

POLLUTION ABATEMENT BY MORE  
EFFECTIVE LIGNIN UTILIZATION:  
GRAFTING TO LIGNIN AND LIGNIN -  
CONTAINING PULPS

by

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January 1970

The work upon which this publication is based was supported in part by funds provided by the Office of Water Resources Research, Department of the Interior, through the Water Resources Research Institute of the University of North Carolina as authorized under the Water Resources Research Act of 1964.

Project No. A-032-NC

Agreement Number - 14-01-0001-1853



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## SUMMARY

The problem of increased utilization of lignin has been approached from two directions: first, a procedure has been developed for grafting vinyl monomers to isolated lignin; second, grafting of hydrophilic monomers to pulps containing substantial amounts of lignin (high yield pulps) has been attempted.

In the first case, styrene was successfully grafted by radiation to a commercially available lignin. In the more successful cases, the grafted product has the solubility behavior of polystyrene. While the reaction proceeds adequately in the presence of good swelling agents for the lignin, the expenditure of radiation is great ( $16 \times 10^6$  rads); on the other hand, grafting in the presence of large amounts of methanol speeds the reaction ( $3 \times 4 \times 10^6$  rads), presumably because of a hindered radical termination rate.

It was found that acrylamide could not be significantly grafted to unbleached kraft pulps containing even only 4% lignin. Consequently, a study was made of the strength properties of blends of highly grafted pure cellulose pulps and the ungrafted high yield kraft pulps. While the blends significantly improved the strength properties of the high yield pulp, the radiation involved and the amounts of the grafted pulp required were great, thus casting doubt on the economic feasibility of such a combination.



## I - INTRODUCTION

Lignin is the major non-cellulosic component of wood, comprising approximately 20% of the weight of hardwoods, and about 30% of softwoods. In chemical pulping processes, only about 50% of the wood is actually utilized as pulp, the remaining 50%, including most of the lignin, is either discarded as a waste product, or recovered as a by-product. The former procedure is clearly the less acceptable of the two; it is not only wasteful, but is a major source of water pollution. Consequently, the pulp and paper industry has continuously sought uses for this most abundant raw material.

An obvious, and probably the most profitable, utilization of lignin is to retain the material in the pulp, a process which also eliminates the pollution problem. Because of the adverse effect of lignin on paper strength and color, this concept presents some difficulties: The presence of lignin, a highly hydrophobic material, decreases the swelling of cellulose fibers, and ultimately the fiber-fiber bonding, one of the major factors affecting paper strength.

Presently, high lignin content pulps, notably groundwood (produced by the mechanical defibration of wood), are blended with very highly hydrophilic fibers before formed into a sheet. Still, as evidenced by the strength of, say, newsprint, this paper has poor strength properties. One means of improving the strength of the sheet made from blended fibers is to increase the hydrophilicity of the additive fibers. This can be done in several ways, one of the most promising being grafting, or chemically bonding, of a hydrophilic polymer to the additive fibers. For example, acrylamide grafted to cellulose has greatly improved the water retention properties of the cellulose alone. The literature on grafting to cellulose is quite large, and has been the subject of several comprehensive reviews (1-4).

Because lignin can easily be isolated from the pulping liquor (though highly modified from the structure of lignin in wood), research in lignin utilization has invariably been directed toward the discovery of modifications of isolated lignins which give some specially desirous properties.

The pulping liquor, or isolated lignin can be used as follows:  
(1) discarded, (2) burned for fuel value, (3) utilized for its physical

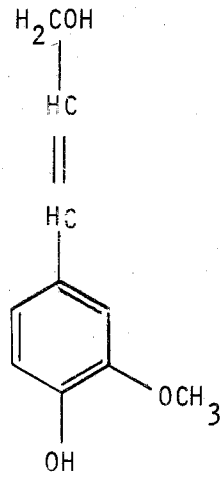
properties, or (4) utilized as a source for marketable chemicals, notably vanillin and dimethyl sulfoxide.

