

The Graft Copolymerization of Styrene and Lignin. III. Chain Transfer Reactions of Lignin and Lignin Model Compounds

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Synopsis

The effect of addition of lignin model compounds on the polymerization rate and molecular weight of polymer in the radiation-induced polymerization of styrene was studied. Guaiacol, a model for softwood lignin, reacted slowly with styrene radicals, while 2,6-dimethoxyphenol, a hardwood lignin model, was a much more efficient chain transfer agent. Studies with isoeugenol indicate that allylic or phenoxy radical stability in a conjugated system may terminate polymerization quite effectively. The results are discussed in the light of new and previous data with isolated lignins; they are consistent with the previously presented grafting scheme.

INTRODUCTION

Previous parts of this series have reported the graft copolymerization of styrene with hydrochloric acid¹ and kraft² lignins isolated from softwood species, using radiation and chemical means of initiation. Evidence was presented¹ that hydrochloric acid (HCl) lignin, the residue from the acid hydrolysis of wood meal, grafted predominantly through chain transfer of growing polystyrene radicals with the phenolic lignin units. A reaction scheme was proposed which accounted well for the data obtained in this laboratory with hydrochloric acid and kraft lignins and styrene, and the results previously reported³ by Japanese researchers with styrene and other monomers. The grafting scheme hypothesized that, apart from accessibility considerations, the grafting efficiency depends strongly on the balance of the ease of phenolic hydrogen abstraction and phenoxy radical stability. This balance, of course, is highly dependent on the structural environment of the phenolic hydroxyl. According to the scheme, highly reactive monomers, as opposed to reactive polymer radicals derived from relatively

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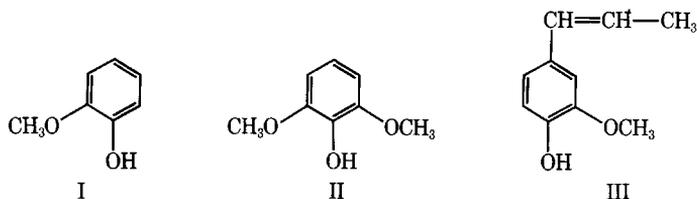
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stable monomers, would graft more effectively with phenolic lignins, a proposition which is supported experimentally by high levels of grafting with styrene,^{1,3} methyl methacrylate,⁴ and acrylonitrile,⁵ but apparent lack of grafting with vinyl acetate.⁴ Acrylamide,⁶ although a highly reactive monomer, also did not react but probably because of accessibility reasons, since a highly aqueous medium was used.

To further test the theory, model compounds chemically characteristic of lignin structural units were chosen to represent the lignin polymer backbone of the grafting system. In the present paper, the chain transfer reactions of these materials are analyzed, and the findings are correlated with the experimental results and hypotheses presented in parts I and II of this series.^{1,2}

RESULTS AND DISCUSSION

In order to better understand the nature of the chain transfer reactions proposed in part I,¹ three model compounds were selected for further study: guaiacol (I) was chosen as a model for simple softwood lignin structural units; 2,6 dimethoxyphenol (II), to represent the characteristic hardwood lignin syringyl moiety; and isoeugenol (III), to examine the effect of conjugated double bonds on the chain transfer reaction:



The compounds were added in various quantities to styrene monomer, and the mixtures irradiated in vacuo by γ -radiation from a cobalt 60 source. The polymerization rates and the molecular weights of the ensuing polymers formed were determined and compared to values obtained for pure styrene polymerized in the same manner. By these comparisons,

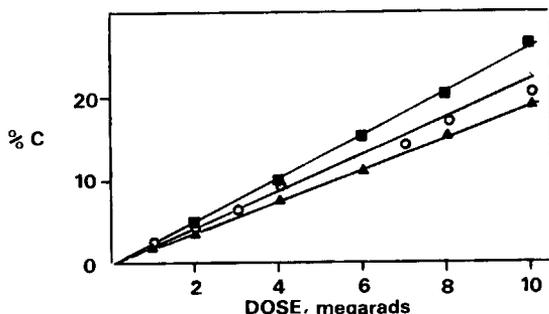


Fig. 1. Effect of guaiacol (■) and 2,6-dimethoxyphenol (▲) on the polymerization of styrene (○ = pure styrene).

the effects of substituents may be judged and related to results obtained with lignin preparations.

