The Graft Copolymerization of Styrene and Lignin. II.   Kraft Softwood Lignin

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Synopsis

The radiation-induced graft copolymerization of styrene and various kraft softwood lignins was studied.   Expression of the results as the usual "per cent graft" was impossible, because grafting caused the lignin to become extractable in solvents for the styrene homopolymer.   However, evaluation of the effects of various solvents on the degree of reaction was made through an indirect, and possibly more characteristic, measure. Grafting was least pronounced under conditions of low lignin accessibility (e.g., when less than 10% methanol was present), but increased with the addition of better lignin solvents or with higher methanol concentrations.   The precipitating nature of the latter conditions was also found to contribute to an accelerated rate of grafting.   Surprisingly, the graft copolymer was found to degrade at higher doses.   Proof of grafting is offered in a fractionation scheme.   Measurement of the molecular weight of the polystyrene separated from the lignin backbone allows the estimation of approximately one polystyrene graft per lignin molecule in benzene-extractable copolymers.   Two glass transition temperatures could be detected in several fractionated copolymers.

INTRODUCTION

The first part of this series[1] was concerned with grafting to hydrochloric acid lignin.   This was chosen for the initial work since extensive studies had been reported in the literature[2] and had appeared to show rather conventional grafting behavior in that the per cent graft could be determined after extraction of the reaction products with benzene.   This removed the homopolystyrene, subject to the usual limitation that inextractable occluded homopolystyrene could also be present.   Initial experiments with kraft lignin, however, revealed rather anomalous behavior in that the weight of the reaction products after benzene extraction was in many instances less than that of the weight of benzene-insoluble lignin originally present.

While this circumstance makes interpretation of results rather difficult in terms of the reaction sequence proposed in part I, the effect of various modifications of the kraft lignin and of the use of different solvents could

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nevertheless be deduced from an indirect, and possibly more informative, measure of the actual grafting that occurred.

EXPERIMENTAL

Kraft Softwood Lignin

A sample of a commercially available kraft softwood lignin, known as Reax 20, was kindly donated by Dr. S. I. Falkehag of the Westvaco Research Center, North Charleston, South Carolina. The material is produced by the Westvaco Polychemicals Division and is obtained by partial acidification of the black liquor of that company's kraft pulping process. The sample, as received, was a fine brown powder, containing a small fraction of particularly low molecular weight material. The original lignin was found to be 3–4% extractable by benzene in a Soxhlet apparatus, and 5–6% extractable after irradiation in vacuo from a ^{60}Co source of γ-radiation for a dose of 10^7 rads. The extractable portion of this lignin was removed prior to use in the grafting experiments. The methoxyl contents of the original and extracted lignins were essentially the same, 13.99%, while the irradiated material had a slightly lower —OCH$_3$ content, 13.88%.

Methylated Kraft Lignins

The lignin described above was successively methylated with diazomethane in ether (—OCH$_3$, 16.8, followed by a treatment with dimethyl sulfate in 30% NaOH (—OCH$_3$, 22.4%). Complete procedural details may be found in ref. 4.

Crosslinked Lignins

Two crosslinked lignins were prepared by Westvaco according to their proprietary procedure. One was labeled "lightly crosslinked with formaldehyde," the other "highly condensed with ethylene diamine." No sol fraction was obtained by extraction of these lignins with benzene.

Fractionated Kraft Softwood Lignin

The original kraft softwood lignin was extracted for 48 hr with acetone to remove a lower molecular weight fraction. Both fractions were then evaporated to dryness in a hood, followed by drying at room temperature in a vacuum oven. The fractions were milled in order to reduce the particle size to its original state.

Procedures

The same grafting procedures and equipment were used as described in Part I (1). Methoxyl determinations were made by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany.

Isolation of Grafted Polystyrene Chains

Kraft lignin–polystyrene graft copolymers of known composition were subjected to nitrobenzene oxidation in order to separate the two components. For each gram of copolymer, 60 ml of $2N$ sodium hydroxide was added. In no case was complete dissolution possible, and wetting was difficult even in the case of slightly grafted fractions. Ungrafted lignin is easily dissolved in $2N$ NaOH. To the suspension of copolymer was added 8 ml nitrobenzene (Matheson Coleman and Bell); 15-ml portions of this mixture were poured into stainless steel autoclaves, which then were placed in an aluminum heating block at 180°C, for 3 hr.