It is the third category above which is an area of interest for the present research. A recent technical bulletin distributed by the West Virginia Pulp and Paper Company (5) gives a partial listing of the uses for some 25 "lignochemicals" recovered from that company's kraft pulping process. These lignin modifications are used as dispersants, resin co-reactants, emulsifiers, stabilizers, sequestrants for polyvalent metals, reinforcing agents for rubber, and oxygen scavengers. Since most of the above uses involve the existence of the lignin with other components or phases, the lignin could be more effective in some cases if it were more compatible with the other components. Again, the grafting of some polymer (which would be chosen on the basis of its compatibility with the primary component) to the lignin could give a product with greatly enhanced properties. Thus, two approaches to improving lignin utilization were taken in this research. The first involved the grafting of the hydrophobic monomer styrene to a commercially available lignin isolated from the kraft process. Styrene was chosen as the monomer because of the wealth of knowledge about the behavior of this material, and the unknown nature of the grafting reaction. The second approach was to graft highly hydrogen bonding hydrophilic side chains of polyacrylamide directly to high yield pulp, or develop a highly hydrophilic grafted pulp which could be blended with high-yield kraft pulp to give a sheet with improved strength properties.

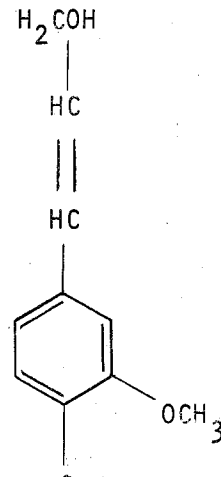
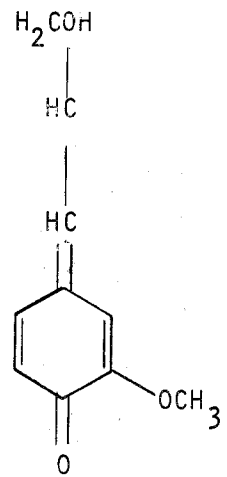
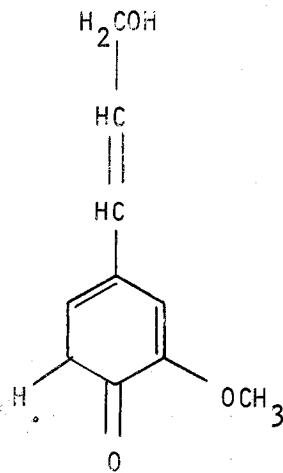
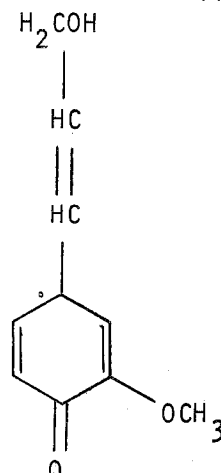
## II - GRAFTING TO LIGNIN

II - 1 General

Lignin in wood is believed to be synthesized by the enzymatic dehydrogenation of the substance coniferyl alcohol (I), the radical of which can exist in four mesomeric forms (II-V) (6)



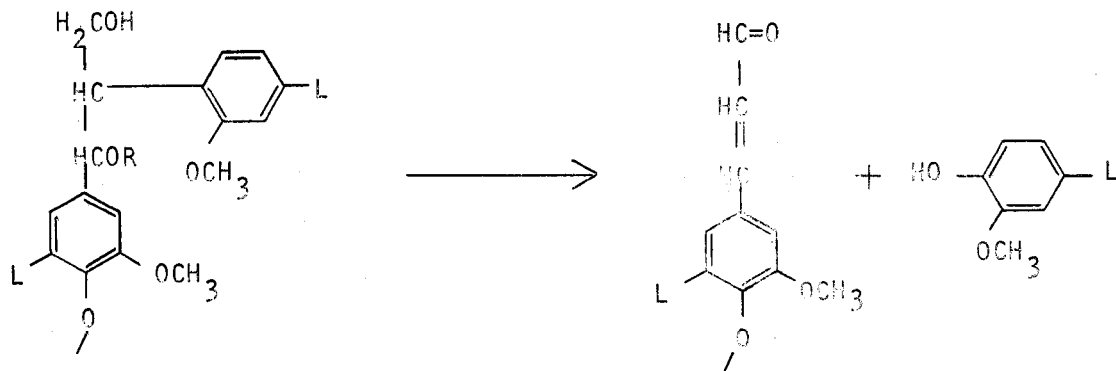
I

II  
R<sub>1</sub> phenoxyIII  
R<sub>3</sub>IV  
R<sub>5</sub>V  
R<sub>1</sub>

Because these mesomers combine in a statistical manner, it is doubtful that lignin in wood can ever be completely represented by a single structural formulation. The uncertainty about lignin in wood exists to the degree that it is unknown whether or not lignin is chemically bonded to carbohydrates in wood, or whether it exists simply as an entangled mixture.

