

## The Graft Copolymerization of Styrene and Lignin. I. Hydrochloric Acid Lignin

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### Synopsis

The effects of methylation of phenolic hydroxyl groups and addition of solvent on the radiation and chemically initiated graft copolymerization of styrene and hydrochloric acid softwood lignin were studied. In the radiation-induced experiments, methylation is found to increase the maximum per cent graft obtainable two or threefold, while methanol addition may increase the value tenfold. Chemically initiated experiments indicate that the main effect of methanol addition is to increase the accessibility of the lignin particles. A mechanism of graft copolymerization of polystyrene and lignin is proposed which requires the reaction to proceed primarily by chain transfer of a polystyrene chain radical to lignin and the subsequent reinitiation of polymerization (i.e., initiation of graft copolymerization) by the lignin radical. The grafting of lignin modifications is then dependent on the type of radical formation (i.e., phenoxy or benzylic) most favored, as well as the usual accessibility considerations.

### INTRODUCTION

Lignin is the major noncellulosic component of wood, comprising approximately 20% of the weight of hardwoods and about 30% of softwood trees. In chemical pulping processes, only about 50% of the wood is actually recovered as pulp, the remaining half, including most of the lignin, is either discarded as a waste product or retained for further utilization. The former procedure is clearly the less acceptable of the two, being not only wasteful, but a source of water pollution. Consequently, the pulp and paper industry has continuously sought uses for this most abundant raw material, either as found in the black liquor of the pulping process or in an isolated form.

A recent technical bulletin distributed by the Westvaco Corporation<sup>1</sup> gives a partial listing of uses for some 25 "ligno-chemicals" recovered from that company's kraft pulping process. These lignin modifications are sold as dispersants, resin coreactants, emulsifiers, stabilizers, sequestrants for polyvalent metals, reinforcing agents for rubber, and oxygen

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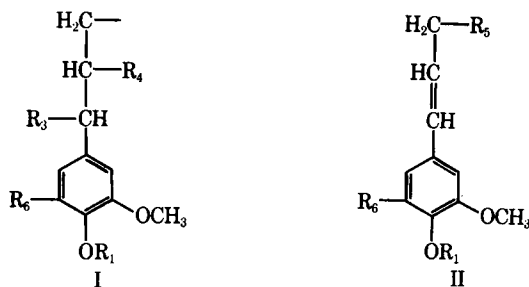
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scavengers. Since most of the above uses involve the existence of lignin in solution or admixture with other components or phases, the lignin conceivably could be made more effective if the compatibility between it and the other compounds could be improved. Grafting, or chemical bonding, of a new polymer to the backbone is one proven method of improving compatibility in polymeric systems.

The prospect of grafting to an isolated form of lignin presents several intriguing problems not normally encountered in grafting studies. First, the structure of the backbone polymer is not as precisely defined as in most systems, and is known to vary considerably according to the particular pulping process or method of isolation of lignin.<sup>2</sup> Numerous laboratories, e.g., those of Freudenberg<sup>3</sup> and Adler,<sup>4</sup> have increased the understanding of the constitution of native, or only slightly modified, lignin, while the work of Marton<sup>5,6</sup> has clarified the nature of isolated kraft softwood lignin.

Using models I and II, it is possible to point out several structural features which ultimately determine the grafting reactions of different lignin modifications:



In high molecular weight lignins (model I), such as the one obtained by the hydrolysis of cellulose in wood from the lignin backbone (e.g., "hydrochloric acid lignin"), it is quite likely that  $\text{R}_1$  and either  $\text{R}_3$  or  $\text{R}_4$  are linkages to other lignin structural (guaiacyl) units. In a smaller number of units, one would find free phenolic hydroxyl groups (i.e.,  $\text{R}_1 = \text{H}$ ). On the other hand, in a highly degraded form of lignin, such as that obtained from the kraft pulping process, the molecular weight is low ( $M_n = 900-1600$ )<sup>6,7</sup> and the phenolic hydroxyl content is high.<sup>5</sup> Moreover, a high percentage of guaiacyl units is known to contain conjugated double bonds in the propyl side chain (model II).<sup>6</sup> The nature of the substituents  $\text{R}_1$  to  $\text{R}_6$  shall later be seen to dictate the likely reactions that a particular guaiacyl unit would undergo.