After the reaction, the autoclaves were cooled and their contents removed by washing with alkali. These products were diluted with an equal volume of water and left in a separatory funnel overnight. The water-insoluble material was collected and washed with several portions of hot water. The gummy polymer was dissolved in benzene and precipitated in a water–methanol mixture. This procedure was repeated until the supernatant of the water–methanol mixture contained none of the brownish color due to the lignin oxidation products. Analysis of the insoluble material revealed less than 1% lignin content.

Koshijima and Muraki[2] had previously determined that pure polystyrene treated in a similar fashion underwent no reduction in molecular weight.

Glass Transition Temperature Measurements

Torsional braid analysis (TBA) was used to determine glass transition temperatures of fractions of grafting reaction products. The TBA instrument manufactured by Metavac Lenscote Corporation, and described by Gillham,[5] provides an assessment of the temperature-dependent mechanical properties of polymers. A 50% solution of the graft copolymer in dioxane was applied to the multifilament glass braid and allowed to dry first in air and then at higher temperature in the absence of oxygen. These conditions allowed the deposition of 0.01–0.02 g copolymer on the braid.

Analysis of the graphic output allows the calculation of $1/p^2$, the relative rigidity, and $1/n$, the mechanical damping index, at each given temperature. With data obtained in the present study, analysis could be made more clearly with values of $1/n$.

RESULTS AND DISCUSSION

Radiation-Induced Grafting to Modifications of Kraft Lignin in the Presence of Small Amounts of Methanol

In these experiments, it was immediately apparent that kraft lignin behaved in quite a different manner from HCl lignin. Despite extraction of the lignin preparations with benzene prior to the grafting experiments. additional quantities of the lignins could be extracted after the grafting

reaction. Table I summarizes the results of experiments when various lignin modifications were mutually irradiated with styrene in the presence of small quantities of methanol added as a swelling agent for lignin.

TABLE I
Radiation-Induced Graft Copolymerization of Styrene and Modified
Kraft Lignins in the Presence of Small Quantities of Methanol

Lignin preparation	Styrene: MeOH vol ratio	Conversion, %		Weight change,[a] %	
		5 Mrad	10 Mrad	5 Mrad	10 Mrad
Unmodified kraft softwood					
lignin	98:02	21.1	47.4	+2.3	+2.0
	97:03	26.6	58.5	−4.8	+11.6
	97:05	23.0	52.6	−5.9	+4.0
	90:10	14.9	46.0	+1.6	+14.3
Diazomethane-methylated kraft	95:05	23.2	48.3	−3.9	−4.3
Dimethyl sulfate-methylated					
kraft	98:02		41.2		−39.3
Low molecular weight kraft	98:02		45.7		−6.7
High molecular weight kraft	98:02		48.6		0.0
Lightly crosslinked kraft	98:02		88.0[b]		+26.3[b]
Highly crosslinked kraft	98:02		88.2[b]		+1.7[b]

[a] Value given is the weight gain (+) or loss (−) of original lignin after extraction of reaction products with benzene.

[b] Dose = 12 Mrads.

No pattern is immediately obvious from these data, certainly not in terms of the results displayed in part I. In some cases (e.g., unmodified kraft lignin, 90:10 styrene:methanol), the weight of grafted material increases with dose, as was found in the grafting reactions of HCl lignin, while in other cases (e.g., dimethyl sulfate–methylated kraft lignin), more original lignin was extracted than can be explained simply by radiation degradation (shown by separate experiments to be quite small).

On the basis of these data, and more so on those to be presented later in this paper, the following explanation is advanced: the solubility of lignin in benzene at a given temperature is a function of both the degree of polymerization of a given lignin molecule and the interaction of its structural units with solvent molecules. For ungrafted lignin chains, the latter effect is quite small; indeed, Brown[6] found this type of kraft lignin to be highly associated, even in good lignin solvents such as dimethylformamide or dimethyl sulfoxide.

When polystyrene is grafted onto the lignin, however, the graft copolymer can then assume solubility more characteristic of the extended polystyrene chains. The degree of copolymer–solvent interaction should depend on the length of the lignin backbone and the length and number of polystyrene branches. This solubilization of kraft lignin is probably possible only because of its low molecular weight (M_n = 900–1600)[6,7] and should not be

