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Guo-Zhen Zheng[ab]; Bian-An Zhao[a]; Shu-Jie He[a]; Jie Gao[a]
[a] Guaugzhou Institute of Chemistry Chinese Academy of Sciences Guangzhou, Guangdong, People's Republic of China [b] Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Toyko, Japan

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INITIATION OF GRAFT COPOLYMERIZATION BY DIRECT OXIDATION OF LIGNOCELLULOSE WITH $KMnO_4$ AND ITS MECHANISM

GUO-ZHEN ZHENG,*† BIAN-AN ZHAO, SHU-JIE HE, and JIE GAO

Guaugzhou Institute of Chemistry
Chinese Academy of Sciences
Guangzhou, Guangdong, People's Republic of China

Key Words: Grafting; Potassium permanganate; Grafting mechanism of lignin; Lignocellulose; Bagasse pith

ABSTRACT

The oxidation of bagasse pith, a lignocellulose material, with potassium permanganate in dilute sulfuric acid solution creates active sites for grafting onto lignin and holocellulose. The grafted poly(methyl methacrylate) chains on lignin and holocellulose were separated, respectively, by delignification with sodium chlorite and hydrolysis of holocellulose with 72% sulfuric acid, and their molecular weights were measured. Lignin shows quite higher reactivity to grafting than does holocellulose. The roles of phenolic hydroxyl, alcoholic hydroxyl, and carbonyl groups of lignin are discussed by investigating the effect of pretreatments of lignocellulose on grafting, and a suitable grafting mechanism is proposed.

†Present address: Department of Forest Products, Faculty of Agriculture, The University of Tokyo, Toyko, Japan.

INTRODUCTION

Graft copolymerization has been known as a useful way to improve the properties of many natural polymers with the goal of extending their applications. Up to now, many initiation systems, such as Ce^{4+} [1, 2], xanthate-Fe^{2+}-H_2O_2 [3], Fe^{2+}-H_2O_2 [4-6], $NaHSO_3$-soda lime glass [7, 8], $KMNO_4$ [9, 10] and irradiation techniques [11], have been adopted in the modification of lignocellulose materials, including bamboo, unbleached pulp, and bagasse and jute fiber.

Lignocellulose mainly consists of cellulose, hemicellulose, and lignin. In order to convert bagasse pith (a waste removed from bagasse before cooking in a paper mill) into a thermoplastic material, we investigated Fe^{2+}-H_2O_2-initiated graft copolymerization and revealed that the lignin of bagasse pith is more reactive to graft copolymerization than is holocellulose [12], though phenolic hydroxyl groups, which lignin contains, were found to be unfavorable to radical graft copolymerization. The higher reactivity of lignin to graft copolymerization is ascribable to the high reactivity of the aromatic nuclei of lignin to attack by hydroxyl radicals.

By contrast with Fe^{2+}-H_2O_2 redox, $KMnO_4$ cannot initiate graft copolymerization by itself but instead does so via the oxidation of substrate. The oxidation of cellulose by $KMnO_4$ and consequent grafting have been studied extensively [13-15] while the oxidations of lignin are still unknown, though it has been pointed out that the chemical structures of lignin play an important role in the graft copolymerization of lignocellulose initiated by oxidation with $KMnO_4$ [9, 10]. During graft copolymerization onto lignocellulose, lignin doesn't behave as simply as does cellulose due to its more complex structure. The purpose of this study is to reveal the roles of alcoholic hydroxyl, phenolic hydroxyl, carbonyl groups, and aromatic nuclei of lignin in the formation of graft sites.

EXPERIMENTAL

Purification of Bagasse Pith

Bagasse pith was pulverized, and the 40-60 mesh part was extracted with a benzene-ethanol mixture (2:1 v/v) for 6 hours in a Soxhlet apparatus and then with hot deionized water three times in a beaker. The klason lignin content was 24.2% and the ash content about 1%.

Methylation of Bagasse Pith with Diazomethane

Diazomethane, prepared from 10 g nitrosomethylurea, was dissolved in 250 mL of 1,4-dioxane, and then 10 g of purified bagasse pith was added. The mixture was kept at 0°C for 4 days, and then the same amount of diazomethane, dissolved in 20 mL diethyl ether, was added again. After storage at 0°C for another 4 days, the reaction mixture was filtered and the residue was washed with de-ionized water. During washing, 0.1% aqueous acetic acid was used to decompose the residual diazomethane.

