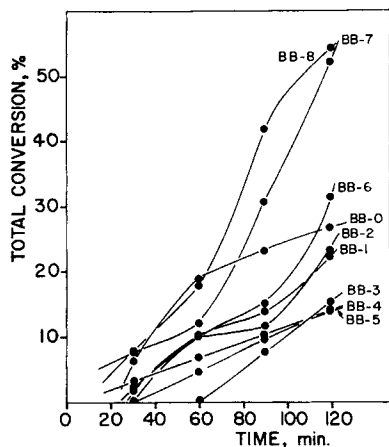


Fig. 5. Total conversion-time curves for pulps with different lignin content.

number of grafts (and their lower average molecular weight), of which a great part may be attached to the lignin moiety.

Because of the complexity of lignin structure and to the different character of lignocellulosic substrates used in the studies cited above, it is difficult to make any general conclusions. A number of factors remain to be evaluated such as the conditions of pulping, wood species, etc. Correlations based on one macroscopic parameter such as the concentration of lignin are bound to have but a limited significance. Other important parameters include the percentage of hemicelluloses, the presence of reactive groups, etc. One interesting phenomenon, which may or may not be coincidental, has been observed in the present work. In Figure 4, copper index (corresponding to the content of reducing groups in pulp) and cation exchange capacity are plotted against lignin content. Both curves show a maximum centering around 15% lignin, i.e., at the same lignin content which gives minimum total conversion

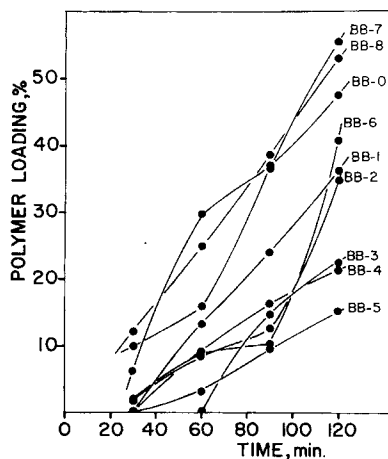


Fig. 6. Polymer loading-time curves for pulps with different lignin content.

and polymer loading in the copolymerization reaction. While some direct correlation appeared to exist in the previous work<sup>7</sup> between the graftability of a sulfite pulp and its exchange capacity, the behavior observed in the present work seems to contradict it. A detailed work with model compounds would be required to further elucidate the mechanism of lignin participation in the copolymerization reaction.

An alternative scheme for grafting on cellulose has been recently brought forth by Gaylord.<sup>13,14</sup> He proposed that cellulose-monomer interaction or complexation plays a major role in the grafting of acceptor monomers such as acrylic esters, amide, or nitrile on cellulose in the presence or absence of catalyst. Although Gaylord has not studied systems involving lignin, it is conceivable that the presence of lignin in the grafting substrate could have an important effect on the character of charge-transfer complexes formed and give rise to the effect observed in the present work. In absence of further evidence, however, the authors of this work consider the radical polymerization and transfer scheme discussed above to be more plausible.

The total conversion data are reinterpreted in the form of time-conversion curves in Figure 5. The curves illustrate the presence of inhibition periods for most samples. The longest inhibition period is observed in the case of the pulp sample BB-3 (15.5% lignin), while the samples BB-7 and BB-8 (6.1% and 3.7% lignin, respectively) show no inhibition periods. Samples containing higher amounts of lignin generally show decreased overall polymerization rate.

In Figure 6, the parameter of polymer loading is plotted against time. A comparison with the foregoing figure reveals even more clearly that it is the homopolymerization reaction, in particular, which is slowed down in the presence of lignin. After an initial inhibition period, the sample with the highest lignin content (BB-0) undergoes a fast copolymerization reaction whose rate is comparable to that observed in the case of the low-lignin samples (BB-7, BB-8). The middle-range samples (BB-3, BB-4, and BB-5) once again show the lowest yields. The results are not sufficient to carry out a complete kinetic analysis, although some deductions can be made about the reactivity of pulps: % lignin < 7%, no inhibition period, some retardation of homopolymerization; 7 < % lignin < 18, a prolonged inhibition period followed by retardation, minimum rate at 11–15% lignin; % lignin > 18, an inhibition period followed by fast copolymerization, homopolymerization retarded.

It would thus appear that in the present work, the lignin in the pulp in fact improves the "true" grafting reaction by partly eliminating the formation of homopolymers. This effect appears to be of a great importance for future applications of grafting onto wood pulp and cellulose. Further studies are carried out in this laboratory to cast more light on the mechanisms which give rise to the occurrence of the effects observed in the present study.

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