$L_0 + S + M_0$

$L_0 + P_0 + M_1$
$+$
S

evaporation

$M_1 + S$

Benzene

$L_0 + P_0$

inextractable
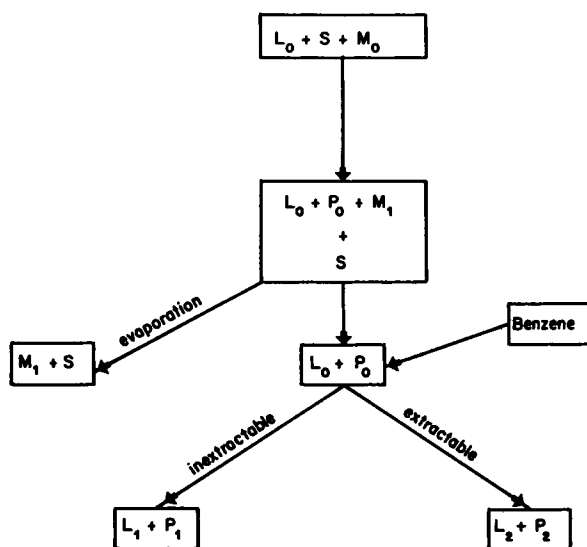
extractable

$L_1 + P_1$

$L_2 + P_2$

Fig. 1. Grafting procedure with kraft lignins.

routinely expected with higher molecular weight lignins, even with very high amounts of grafted material.

Thus, it is now emphasized that the extractability of kraft lignin in Table I, and the data to follow, may be used as a measure of grafting. The extraction process, as pictured in Figure 1, is essentially a gross fractionation, separating styrene homopolymer and highly grafted lignin into one (benzene-extractable) fraction, and ungrafted and slightly grafted lignin into another (benzene-inextractable) fraction. Infrared spectra, as well as —OCH$_3$ analysis, confirmed the presence of lignin in the benzene-extractable fraction, which in some cases had a dark-brown color.

To test if the grafting reaction was necessary for increased benzene extractability, a quantity of unmodified lignin was dissolved in dioxane along with five times the amount of pure polystyrene. The solution was then evaporated to dryness, and the solid residue was transferred to a Soxhlet thimble and extracted as before. It was found that the lignin remained inextractable, while all the polystyrene was easily removed. The experiment was repeated by irradiating the dioxane solution in vacuo but the same result was again noted. If lignin was irradiated in the presence of α-methylstyrene, which does not polymerize under the conditions used, no increase in lignin extractability was found. Thus, it appears that the lignin must truly be chemically bonded to polystyrene in order to be extracted, i.e., soluble in benzene.

Polystyrene solvents other than benzene were tried (e.g., toluene, cyclohexane, chloroform), but the graft copolymer was visibly soluble in all.

Clearly, the inability to express per cent graft in the traditional manner of "weight increase due to grafting" presents considerable difficulty. Specifically, one cannot compare grafting under the same conditions be-

tween HCl and kraft lignin if a significant amount of the latter is extracted with benzene. Moreover, the comparison between methylated and unmethylated kraft lignins is impossible because one cannot be certain that graft copolymers of each would be extractable in the identical lignin:polystyrene proportion. Even kraft lignin grafted under a variety of solvent conditions cannot be strictly analyzed because the effect of solvent on polystyrene chain length would change the extractability of the graft copolymer.

On the other hand, one can be confident that graft copolymerization and not simply homopolymerization *in situ* has occurred. With HCl lignin, there is no clear certainty that the weight increase attributed to grafting is not due to inextractable homopolymer. This problem has frequently been mentioned in studies of grafting to films[8] and fibers.[9] With kraft lignin, it is possible that homopolymer is occluded in the inextractable lignin fraction, but it is quite unlikely that this would affect the extracted lignin.

Radiation-Induced Grafting to Kraft Lignin in the Presence of Dioxane and Dimethylformamide

In Table I, little grafting is apparent with unmodified kraft lignin, regardless of the methanol concentration. This may, however, have been due to the hard, gel-like aspect of the lignin–styrene–methanol mixtures. To overcome these conditions unfavorable for the accessibility of monomer to the lignin, dioxane and N,N'-dimethylformamide were selected to replace methanol. With these new solvents, gelation was avoided and the lignin became more or less soluble in the reaction medium, depending on the styrene:solvent ratio. Tables II and III show the results with dioxane and DMF, respectively.

In most samples, the methoxyl contents of the inextractable fractions were measured, from which "per cent graft" of the fraction and "per cent original lignin extracted" can be calculated. When methoxyl contents

TABLE II
Radiation-Induced Graft Copolymerization of Lignin
and Styrene in Dioxane

Styrene:dioxane ratio	Dose, Mrads	Conversion, %	Original lignin extracted, %	Graft of inextractable fraction, %
80:20	5	15.6	17.9	9.1
	10	31.3	19.7	13.5
50:50	5	15.6	−21.0[a]	—
	10	30.7	−32.1[a]	—
20:80	5	25.7	28.9	18.6
	10	42.9	32.6	29.4

[a] —OCH₃ analysis not available; figure given is % weight change after extraction with benzene.