Methylation of Bagasse Pith with CH_3OH-HCl

Bagasse pith (10 g) was added to 250 mL of 2 N methanolic hydrochloric acid, and the methylation was carried out at room temperature for 2 days. The product was purified in the same manner as described above.

Reduction of Carbonyl Groups with Sodium Borohydride

In a three-neck flask, purified bagasse pith (10 g) was reacted with 2.5 g sodium borohydride in 250 mL ethanol under nitrogen atmosphere at room temperature for 24 hours. The same method as described in the methylation section was also used in the purification of the reaction product.

Graft Copolymerization and Separation of Grafted PMMA Chains

Bagasse pith [dry weight (W_0), 0.500 g] was soaked in 25 mL of aqueous $KMnO_4$ solution at the prescribed temperature for 30 minutes and then was washed with de-ionized water in a sintered glass crucible. The residue was transferred into a 50-mL three-neck flask using 20 mL de-ionized water. After the contents were bubbled with nitrogen gas for 15 minutes, 1.0 mL monomer and the other reagents were added. A total of 25 mL of de-ionized water was used as the reaction medium. After reaction under a nitrogen atmosphere with gentle stirring, graft copolymer and homopolymer were collected by filtration with a sintered glass crucible and then were treated with 10% $NH_2OH \cdot HCl$ dissolved in 1 M H_2SO_4 to reduce the oxidants to water-soluble Mn^{2+} ions. The residue was washed and dried under vacuum to a constant weight (W_1). The dried residue was then extracted with acetone in a Soxhlet apparatus for 24 hours to remove homopolymer and dried under vacuum to a constant weight (W_2).

The separation of grafted PMMA chains from lignin and holocellulose has been described elsewhere [12], and its procedure is illustrated by Scheme 1.

The viscosities of the grafted PMMA chains were measured in acetone at 25.00 ± 0.05°C, and the following Mark–Houwink equation, which was calibrated by number-average molecular weight [16], was adopted to calculate the molecular weights.

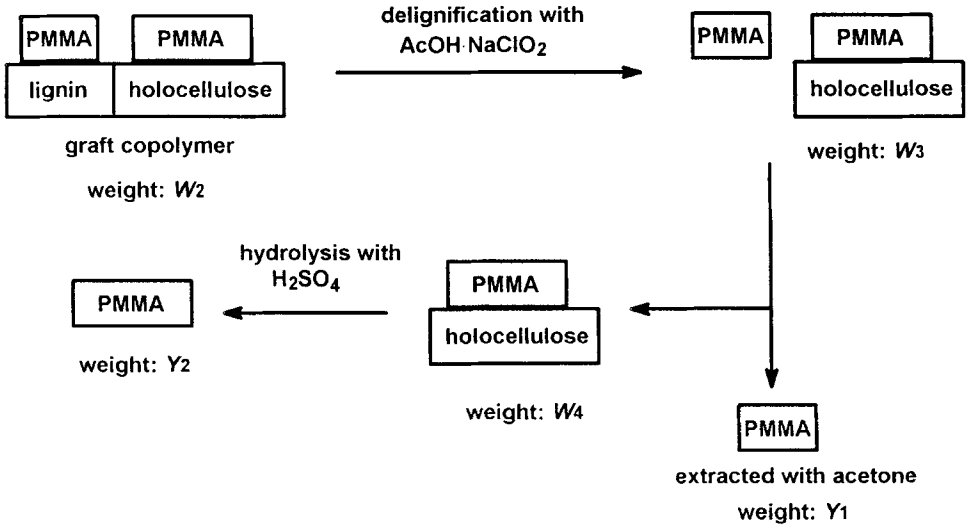
$$[\eta] = 2.45 \times 10^{-5} M^{0.80}$$

Homopolymer yield, percentage conversion of monomer, grafting efficiency, and percentage grafting were calculated using the following equations.

$$\text{Homopolymer yield (\%)} = \frac{W_1 - W_2}{\text{weight of monomer (0.944 g)}} \times 100$$

$$\text{Percentage conversion of monomer (\%)} = \frac{W_1 - W_0}{\text{weight of monomer (0.944 g)}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$



SCHEME 1.