Figure 1 and Table I demonstrate the results obtained with 0.05*M* solutions of I and II irradiated in styrene solutions at an intensity of 41 rads/sec. It is seen that guaiacol had little effect on either the rate of polymerization (Fig. 1) or the molecular weight of the polymer formed (Table I). While the hardwood lignin model 2,6-dimethoxyphenol (II) had a similarly small effect on polymerization rate, the molecular weight of the polystyrene was considerably reduced.

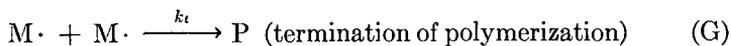
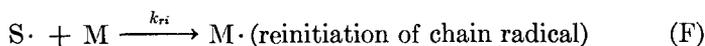
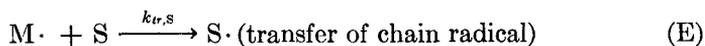
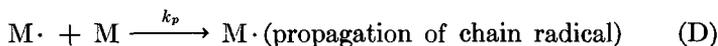
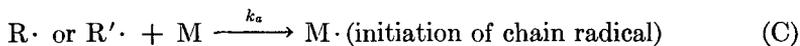
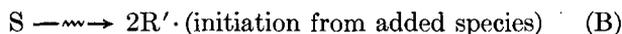
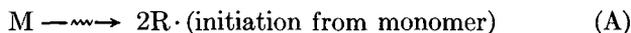
TABLE I
Chain Transfer Constants for Guaiacol (I) and
2,6-Dimethoxyphenol (II) in Styrene^a

Compound	$R_p \times 10^{+7}$, M/sec	\bar{M}_w	\bar{M}_n	\bar{M}_w/M_n	$C_s \times 10^{4b}$
Styrene	72	101,000	51,000	1.98	...
0.05 <i>M</i> Guaiacol	88	100,000	50,200	1.99	69
0.05 <i>M</i> 2,6-Dimethoxyphenol	66	74,000	38,600	1.91	1,150

^a Dose rate 41 rad/sec.

^b Calculated from $\frac{1}{P_n} = \frac{1}{P_0} + C_s \frac{[S]}{[M]}$, where P_n = degree of polymerization of phenol solution reaction; P_0 = degree of polymerization of pure styrene reaction; and $C_s = k_{tr,s}/k_p$.

The significance of these data may be judged in terms of the grafting scheme presented earlier¹ by considering the following sequence of solution polymerization reactions, generally accepted⁷ as representing those occurring in the radiation-induced polymerization of a monomer (M) in the presence of an added species (S):



The analogies are easily seen between the above reactions and the reactions in part I¹: thus, reaction (B) above has its counterpart in reactions (1) and (2) in the grafting scheme in part I.¹ Reaction (E) above is similarly related to grafting reactions (3) and (4), while reaction (F) above is analogous to grafting reactions (5) and (6).

Moreover, it is clear that compound S in the above scheme is in competition with monomer for polymer radicals $M\cdot$, reactions (D) and (E). If S is extremely reactive ($k_{tr,s} \gg k_p$), growing polymer radicals are terminated almost uniquely by reaction (E). If S is a phenolic species, a rapid reaction (E) would imply a relatively stable phenoxy radical $S\cdot$. In such a case, the reinitiation reaction (F) occurs slowly or not at all. If S is moderately reactive ($k_{tr,s} \cong k_p$) reactions (E) and (F) may not affect the polymerization rate, but will nevertheless result in a reduced molecular weight polymer. If S is hardly competitive with monomer for polymer radicals ($k_{tr,s} \ll k_p$), little change in either polymerization rate or molecular weight is found.

It appears from the data in Figure 1 and Table I that guaiacol (I) falls in the latter category, but 2,6-dimethoxyphenol (II) is considerably more competitive with styrene for polystyryl radicals. The chain transfer con-

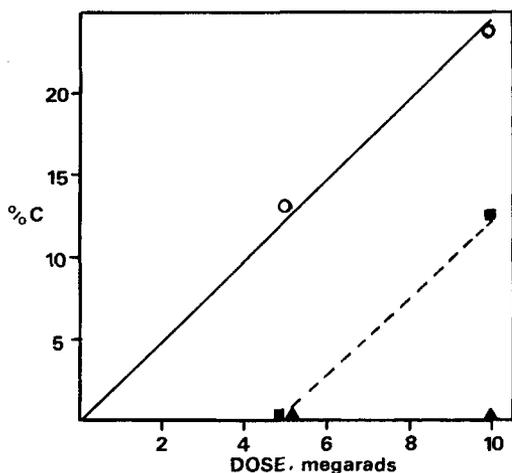


Fig. 2. Effect of guaiacol and 2,6-dimethoxyphenol on the polymerization of styrene in air. Same legend as in Fig. 1.

stant, $C_s = t_{tr,s}/k_p$, calculated as indicated in Table I, gives an approximate measure of the competition between propagation and transfer and is clearly quite different in the two cases. The greater effect in the case of II, according to generally accepted rules,⁸ is due to both the electron-donating effect of the additional methoxyl group and the steric hindrance provided by the two bulky methoxyl groups in retarding the reinitiation reaction (F).