TABLE III
Radiation-Induced Graft Copolymerization of Lignin and Styrene
Dimethylformamide

Styrene:DMF ratio	Dose, Mrads	Conversion, %	Original lignin extracted, %	Graft of inextractable fraction, %
95:05	6.1	18.7	11.2	12.4
	10	28.2	16.8	13.5
	15	100	19.5	16.1
80:20	5	13.8	−24.2[a]	—
	10	28.3	−16.0[a]	—
60:40	14	43.8	32.4	19.9
	20	61.0	63.2	37.7
	25	100	45.4	38.3
50:50	Fig. 2	Fig. 2	Fig. 2	Fig. 2
20:80	1	8.6	16.2	19.5
	5	16.3	16.8	18.2
	10	30.4	20.8	23.9
	15	52.0	28.2	45.4
	16	57.6	25.4	35.7

[a] See Table II.

were unavailable, the data are reported as "per cent weight change" of the benzene-inextractable fraction, relative to the weight of lignin originally present:

% original lignin extracted = 100

$$\times \frac{\text{weight original lignin} - \text{weight inextractable lignin from methoxyl content}}{\text{weight original lignin}}$$

$$\% \text{ weight change} = 100 \times \frac{\text{weight inextractable fraction} - \text{weight original lignin}}{\text{weight original lignin}}$$

From Tables II and III and Figure 2, the following observations can be made:

1. The per cent grafts obtained for the inextractable fractions are undoubtedly a reflection of the distribution of grafting that occurred for the total lignin. It follows that for a *given* styrene–solvent mixture, the highest per cent graft for the inextractable fraction also represents the highest per cent graft to the total lignin, and hence the greatest quantity of benzene–extractable material.

2. Between *different* styrene–solvent compositions for a given solvent, no one-to-one correspondence appears between per cent graft to the inextractable fraction and per cent lignin extracted because of the effect of solvent concentration on grafted polymer chain length and molecular weight distribution. Table IV demonstrated this property.

3. With both DMF and dioxane, extractability appears to be maximum at intermediate solvent concentrations. This can be considered a result of at least three factors: first, increased lignin swelling or solubility at high
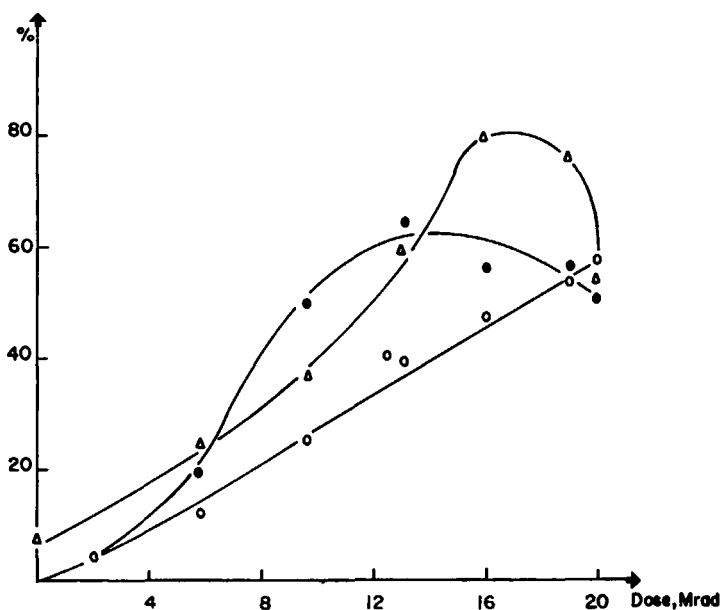
Fig. 2. Graft copolymerization of kraft softwood lignin with styrene in the presence of dimethylformamide (50:50:5 styrene:DMF:lignin):   (△) % original lignin extracted with benzene; (○) % conversion of styrene; (●) % graft of inextractable fraction.

solvent concentration; second, increased termination rate of grafted poly-styryl radicals through chain transfer; and third, diminished monomer concentration.

4.   As expected, grafting initially increased with increasing radiation dose. However, unexpectedly, the per cent graft of the inextractable fraction, as well as the per cent lignin extracted, eventually decreased with higher doses (see, e.g., Fig. 2).   While this effect may be due to degradation by radiation, the degradation cannot occur on the lignin chain, as this would tend to increase the extractability of lignin in benzene.   Moreover, radiation degradation of polystyrene is not normally found,[10] though this phenomenon would well account for the data.   The remaining possibility of degradation would require scission of the lignin–polystyrene bond.   This perhaps results from interaction of the radiation energy and the aromatic lignin units bonded to polystyrene.