One must also consider that lignin exhibits the characteristic stability of aromatic compounds toward radiation,<sup>9</sup> indicating that only a few radicals would be formed on the lignin polymer backbone.

The radiation-induced graft copolymerization of methyl methacrylate,<sup>10,11</sup> styrene,<sup>10,12-16</sup> and vinyl acetate<sup>10</sup> with softwood hydrochloric acid lignin has been reported in a series of papers by Koshijima and Muraki.<sup>10-16</sup> An extensive review of translations of these papers has been made,<sup>17</sup> with the following main findings:

1. Grafting occurs by a free-radical process.
2. Methyl methacrylate grafts more effectively than styrene.
3. Methylation of the lignin (i.e., those R<sub>1</sub> groups which are hydroxyl) raises the maximum per cent graft of polystyrene from 25% to 40%.
4. Addition of 2% methanol to the styrene increases the maximum per cent graft of methylated HCl lignin dramatically from 40% to 430%.
5. Grafting occurs at a site on lignin such that the product of nitrobenzene oxidation of the graft copolymer is not analyzed as vanillin.

Koshijima and Muraki mainly studied the grafting of these monomers to methylated HCl lignin, using radiation and chemical initiation. In the present series of papers, the radiation-initiated and chemically initiated grafting of styrene to various lignin modifications will be described. This first report extends the work of Koshijima and Muraki to the grafting of styrene to unmethylated HCl lignin, using both means of initiation. The results allow the formulation of a probable sequence of reactions.

## RESULTS AND DISCUSSION

As discussed above, it has been found<sup>10,13</sup> that the yields in the radiation-induced graft copolymerization of styrene and HCl lignin are increased by (1) methylation of the phenolic hydroxyls of the lignin and (2) addition of 2% methanol to the reaction medium. In order to clarify and separate these effects, a series of experiments was conducted using unmethylated lignin with a cobalt-60 source of  $\gamma$ -radiation of approximately the same intensity employed in the work of Koshijima and Muraki. The results, presented in Figures 1 and 2, may then be compared to data previously obtained<sup>10,13</sup> for the case of methylated lignin.

In Figures 1 and 2, the following definitions apply:

$$\% \text{ conversion} = 100 \times \frac{\text{wt of polystyrene (graft + homopolymer)}}{\text{wt of original monomer}}$$

$$\% \text{ graft} = 100$$

$$\times \frac{\text{wt of reaction products inextractable in benzene} - \text{wt of original lignin}}{\text{wt of original lignin}}$$

It may be seen that little grafting occurred in a medium of pure styrene (Fig. 1), even after 30 megarads, despite the high per cent conversion ( $\approx 78\%$ ) of monomer to polymer. Moreover, it is apparent that the conversion of styrene is hardly affected by the presence of lignin.

However, when the reaction medium contained 2% methanol, grafting yields are greatly increased (Fig. 2). The marked coincidence of the acceleration of grafting with the acceleration of polymerization indicates that both are under the influence of the gel and other effects. The so-called gel effect arises when the polymerizing medium becomes highly viscous. This leads to a reduced termination rate of the growing chains due to their slower diffusion, leading in turn to higher molecular weights

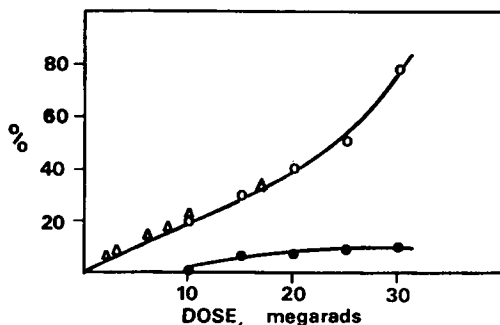


Fig. 1. Radiation-induced graft polymerization of HCl lignin with pure styrene: (●) per cent graft; (○) per cent conversion; (△) per cent conversion when no lignin is present.