Percentage grafting of lignin (%)

$$= \frac{\text{weight of grafted PMMA on lignin } (Y_1)}{\text{weight of lignin } (W_2 - W_3)} \times 100$$

Percentage grafting of holocellulose (%)

$$= \frac{\text{weight of grafted PMMA on holocellulose } (Y_2)}{\text{weight of holocellulose } (W_4 - Y_2)} \times 100$$

Determination of Phenolic and Alcoholic Hydroxyl Groups of Lignin

The milled bagasse pith lignin was prepared according to the Björkman method [17]. The phenolic and alcoholic hydroxyl groups contents were determined according to the literature [18].

RESULTS AND DISCUSSION

Graft Copolymerization

The data in Table 1 show the changes in the grafting percentages and the molecular weights of grafted PMMA chains during grafting. The grafting percentage of lignin is about 3–4 times as high as that of holocellulose although lignin is a phenolic polymer. The molecular weights of grafted PMMA chains on lignin are slightly lower, indicating the higher reactivity of lignin to the formation of graft sites. Moreover, comparison with the data of Fe^{2+}-H_2O_2-initiated graft copolymerization [12] shows that the direct oxidation of lignin by $KMnO_4$ is more favorable to grafting than the attack of lignin by hydroxyl radicals.

During grafting, both the grafting percentages and the molecular weights of grafted PMMA chains on both lignin and holocellulose increase and then level off

TABLE 1. Grafting Percentages and Molecular Weights of Grafted PMMA Chains at Different Stages of Grafting[a]

	Reaction time, minutes				
	5.0	10.0	25.0	45.0	90.0
Homopolymer yield (%)	3.6	12.5	19.4	27.1	28.9
Conversion of monomer (%)	17.2	40.9	60.4	67.2	69.0
Grafting efficiency (%)	78.9	69.5	67.9	59.6	58.2
Percentage grafting of lignin (%)	69.5	123.3	193.6	210.9	201.0
Percentage grafting of holocellulose (%)	25.0	34.4	52.4	50.4	51.0
M_η[b] of PMMA on lignin (10^5)	1.44	2.48	2.94	30.4	2.95
M_η[b] of PMMA on holocellulose (10^5)	1.89	2.99	3.38	3.51	3.32

[a]Bagasse pith was soaked in 0.016 M $KMnO_4$ at 40°C for 15 minutes, and grafting was carried out in 0.015 M H_2SO_4 at 80°C.

[b]Viscosity-average molecular weight.

after 25 minutes. A similar phenomenon was also observed in the investigation of Fe^{2+}-H_2O_2-initiated graft copolymerization [12]. The increase in the molecular weights of grafted PMMA chains with reaction time implies that chain termination is slowed down because of the insolubility of grafted PMMA chains in water.

The extent of oxidation of organic substrates by $KMnO_4$ depends on the nature of the substrate and on the pH of the reaction medium [19], as manifested by the data in Table 2. Lignin and holocellulose show different responses to H_2SO_4 concentration. With an increase in H_2SO_4 concentration from 0 to 0.015 M, the percentage grafting of lignin increases by about 100%, while no evident effect on the percentage grafting of holocellulose is observed. The molecular weights of grafted PMMA chains on lignin and on holocellulose decrease at approximately equal rates.

TABLE 2. Effect of H_2SO_4 Concentration on Grafting[a]

	H_2SO_4 concentration, M				
	0	0.010	0.015	0.050	0.100
Homopolymer yield (%)	2.4	25.2	27.1	30.6	32.7
Conversion of monomer (%)	29.3	63.3	67.2	60.4	61.2
Grafting efficiency (%)	91.1	60.2	59.6	49.3	46.3
Percentage grafting of lignin (%)	100.6	165.3	210.9	150.0	139.3
Percentage grafting of holocellulose (%)	47.0	47.3	50.4	39.3	36.3
M_η[b] of PMMA on lignin (10^5)	4.71	3.32	3.04	2.59	2.21
M_η[b] of PMMA on holocellulose (10^5)	5.60	4.14	3.51	2.92	2.59

[a]Bagasse pith was soaked in 0.016 M $KMnO_4$ at 40°C for 15 minutes, and grafting was carried out at 80°C for 45 minutes.

[b]Viscosity-average molecular weight.

This result implies that the formation of graft sites on lignin is accelerated more readily by H_2SO_4. A further increase in H_2SO_4 concentration from 0.015 to 0.100 M leads to poor grafting efficiency.