TABLE IV
Nature of the Grafts Produced by Different Styrene–DMF Mixtures

Styrene:DMF ratio	Dose, Mrads	Weight polystyrene, g	Lignin extracted, %	Graft inextractable fraction, %
20:80	1	0.156	16.2	19.5
50:50	5.8	0.561	24.8	19.6
60:40	14	2.395	32.4	19.9

Radiation-Induced Grafting to Methylated Kraft Lignin

For comparison with the results of Figure 2, diazomethane-methylated kraft lignin was reacted as in the latter case with a 50:50 styrene:DMF solution. The results, shown in Figure 3, appear to show less degradation of the graft copolymer than that found in the unmethylated case. This would tend to support the previous explanation of the degradation, because, as discussed in part I of this series, the location of the grafted polymer can be different on methylated and highly phenolic lignins. Thus, a greater dissociation energy would be involved in the degradation of a methylated lignin–styrene graft copolymer.
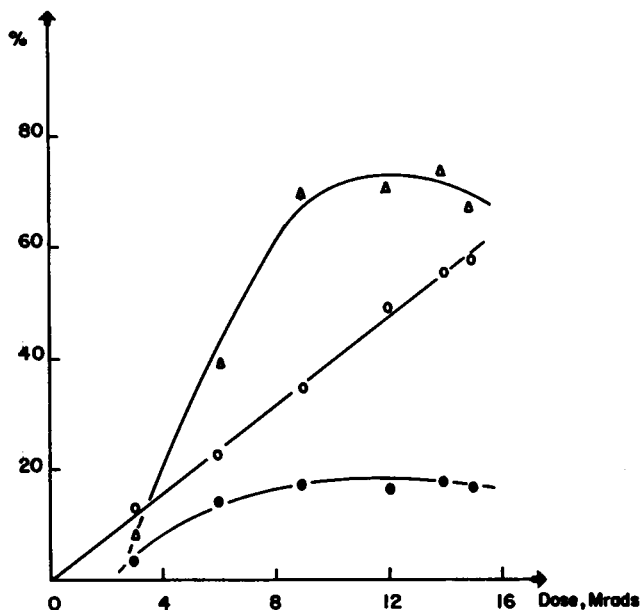

Fig. 3. Graft copolymerization of diazomethane-methylated kraft softwood lignin with styrene in the presence of dimethylformamide. Same conditions and symbols as in Fig. 2.

Radiation-Induced Grafting to Kraft Lignin in Precipitating Medium

Chapiro[11] reported an increase in the rate of radiation-induced polymerization of styrene when the reaction was conducted in a large proportion of methanol, a nonsolvent for the polymer. This effect results from the occlusion of the chain radical by the precipitated polymer coil, reducing the rate of biradical termination. Application of this phenomenon to graft copolymerization has been made by several authors[12,16] and has recently been discussed by Phillips and Stannett.[17]

Use of high proportions of methanol was made in the present work, not only for the primary effect of lowering the rate of termination of grafting, but also to increase the accessibility of the lignin to monomer. Figures
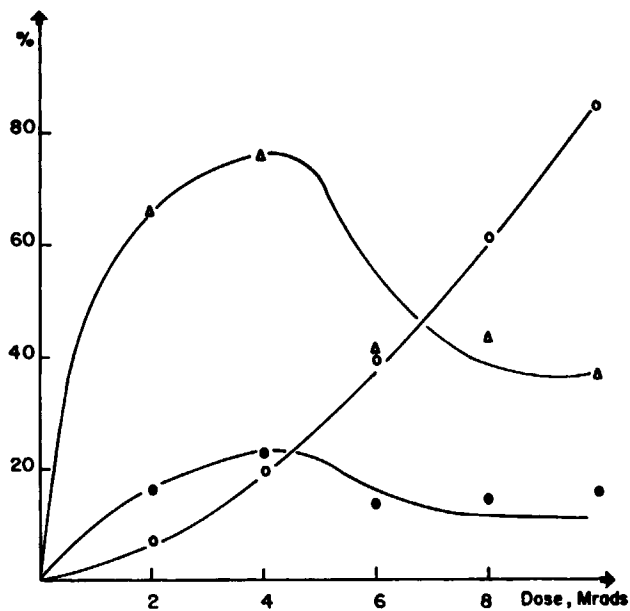
Fig. 4. Graft copolymerization of kraft softwood lignin with styrene in the presence of methanol (50:50:5 styrene:MeOH:lignin).   Same symbols as in Fig. 2.
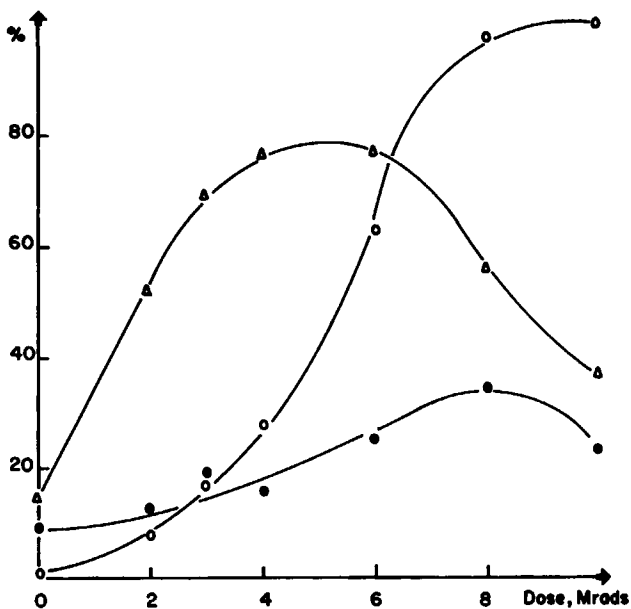