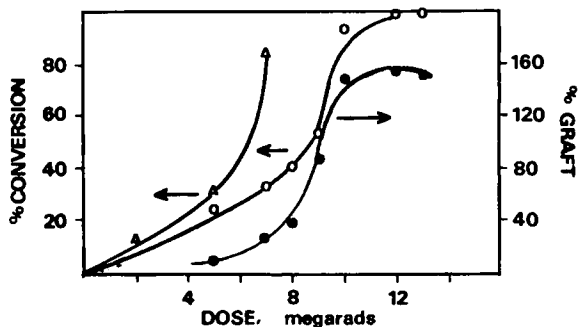


Fig. 2. Radiation-induced graft polymerization of lignin with 98:02 styrene:MeOH mixture: (○) per cent conversion; (●) per cent graft; (△) per cent conversion with no lignin present.

and higher rates of polymerization. The accelerating effects of small amounts of methanol on the radiation-induced polymerization of styrene have been discussed in detail by Chapiro<sup>18,24</sup> and by Phillips and Stannett.<sup>25</sup>

Table I confirms the occurrence of a small gel effect, collecting the intrinsic viscosities of the homopolymer extracted from the reaction products. It must be considered that these intrinsic viscosities represent homopolymer formed, to a large extent, away from the influence of the lignin particles. Within the lignin substrates, at any stage of the reaction, one would expect to find the viscosity higher than the bulk value, and thus a magnified, but quantitatively unknown, local gel effect. This phenomenon is discussed by Chapiro<sup>18</sup> and many other authors.

Returning to Figure 1, it is seen that a gel effect also was present in the system of pure styrene in the presence of lignin, but only a slight increase in the per cent graft resulted. This suggests that styrene when alone is not readily accessible to the depths of lignin particles, and only surface grafting may be possible. Addition of only 2% methanol, then, is believed to increase the swelling of the lignin particles.

It must also be realized that one other effect of methanol addition in the

TABLE I  
Intrinsic Viscosities of Homopolymer Extracted from HCl Lignin  
Grafting Reaction Products

MeOH, %	Dose, megarads	Conversion, %	( $\eta$ ) <sup>a</sup>	$M_v$ <sup>b</sup>
0	15	29.4	0.419	81.000
0	20	38.7	0.406	79.500
0	30	77.5	0.528	112.000
2	5	24.1	0.388	74.000
2	7	33.7	0.392	77.500
2	8	40.5	0.416	81.000
2	9	53.2	0.516	110.000
2	10	93.4	0.641	151.000

<sup>a</sup> Determined in benzene at 30°C.

<sup>b</sup> Calculated from ( $\eta$ ) =  $0.97 \times 10^{-4} M_v^{0.74,19}$

radiation-induced reaction is to increase the production of primary radicals.<sup>18</sup> Thus the rate of this initiation would be

$$R_i = I(\theta_M[M] + \theta_S[S] + \theta_L[L])$$

where  $I$  = radiation intensity in rads/sec,  $\theta$  = radiation yield per unit volume of material exposed to the radiation field, and  $[M]$ ,  $[S]$ , and  $[L]$  are monomer, solvent, and lignin concentrations, respectively.

Methanol addition, then, would hasten the onset of the gel effect (ca. 8 versus 25 megarads for 2% MeOH and 0% MeOH, see Figs. 1 and 2). In order to isolate the swelling from this radiolysis effect, companion experiments were made, employing benzoyl peroxide as initiator and used which, when decomposed at 60°C, closely approximates the rate of initiation<sup>19</sup> of styrene when the pure monomer was irradiated at room temperature. Figure 3 clearly indicates that grafting is more efficient in the presence of methanol, even though, as shown in Figure 4, the polymerization of the pure monomer is a little more rapid. Thus, it appears that the major effect of solvent addition is to promote swelling of the lignin particles. It is interesting to note that, for a given per cent conversion of monomer, the chemically initiated grafting at 60° was more effective than the radiation-induced grafting at room temperature. This may be accounted for by the high temperature favoring monomer diffusion.