The data in Table 3 show the effect of $KMnO_4$ concentration of grafting. It is apparent that the grafting percentage becomes higher because more active sites are created when $KMnO_4$ concentration increases from 0.004 to 0.016 M. Any further increase in $KMnO_4$ concentration produces a negative effect on grafting due to accelerated homopolymerization. When more graft sites are formed at higher $KMnO_4$ concentrations, grafted PMMA chains become shorter, as shown by the data in Table 3. However, an exception was found at 0.004 M $KMnO_4$, and the lower than expected molecular weight value is ascribable to the inhibition effect of some lignin structures which can be eliminated by oxidation with $KMnO_4$ at higher concentration.

The result that active sites for grafting can also be created in a neutral medium (Table 2) suggests that the active sites may already be formed during soaking in aqueous $KMnO_4$. Apparently the formation of active sites in soaking is unfavorable to grafting, as indicated by the result that a higher soaking temperature results in a lower grafting percentage of lignin (Table 4). However, the grafting percentage of holocellulose doesn't show as evident a change.

Grafting Mechanism

In order to reveal the grafting mechanism of lignin, we changed the chemical structure of lignin by pretreatment of bagasse pith before grafting. The results are summarized in Table 5.

The methylation of bagasse pith with CH_2N_2 results in a decrease in phenolic hydroxyl groups per phenylpropane unit of lignin from 0.36 to 0.12. The grafting percentages of lignin and holocellulose increase by 146 and 38%, respectively, and the molecular weights of grafted PMMA chains change slightly when some phenolic

TABLE 3. Effect of $KMnO_4$ Concentration in Soaking on Graft Copolymerization[a]

	$KMnO_4$ concentration, M				
	0.004	0.008	0.016	0.030	0.045
Homopolymer yield (%)	2.7	9.5	27.1	37.3	46.4
Conversion of monomer (%)	17.4	49.1	67.2	67.8	60.9
Grafting efficiency (%)	84.4	80.6	59.6	45.0	23.9
Percentage grafting of lignin (%)	69.8	195.2	210.9	184.7	114.6
Percentage grafting of holocellulose (%)	19.3	41.5	50.4	41.2	29.1
M_η[b] of PMMA on lignin (10^5)	5.12	6.16	3.04	2.66	2.05
M_η[b] of PMMA on holocellulose (10^5)	4.77	6.26	3.51	2.50	1.89

[a]Bagasse pith was soaked at 40°C for 15 minutes, and grafting was carried out in 0.015 M H_2SO_4 at 80°C for 45 minutes.

[b]Viscosity-average molecular weight.

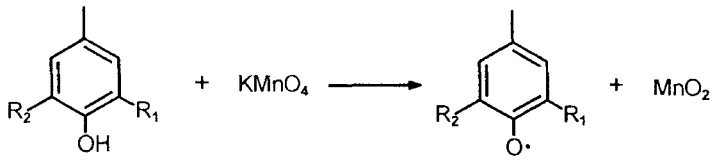
TABLE 4. Relationship between Soaking Temperature and Graft Copolymerization[a]

	Soaking temperature, °C				
	20	30	40	60	80
Homopolymer yield (%)	12.6	15.3	27.1	29.7	26.7
Conversion of monomer (%)	58.0	59.1	67.2	68.5	65.1
Grafting efficiency (%)	78.3	74.1	59.6	56.6	59.0
Percentage grafting of lignin (%)	237.0	220.7	210.9	196.8	182.6
Percentage grafting of holocellulose (%)	54.3	52.7	50.4	49.1	54.0
M_η[b] of PMMA on lignin (10^5)	3.16	3.20	3.04	3.25	3.29
M_η[b] of PMMA on holocellulose (10^5)	3.62	3.59	3.51	4.11	4.01

[a]Bagasse pith was soaked in 0.016 M $KMnO_4$ for 15 minutes, and graft copolymerization was carried out in 0.015 M H_2SO_4 at 80°C for 45 minutes.

[b]Viscosity-average molecular weight.

hydroxyl groups of lignin are methylated. During soaking of unmethylated bagasse pith, the purple color of aqueous $KMnO_4$ solution disappears and the white bagasse pith becomes brown, indicating the reduction of $KMnO_4$ to MnO_2 during soaking, perhaps via the following reaction.