Fig. 5. Graft copolymerization of kraft softwood lignin with styrene in the presence of methanol (25:75:5 styrene:MeOH:lignin).   Same symbols as in Fig. 2.
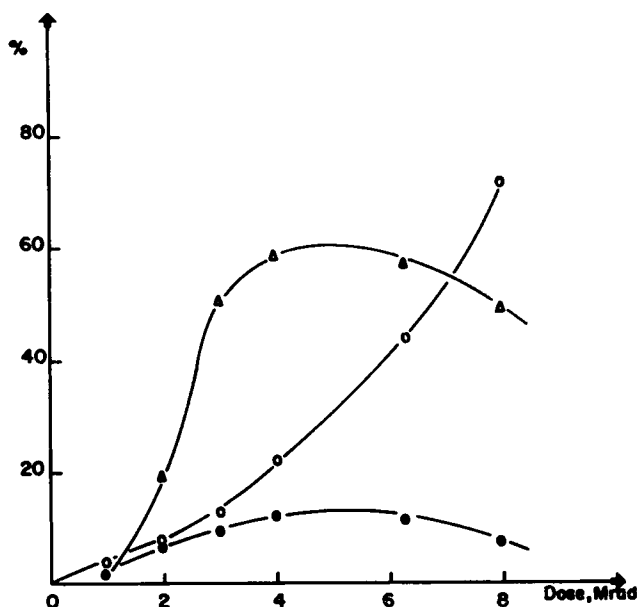
Fig. 6. Graft copolymerization of kraft softwood lignin with styrene in the presence of methanol (20:80:5 styrene:MeOH:lignin). Same symbols as in Fig. 2.

4 to 6 appear to bear out these expectations; for example, with 25:75 styrene:methanol (Fig. 5), almost 80% of the lignin could be extracted with benzene after a dose of 4 megarads, compared to the 16 megarads required to achieve the same level when DMF was employed (Fig. 2). Figure 6 indicated that lower monomer concentration eventually causes grafting to decrease, possibly through termination by primary radicals.[17]

Fractionation of the Graft Copolymer

In order to characterize the kraft lignin–polystyrene graft copolymer, the conditions responsible for the maximum of lignin extractability in Figure 5 were chosen for the synthesis of a large-scale sample. Thus, 5.0 g unmodified lignin was sealed under vacuum with 25 ml styrene and 75 ml methanol. The contents were continuously stirred during an irradiation period of 4 megarads.

As shown in Figure 7, the reaction products containing 33.2% lignin could be dissolved in an 80:20 benzene:methanol mixture. Further addition of methanol caused precipitation of polystyrene-rich material, fraction IA. The soluble portion, fraction IB, was evaporated to dryness and further fractionated as shown in Figure 7.

Fraction IA was suspended in cyclohexane at a 1% solids concentration at 70°C for 24 hr. Normally, this procedure is sufficient to dissolve all styrene homopolymer (as verified with a physical mixture).