Any procedure to isolate lignin from wood must necessarily modify the structure of the original lignin. Most structural studies on lignin have been made with milled wood lignin (MWL) (7) which is obtained by mechanical milling of wood, followed by extraction with neutral solvents for long periods of time; this form of lignin is probably the least altered from that of lignin in wood. The results of these studies, made mainly by Freudenberg (6) and Adler (8) have shown that softwood lignin consists of many units similar to coniferyl alcohol (1), but linked together in many different fashions.

Studies by Marton and co-workers (9-11) have shown that the structure of kraft lignin is degraded from that of MWL. The kraft pulping chemicals attack lignin in wood in a manner shown below.



This lignin may be isolated by partial acidification of the black liquor, and can be obtained in the form of a fine brown powder. Reactions of the type shown above produce a lignin highly phenolic in character; this property is dramatically seen in Table I which compares the functional groups present in kraft and milled wood lignin from softwood species.

Table I

## Functional groups in lignin (11)

Groups in 100 C <sub>6</sub> - C <sub>3</sub> Units	Spruce MWL	Kraft Pine
Total OH	120	120
Guaiacyl OH	30	60
2 X Catechol	-	12
Aliphatic	90	48
Total COOH	5	16
Total CO	20	15
Coniferyl Aldehyde	3	-
$\alpha$ - C = O	7	5
$\beta$ - and other C = O	10	10

The degraded nature of kraft lignin is evident from comparison of the molecular weights of the same lignins, including hardwood kraft:

Table II

## Molecular weights of lignins (10)

Type Molecular Weight	Spruce MWL	Kraft Pine	Kraft Hardwood
Number Average	2100	1600	1050
Weight Average	7000	3500	2900
Mw/Mn	3.3	2.2	2.8

Utilizing the data of Tables I and II, Marton (11) has proposed the following constitutional scheme for the structure of softwood kraft lignin (Fig. 1):

It should be emphasized that this structure is a statistical representation which contains the correct percentages of functional groups, and is linked according to possible reactions in alkaline pulping.

The isolated form of kraft lignin presents several difficulties as a polymer backbone in a grafting system. The first requirement for a grafting