R_1, R_2 = hydrogen or methoxy

Methylated bagasse pith and $KMnO_4$ solution are purple after soaking. The higher grafting percentages of lignin and holocellulose can only be attributed to $KMnO_4$ adsorbed by methylated bagasse pith. Although MnO_2 and Mn^{3+} ion are generally considered to react with cellulose to form graft sites in $KMnO_4$-initiated graft copolymerization [14, 15], the direct oxidation of holocellulose and lignin by $KMnO_4$ may also create graft sites since some free-radical mechanisms involving the oxidation of organic compounds by $KMnO_4$ have been proposed [20, 21].

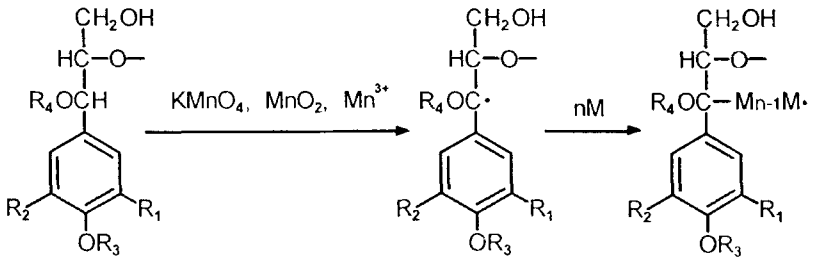
Benzylic C—H bonds and aromatic nuclei of lignin may be the key to why lignin shows quite high reactivity to grafting. Another result is that graft sites on lignin increase more significantly than those on holocellulose when an appropriate amount of H_2SO_4 is added, as indicated by the data in Table 2, which may also be attributed to benzylic C—H bonds and aromatic nuclei of lignin. Benzyl radicals are generally regarded as intermediates in the oxidation of organic compounds by MnO_2 [22, 23] or by Mn^{3+} [24]. Therefore, the formation of graft sites on α-carbons of phenylpropane units and consequent chain propagation can be expressed by

TABLE 5. Effect of Pretreatments on Graft Copolymerization[a]

No.	Pretreatment	Percentage grafting of holocellulose, %	M_η[b] of PMMA on holocellulose (10^5)	Percentage of grafting on lignin, %	M_η[b] of PMMA on lignin (10^5)	Hydroxyl groups per phenylpropane unit	
						Phenolic	Alcoholic
1	Untreated	34.0	4.38	110.0	3.93	0.36	0.87
2	CH_2N_2	47.0	3.94	271.0	4.05	0.12	0.98
3	$CH_3OH-HCl$	48.0	4.88	143.0	4.28	—	—
4	$NaBH_4$	38.0	4.15	94.0	3.69	0.34	1.04

[a]Bagasse pith was soaked in 0.006 M $KMnO_4$ at 40°C for 15 minutes, and graft copolymerization was carried out in 0.015 M H_2SO_4 at 80°C for 30 minutes.

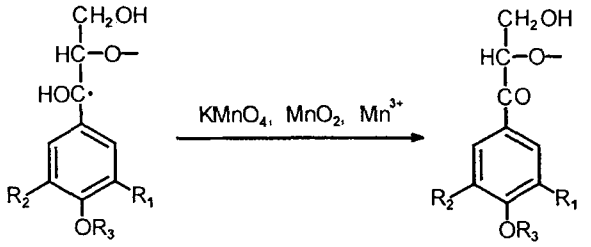
[b]Viscosity-average molecular weight.



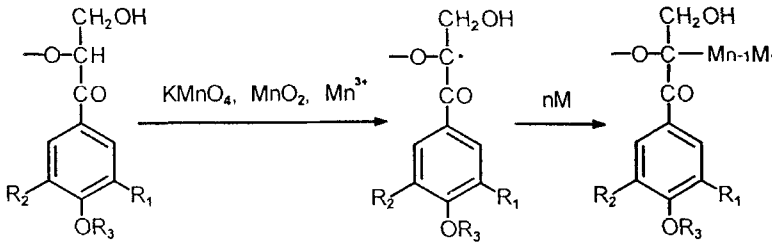
[I]

R_1, R_2 = hydrogen or methoxy
R_3 = hydrogen, alkyl or aryl
R_4 = hydrogen or aryl
M = monomer

When α-hydroxyl groups (R_4 = H) of phenlpropane units are methylated by pretreatment with methanolic hydrochloric acid [25], the grafting percentage of lignin increases by 30% while the molecular weight of grafted PMMA increases only by 9%, indicating more graft sites are formed. This result suggests that more benzyl radicals could initiate graft copolymerization because the further oxidation of benzyl radicals, as shown below, becomes quite difficult when α-hydroxyl groups are methylated.