However, fraction IIA, the material insoluble at 70°C, contained 68.8% polystyrene, which must then be graft copolymer. As the temperature of
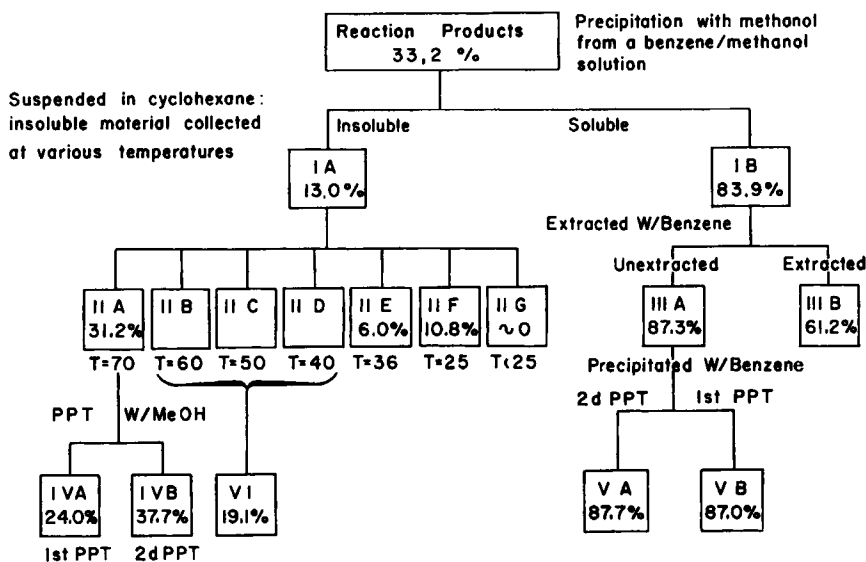
Reaction   Products
33,2 %

Precipitation with methanol
from a benzene/methanol
solution

Suspended in cyclohexane:
insoluble material collected
at various temperatures

Insoluble   Soluble

I A
13.0%

I B
83.9%

Extracted W/Benzene

Unextracted   Extracted

II A
31.2%   II B   II C   II D   II E
6.0%   II F
10.8%   II G
~0

III A
87.3%   III B
61.2%

T=70   T=60   T=50   T=40   T=36   T=25   T<25

Precipitated W/Benzene

2d PPT   1st PPT

PPT   W/MeOH

I VA
24.0%   I VB
37.7%   V I
19.1%

V A
87.7%   V B
87.0%

1st PPT   2d PPT

Fig. 7. Fractionation of graft plus homopolymer from reaction under the conditions of Fig. 5 (dose = 4.0 × 10⁶ rads). Numbers in boxes indicate percentage lignin present in fraction.

the mixture was lowered further (remaining at each indicated temperature for 24 hr), the probability of precipitated homopolymer increases. Fraction IIG, however, was the only one collected containing substantially lignin-free polystyrene. This fraction accounted for 10% of the weight of the reaction products.

Molecular Weight of Grafted Polystyrene

Using the nitrobenzene oxidation procedure described in the experimental section of this paper, polystyrene branches may be isolated relatively free of the lignin portion. For the calculation of the number of branches per lignin molecule, several assumptions must be made: (1) the sample can contain no homopolymer; (2) all of the polystyrene, particularly the low molecular weight material, can be recovered; (3) the molecular weight measurement by gel permeation chromatography of the polystyrene is not affected by a guaiacyl endgroup; (4) the molecular weight of the kraft lignin by be satisfactorily represented by the value $M_n = 1600$ in a poor solvent.[6]

In an earlier report,[4] a fractionation scheme similar to that in Figure 7 gave rather low ratios of chains of polystyrene to chains of lignin. Using an improved method of polymer isolation, however, fraction VI (which should contain no homopolymer and only grafted lignin chains) was oxidized with nitrobenzene, and the polystyrene was isolated and purified by several washings and reprecipitations. Care was taken, however, to retain low molecular weight polystyrene. Comparison of the gel permeation chro-

matogram of the product obtained by this procedure with those of mono-disperse polystyrene samples allows one to calculate[18] a value of $\bar{M}_n = 7050$ for the homopolymer. Then, using $\bar{M}_n = 1600$ for kraft softwood lignin, one may calculate approximately 1.1 for polystyrene chain/lignin chain. A rather high ratio of $\bar{M}_w/\bar{M}_n = 2.6$ was obtained (as compared to values less than 2 when the low molecular weight material was neglected as in the earlier report[1]).

Glass Transition Temperatures of the Graft Copolymers

Torsional braid analysis was made of several of the fractions of graft copolymer described in Figure 8. The results, expressed as the damping index at various temperatures, are shown in Figure 8. It is evident that both components have a minimum concentration below which there is no apparent contribution to the damping behavior of the fraction. Thus, polystyrene does not appear in the spectrum of sample VB, which contains 13.0% polystyrene, while lignin seemingly does not make any contribution to IIF, containing 10.8% lignin. It is not at all surprising that kraft lignin shows only a broad peak (VB), when one considers the varied chemical nature of lignin structural units as well as the nonlinearity of the total molecule.