To demonstrate that radical attack truly involves the phenolic hydroxyl, the above experiments were repeated with all conditions identical, except that the polymerizations were conducted in the presence of oxygen. The data shown in Figure 2 indicate that both compounds I and II strongly inhibited the polymerization of styrene ($k_{tr,s} \gg k_p$), but II again was more reactive than guaiacol. The reaction mixtures (originally colorless) of the

samples during the inhibition period was the characteristic yellow color of quionones, and infrared spectra confirmed the presence of C=O, not originally present nor present in the pure styrene samples irradiated in air. However, the mixtures containing guaiacol later returned to colorless, indicating that the quinone had been consumed, and polymerization could proceed. In similar experiments made with cresols, Minoura et al.⁹ proposed that the phenols were rapidly oxidized to the quinone form, that product being the actual inhibitor.

A similar order of reactivity was found when lignin preparations were used in place of the model compounds. Samples of kraft hardwood or softwood lignin (0.5 g) were dissolved in 5 ml dioxane and subsequently added to 5 ml styrene. After irradiation in vacuo, the per cent conversion was determined and compared to the value obtained with the mixture in the absence of lignin. These results are shown in Figure 3 and reflect a significant retardation of polymerization by both varieties of lignin, but certainly more pronounced in the case of hardwood lignin. These results

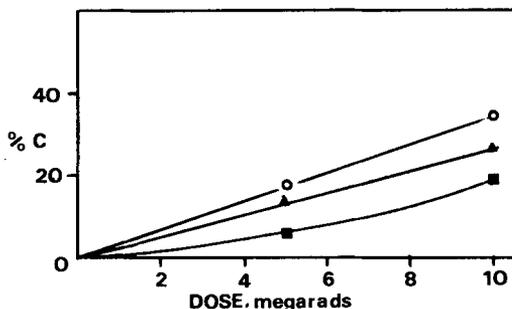


Fig. 3. Retardation of the polymerization of styrene by softwood (▲) and hardwood (□) kraft lignins in 50:50 styrene:dioxane mixture (○ = no lignin).

are consistent with the model compound studies and may account for the results of Koshijima and Muraki,⁴ who found that a hydrochloric acid lignin of a hardwood species failed to graft significantly with styrene.

Kraft lignin is known¹⁰ to contain a higher concentration of alkyl double bonds conjugated with the aromatic portion of the structural units. To characterize the effect of this configuration on grafting reactions, isoeugenol (III) was used in the same manner as previous experiments with I and II. The same radiation source was not available for this series of reactions, but instead, a ⁶⁰Co source of somewhat higher intensity (278 rad/sec) was employed; this should not influence the results, however.

Previous investigations^{11,12} have determined that isoeugenol alone forms only very low molecular weight products when a free-radical initiator is present. Similar products were obtained with the methyl ether of isoeugenol,¹³ indicating that the failure to polymerize is attributable to the presence of allylic as well as phenolic hydrogens. In addition, there will be considerable steric hindrance in the polymerization of such a 1,2-sub-

stituted vinyl compound. On the other hand, Whitby and Katz¹⁴ discovered that ionic catalysts gave a much higher molecular weight product. Our experiments with γ -radiation confirmed the earlier observations with other free-radical initiators. However, a small amount of polymer could be isolated by precipitation in petroleum ether when isoeugenol was irradiated in air with γ -radiation or with UV radiation.¹⁵

Copolymerization studies of styrene and isoeugenol were made by preparing standard solutions of the two components and irradiating them as in previous experiments. Figure 4 shows the per cent polymer obtained, based on the weight of styrene originally present in the reaction mixture. This measure was chosen because subsequent analysis of the polymers for OCH_3 revealed that very little of the isoeugenol had actually reacted. Thus, Figure 4 illustrates the retardation of the polymerization of styrene by isoeugenol, apart from simple dilution effects (see also Table II).