Examining Figures 2 and 3, it is evident that the overall polymerization of styrene is retarded somewhat when graft polymerization is significant, but not, as reflected in Figure 1, when grafting is unimportant. Evidently, the rate of the grafting reaction is slower than homopolymerization.

If Koshijima and Muraki's results are now reexamined in light of these findings, it would appear quite reasonable that methyl methacrylate grafted more efficiently than styrene to unmethylated lignin. First, methyl methacrylate is more polar than styrene and would swell the lignin more. Secondly, methyl methacrylate is known to be influenced by the gel effect almost immediately after polymerization is initiated,<sup>20</sup>

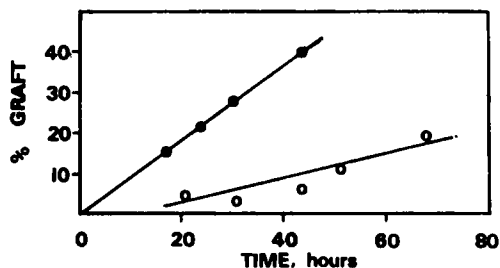


Fig. 3. Benzoyl peroxide-initiated graft polymerization of styrene and unmethylated HCl lignin: (●) 2% methanol present; (○) no solvent.

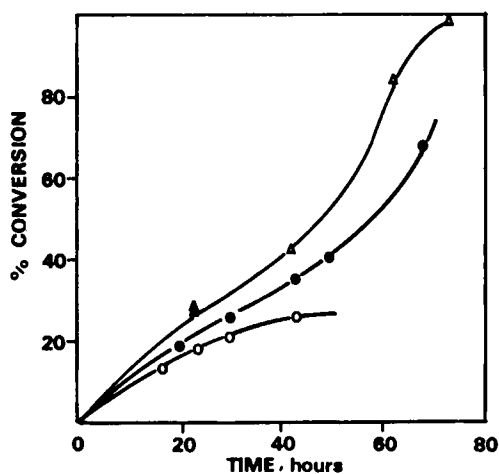


Fig. 4. Per cent conversion of styrene monomer to polymer in benzoyl peroxide-initiated experiments: (Δ, ▲) no lignin present; (●) 2% methanol present; (○) no solvent.

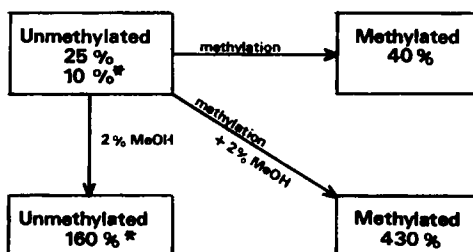


Fig. 5. Effects of methylation and solvent addition on the maximum per cent graft obtained with styrene and HCl lignin: (\*) indicates values obtained in present research, others obtained by Koshijima and Muraki.<sup>10,13</sup>

whereas this phenomenon occurs with styrene only at ca. 30–50% conversion.

Moreover, the swelling of methylated HCl lignin in styrene would also be more enhanced than would be the case of unmethylated OH groups,

perhaps accounting for some of the accelerated grafting rates found after methylation.

The relative effects of methylation and swelling are summarized in Figure 5, which indicates that methylation increases the maximum per cent graft obtainable to ca. 2-3 times the unmethylated value, while solvent addition increases the maximum per cent graft tenfold.