Samples IIIB (61.2% lignin) and IVB (37.7% lignin) have the only spectra with two clearly defined peaks. The polystyrene transitions appear to occur at 82°C and 99°C, respectively, while those due to lignin may be estimated at 147°C and 164°C. If these relative differences are assigned to molecular weight influence on T_g, then IIIB would contain shorter
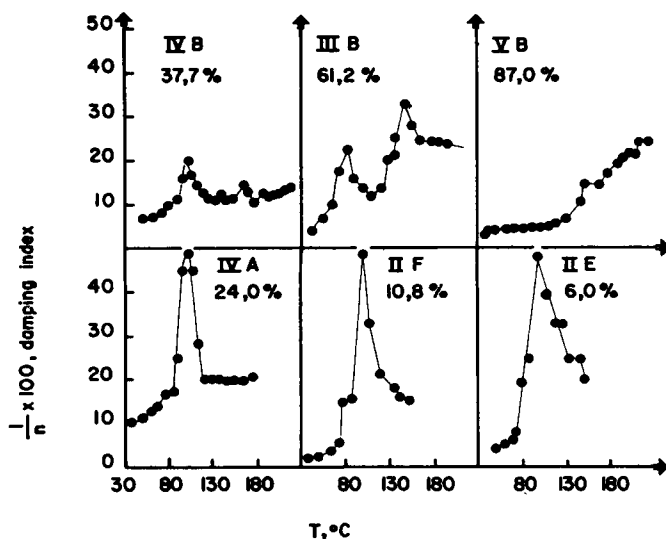

Fig. 8. Damping indices of various fractions (Fig. 7), determined by torsional braid analysis at various temperatures. Numbers in boxes indicate percentage lignin present in fraction.

polystyrene segments than does IVB, a finding consistent with the fractionation scheme of Figure 7.

Within experimental error, fractions IVB, IVA, IIF, and IIE each registered a T_g near 100°C. This result is particularly interesting since all four fractions were obtained from fraction IA and perhaps differ from one another only in the number of polystyrene chains grafted to each lignin molecule.

CONCLUSIONS

The radiation-induced graft copolymerization of styrene and kraft softwood lignin is a diffusion-controlled reaction which produces few short-chained polystyrene grafts. Nevertheless, because of the low molecular weight of the starting lignin backbone, a benzene-soluble graft copolymer can be produced. The efficiency of the grafting process can be significantly increased by conducting the reaction in a medium precipitating for the grafted polystyrene chains.

References

1. R. B. Phillips, W. Brown, and V. Stannett, *J. Appl. Polym. Sci.*, **15**, 2929 (1971).

2. T. Koshijima and E. Muraki, *J. Polym. Sci. A-1*, **6**, 1431 (1968).

3. Technical Bulletin, *Lignochemicals*, Westvaco Corporation, Polychemicals Division, North Charleston, S. C.

4. R. B. Phillips, Ph.D. Thesis, North Carolina State University, Raleigh, N. C., 1970.

5. J. K. Gillham, *Appl. Polymer Symposia*, **2**, 45 (1966).

6. W. Brown, *J. Appl. Polym. Sci.*, **11**, 2381 (1967).

7. J. Marton and T. Marton, *Tappi*, **47** (8), 471 (1964).

8. S. Munari, G. Tealdo, F. Vigo, and C. Rossi, *Eur. Polym. J.*, **4**, 241 (1968).

9. V. Stannett and H. B. Hopfenburg, in *Cellulose and Cellulose Derivatives*, N. Bikales and L. Segal, Eds., Interscience, New York, 1971.

10. A. Chaprio, *Radiation Chemistry of Polymeric Systems*, Wiley, New York, 1962.

11. A. Chaprio, *J. Chim. Phys.*, **47**, 747 (1950).

12. G. Odian, T. Acker, E. Ratchik, M. Sobel, and R. Klein, AEC-RAI-301, 1962.

13. G. Odian, T. Acker, and M. Sobel, *J. Polym. Sci.*, **7**, 245 (1963).

14. G. Odian, M. Sobel, A. Rossi, and R. Klein, *J. Polym. Sci.*, **55**, 663 (1961).

15. S. Dilli, and J. L. Garnett, *J. Appl. Polym. Sci.*, **11**, 839 (1967).

16. S. Dilli, and J. L. Garnett, *J. Appl. Polym. Sci.*, **11**, 859 (1967).

17. R. B. Phillips and V. Stannett, to be published.

18. J. Cazes, *J. Chem. Educ.*, **43** (7), 567 (1966).