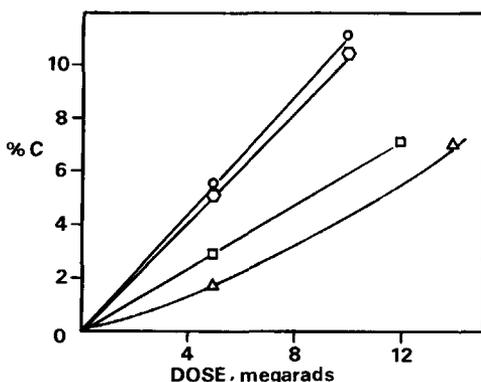


Fig. 4. Polymerization of styrene-isoeugenol mixtures; per cent conversion based on styrene only. Symbols given in Table II.

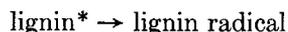
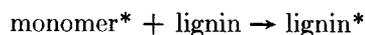
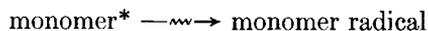
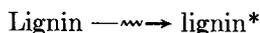
Accompanying the retardation is an expected reduction of the molecular weight of the polymer produced. Most significant, however, is the finding that, on the average, only two to 2.5 isoeugenol molecules are present per polymer chain. These may be accounted for by assuming that a polystyrene chain is initiated and grows relatively unimpeded until stopped by an isoeugenol molecule. The radical end is evidently rather stable, or otherwise this process could be repeated a number of times without reduction in polymerization rate more than that expected from the reduction in styrene concentration by isoeugenol. More likely, the stable radical couples with another isoeugenol radical, either of the same polymeric variety or another growing chain or a primary radical formed by radiation. The number of isoeugenol units per chain strongly suggests that the combination of two stable isoeugenol adduct radicals provides the main termination mechanism. Certainly, other combinations and possibilities exist, but it is difficult to envision them resulting in a high polymer.

TABLE II
Analysis of Styrene (M_1)-Isoeugenol (M_2) Copolymer Data^a

Symbol in Fig. 4	$[M_1]$	$[M_2]$	\bar{M}_n	\bar{M}_w/\bar{M}_n	$R_p \times 10^{+7}$, M/sec	M_2 in polymer, wt-%	M_2 , mole-%	M_2 units per polymer molecule
○	8.60	0	27,334	2.17	269	0	0	0
○	8.55	0.05	23,800	2.00	240	ND	...	ND
□	6.1	2.0	7,940	1.68	106	5.24	3.39	2.5
△	4.4	3.6	5,528	1.44	39	6.98	4.54	2.4

^a Dose rate 278 rad/sec. ND = not determined.

In the above discussion of the grafting and other reactions, energy transfer effects⁷ have not been included. It is clear however that they may play a considerable role in the initiation steps, i.e.,



where the asterisk represents an excited species. Such effects will affect the relative yields of the two initiating species but will not affect otherwise the various mechanism discussed earlier. A more detailed discussion of energy transfer effects will be included in part IV of this series, where the role of methanol in the grafting reaction will be considered.

EXPERIMENTAL

Materials. Kraft and styrene purification have been described.^{1,2} Guaiacol (mp 28.8°C) and 2,6-dimethoxyphenol (mp 56.0°C) were kindly donated by Professor K. V. Sarkanen of the University of Washington, Seattle, and were used without further treatment. Isoeugenol (practical grade) was obtained from Eastman Organic Chemicals and was used without purification, as the main impurity was found to be eugenol.

Procedure. With the exception of experiments involving isoeugenol, per cent conversion was measured as in previous reports.^{1,2} In the remainder of the experiments, methanol-water or petroleum ether was used to precipitate polymer from its styrene solution. Some yellowish low molecular weight oil was evidently lost by this procedure.

Molecular Weight Measurements. Weight- and number-average molecular weights were calculated from the gel permeation chromatograms obtained with a Model GPC-300 instrument manufactured by Waters Associates, Framingham, Mass. The apparatus was equipped with five columns in series, each with gel of different pore sizes, capable of effecting separation of polystyrene molecules of dimensions in toluene corresponding to less than 2×10^6 molecular weight. In view of the small amounts of model compounds incorporated into the polymers, monodisperse polystyrene standards were used for molecular weight evaluation.

CONCLUSIONS

Model compounds for lignin containing free phenolic hydroxyl groups behave as effective chain transfer agents or polymerization retarders with styrene. Substituent effects are consistent with results obtained with lignin preparations and indicate that syringyl-type and isoeugenol-type configurations are not likely to result in significant graft copolymerization.

Guaiacyl structures unsubstituted para to the phenolic hydroxyl show less ability to react with styrene. Intermediate behavior would be most effective in a grafting system and can be no doubt attained by judicious pretreatment of the lignin preparation.

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