The swelling phenomenon, found to control numerous grafting reactions, cannot be overemphasized. The different reactivity of the methylated lignin over the unmethylated cannot be the sole effect of the blocking of phenolic hydroxyl groups; indeed, Koshijima and Muraki<sup>10</sup> found that acetylation of these groups resulted in a drastic decrease in the amount of grafting. Moreover, in a recent paper by Simionescu and Anton,<sup>21</sup> the grafting of acrylonitrile to reed lignin was found to decrease with both methylation and acetylation. Solvent effects will be quite different in both these cases.

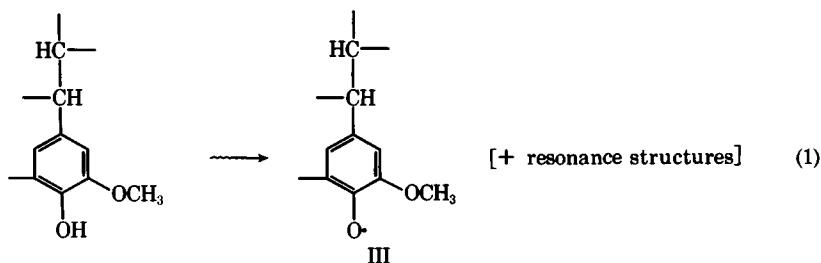
Thus, it seems clear that methylation of phenolic hydroxyls should have at least two major effects on the grafting to lignin: (1) the accessibility of the lignin particles to the surrounding monomer solution is changed; (2) the reactivity of any particular lignin structural unit is modified.

The first factor makes it difficult to prove any particular reaction mechanism; but a consideration of certain experimental findings, as well as data for the polymerization of styrene in the presence of various model compounds, make a plausible formulation possible.

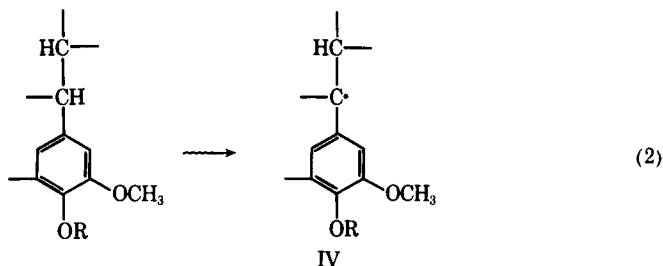
### Proposed Grafting Scheme

Grafting does not occur at the methoxyl groups, because the number of these functions remains constant during the reaction. Koshijima and Muraki presented evidence<sup>15</sup> that grafting must occur at a location such that the grafted guaiacyl residue is not oxidized by nitrobenzene to vanillin; this eliminates grafting to purely aliphatic portions of the molecule, and limits the reaction to either the ring itself or at a benzylic carbon.

When either methylated or unmethylated HCl lignin is irradiated, the bulk of the energy will probably be absorbed by the aromatic guaiacyl units. The energy is absorbed equally throughout the conjugated system and may result in the homolytic rupture of a bond, those having the lowest dissociation energies being most probable. In the unmethylated case, this would appear to favor the formation of phenoxy radicals:

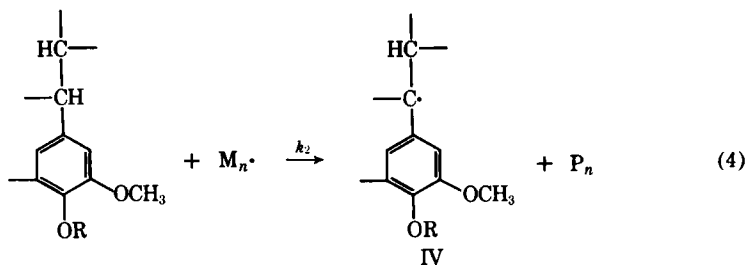
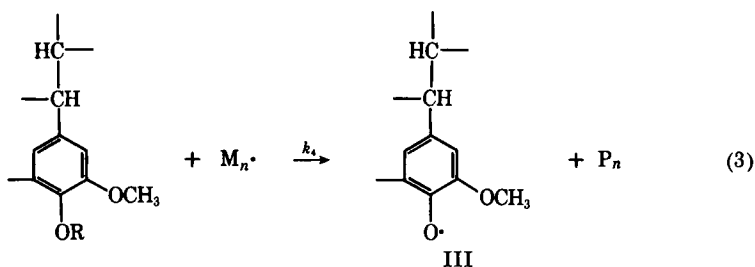


with some smaller probability of benzylic radical formation:



On the basis of their higher bond dissociation energies and Koshijima and Muraki's findings with vanillin yields, consideration need not be given to purely aromatic or aliphatic radicals.