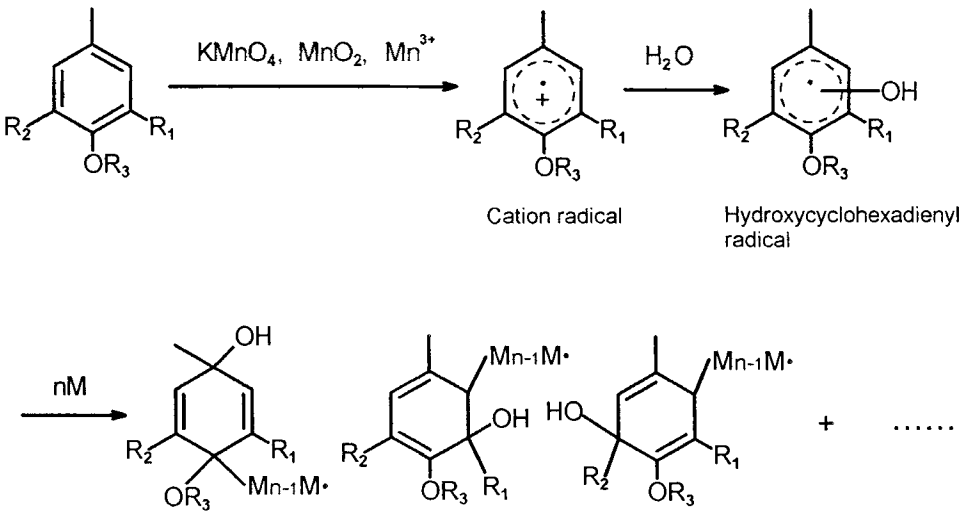


After the reduction of bagasse pith with sodium borohydride, alcoholic hydroxyl groups increase from 0.87 to 1.04 per phenylpropane unit. This can be ascribed to the reduction of α-carbonyl groups (structure II) to α-hydroxyl groups. The grafting percentage of lignin and the molecular weights of grafted PMMA chains decrease by 15 and 6%, respectively, as a result of a decrease in α-carbonyl groups. This result implies that one important grafting path may be



[II]

In addition, we propose the following mechanism for grafting onto the aromatic nuclei of lignin to account for the higher reactivity of lignin to grafting compared with holocellulose.



Since $KMnO_4$, MnO_2, and Mn^{3+} have quite high standard potentials, they could withdraw one electron from an aromatic nucleus to produce a cation radical intermediate, followed by reaction with water to form a hydroxycyclohexadienyl radical onto which graft copolymerization occurs. Some mechanisms concerning the oxidation of aromatic compounds were proposed to involve an electron-transfer process from aromatic nuclei to oxidants, producing cation radicals because of the relatively low ionization potentials of aromatic compounds [26, 27].

$KMnO_4$ and MnO_2 are not very powerful oxidants in a neutral medium, and dark MnO_2 still remains after the reaction. Dark MnO_2 gradually disappears during grafting in the presence of H_2SO_4, indicating the strong oxidizing capabilities in an acid medium. The formation of cation radicals seems to need oxidants of high potential. This may be the reason why the grafting of lignin is more sensitive to H_2SO_4 concentration than is that of holocellulose.

CONCLUSIONS

The oxidation of lignocellulose by $KMnO_4$ is an efficient route to the formation of graft sites. Graft copolymerization can occur in neutral media, and it is accelerated by an appropriate addition of H_2SO_4. Although lignin is a phenolic polymer, it shows quite higher reactivity to grafting and is more sensitive to H_2SO_4 concentration than is holocellulose.

The high reactivity of lignin to grafting may be partly attributed to benzylic C—H bonds. The methylation of α-hydroxyl groups of phenylpropane units makes benzyl radicals escape further oxidation, as indicated by the more graft sites formed. The reduction of α-carbonyl groups to α-hydroxyl groups is unfavorable for the

grafting of lignin, suggesting that graft sites may also be created on β-carbons adjacent to α-carbonyl groups. Phenolic hydroxyl groups are found to have a negative effect on grafting via reduction of $KMnO_4$ in soaking.

In addition, the high reactivity of lignin to grafting may be partly ascribable to the aromatic nuclei of lignin. Aromatic nuclei could be converted into cation radicals via a one-electron transfer process, and the addition of H_2O to cation radicals creates hydroxycyclohexadienyl radicals which initiate grafting.

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