In the case of methylated lignin, the order would be just the opposite. Formation of compound III would be more difficult for methylated lignin because of the higher energy required for  $\text{PhO}-\text{CH}_3$  scission, as opposed to  $\text{PhO}-\text{H}$ . This is supported by the higher  $G_R$  values (number of radicals formed per 100 eV of radiation) found by Koshijima and Muraki<sup>10</sup> for unmethylated HCl lignin with respect to the methylated case. Further, Kringstad and Lin,<sup>22</sup> who studied the UV irradiation of lignin model compounds, found that, for a given exposure, methylated lignin models have significantly lower free-radical content than the corresponding unmethylated compound. A considerable number of benzylic radicals (IV) may have been formed, but their reactivity precluded measurement. Reactions (1) and (2), however, cannot be the only source of radicals III and IV, since grafting was highly significant in the chemically initiated system. The chain transfer reactions of the lignins with growing polystyrene chain radicals ( $M_n$ ) would be another, and probably the most important, source of lignin radicals:

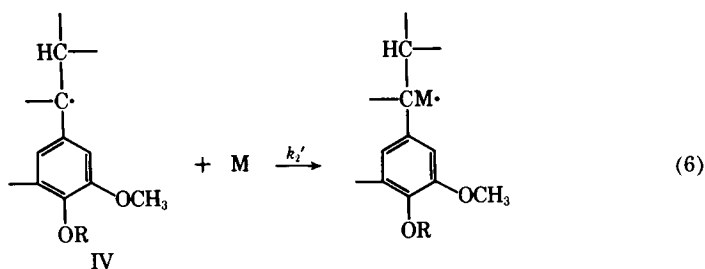
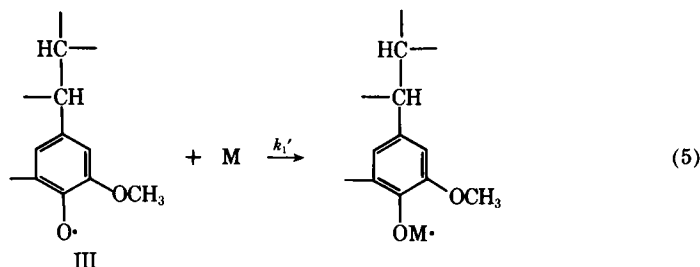




Here, it is quite well known that reaction (3) will proceed very rapidly when  $R = H$ , and more slowly when  $R = CH_3$ , and that reaction (4) will be more favored in the methylated case. This is based on values of chain transfer constants of model substances (e.g.,  $C_{S_{phenol}} = 4 \times 10^{-48}$ ;  $C_{Stoluene} = 0.12 \times 10^{-423}$ ), which indicate that the magnitudes of  $K_1$  and  $K_2$  are vastly different for phenolic and benzylic hydrogen abstraction. With methylated HCl lignin, homolytic aromatic substitution, as proposed by Koshijima and Muraki,<sup>15</sup> may be possible, but this reaction, which involves two rather slow steps, should not be as significant as the reactions described above. For example, Szwarc<sup>26</sup> reported that toluene underwent chain transfer five times more rapidly than aromatic substitution with highly reactive methyl radicals. With resonance-stabilized polystyryl radicals, the ratio should be even higher.

With unmethylated lignin, our work with model compounds, to be published later, and numerous studies, for example ref. 8, with phenols have indicated chain transfer with the phenolic hydrogen to be the main reaction.

But thus far, reactions (1) through (4) have been concerned only with the formation of lignin radicals and would show that unmethylated lignin is highly favored from this aspect. However, the formation of graft copolymer requires that radicals III and IV reinitiate a polymer chain:



Here, the high reactivity of the benzylic radical makes  $K_2'$  on the order of the rate constant for propagation of styrene,  $K_p$ , while  $K_1'$  may vary from 0 to  $K_p$ . In their study of the effect of phenols on the polymerization of styrene, Godsay et al.<sup>8</sup> found that, depending on the substituents present with the OH group, phenols may act simply as chain transfer agents ( $K_1' \simeq K_p$ ) or as inhibitors ( $K_1' = 0$ ).

The exact behavior of HCl lignin cannot be known, but the retardation of polymerization shown in Figure 2 is accounted for by the above series

of reactions, which also are consistent with the remaining experimental data of this paper and those of Koshijima and Muraki. This includes the finding by the latter authors that hardwood HCl lignin ( $R_1 = \text{OCH}_3$  in model I), methylated or not, failed to graft substantial amounts of styrene or methyl methacrylate.

## CONCLUSIONS

Referring once again to models I and II, the participation of any lignin structural unit in a grafting reaction depends first on the ease and location of radical formation. In the case of unmethylated lignin,  $R_1 = \text{H}$ , relatively stable phenoxy radicals are easily formed, whereas with  $R_1 \neq \text{H}$ , fewer numbers of more reactive benzylic radicals are initiated. The effectiveness of these radicals in subsequent reactions, however, depends on (1) the initiation of polymerization by the lignin radicals (in which reaction benzylic radicals are more effective than phenoxy radicals); (2) accessibility of styrene to the lignin radicals (enhanced either by methylation or addition of solvent); and (3) rate of termination of grafted chain radicals (which is reduced by the high viscosity of the reaction medium).

## EXPERIMENTAL

### Hydrochloric Acid Lignin

This material was kindly donated by Dr. T. Koshijima of the Government Industrial Research Institute, Osaka, Japan, and was identical to the preparation used in his own work.

### Styrene

Monomer, stabilized with *tert*-butylpyrocatechol, was obtained from Eastman Organic Chemicals. The inhibitor was removed by distillation in a 4-ft packed column under vacuum (40°C, 20 mm Hg). Large quantities were routinely distilled and stored over Drierite in stoppered bottles with refrigeration. On the day of use, a final cold distillation was made to remove any polymer that may have formed.

### Grafting Procedure

Samples for chemical and radiation grafting experiments were prepared in the same manner, except for the addition of initiator to the styrene in the former case. Approximately 0.5 g of dry lignin powder was placed in a glass ampoule which could be fitted to a high-vacuum system. After the desired amount of lignin was added, the styrene-methanol mixture (10 ml) was pipetted into the ampoule. The ampoules were then attached to the vacuum system and the oxygen removed by four successive freeze-thaw cycles. After the fifth freezing, the ampoules were sealed, with the pressure usually less than  $10^{-5}$  mm Hg.

The ampoules were then either placed in the radiation source or in a constant temperature bath (60°C) for the desired length of time. After the reaction, the ampoules were broken open and the contents transferred, with benzene, to tared beakers. The contents were then evaporated to dryness, first in a hood, then by placing them in a vacuum drying oven at 60°C for 24 hr. The dried beakers were reweighed to determine per cent conversion of monomer.

After this determination, the contents were transferred, again with benzene, to tared Whatman extraction thimbles and extracted for 72 hr in a Soxhlet apparatus, with benzene.

### Radiation Procedure

The source, manufactured by Atomic Energy of Canada, Ltd., had been previously calibrated to have an intensity of  $0.14 \times 10^6$  rad/hr. The temperature could not be controlled, but varied between 20° and 25° during these experiments. The authors are grateful to Dr. W. K. Walsh of the School of Textiles for the generous allotments of time with the source.

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