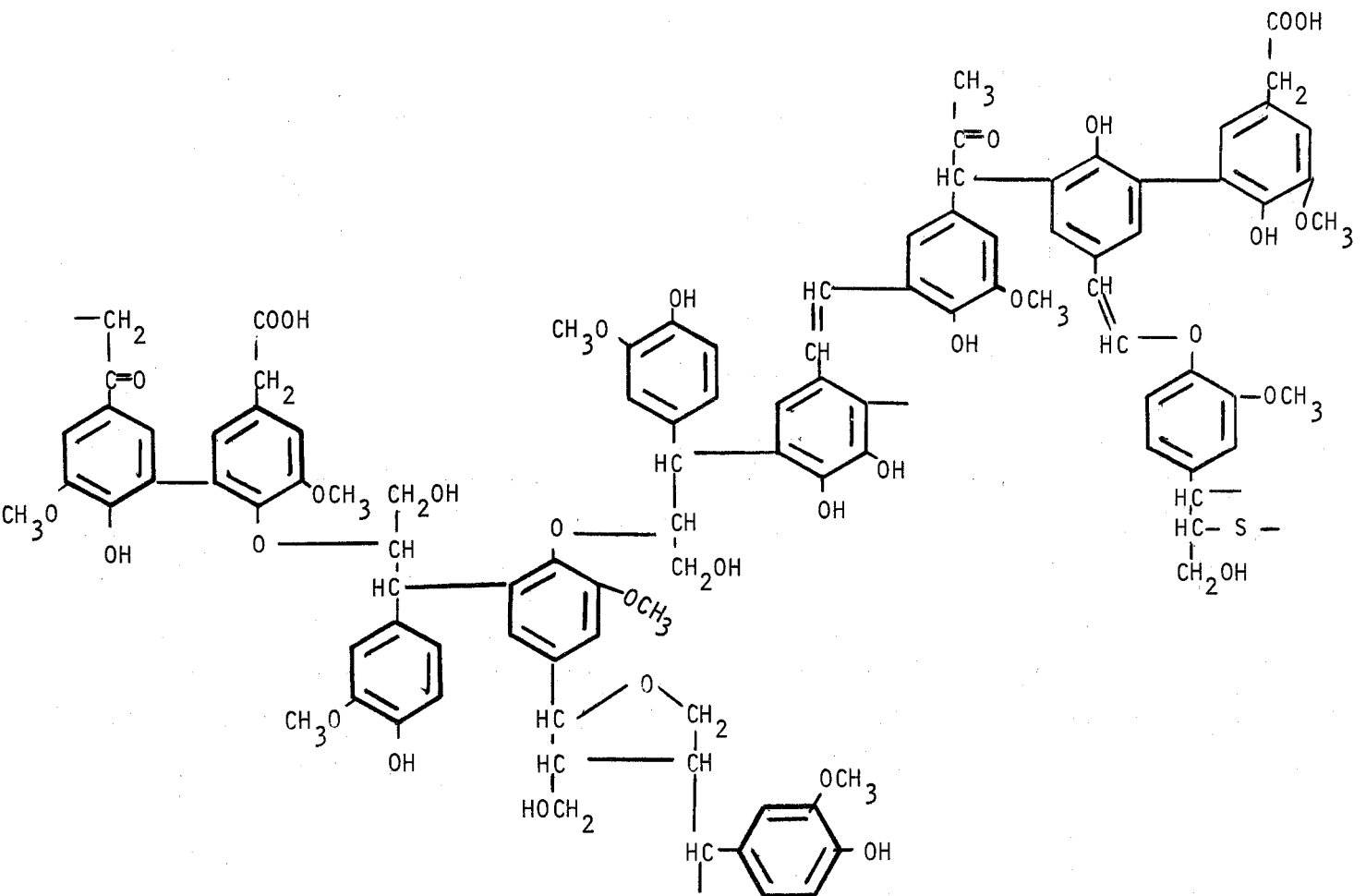


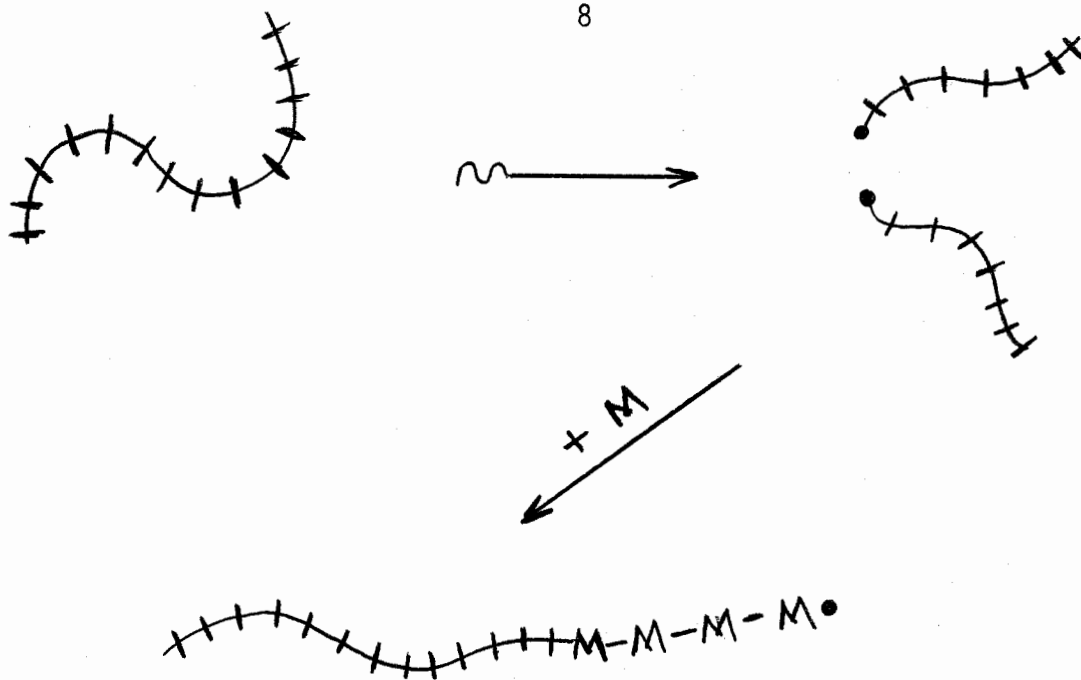
Figure 1. Constitutional scheme of kraft pine lignin

reaction to proceed is for formation of radicals on the backbone; examination of Fig. 1 shows that kraft lignin is highly conjugated, and chemical production of radicals would probably yield mainly stable phenoxy radicals. Even though high energy radiation is insufficient to create large numbers of radicals, this latter means was chosen for two reasons: (1) the non-specificity of radiation would promote radical production on all portions of the lignin molecule (as opposed to the specificity of chemical attack); and (2) the availability of  $\gamma$  - radiation sources for increasingly lower costs makes this means of radical initiation particularly attractive.

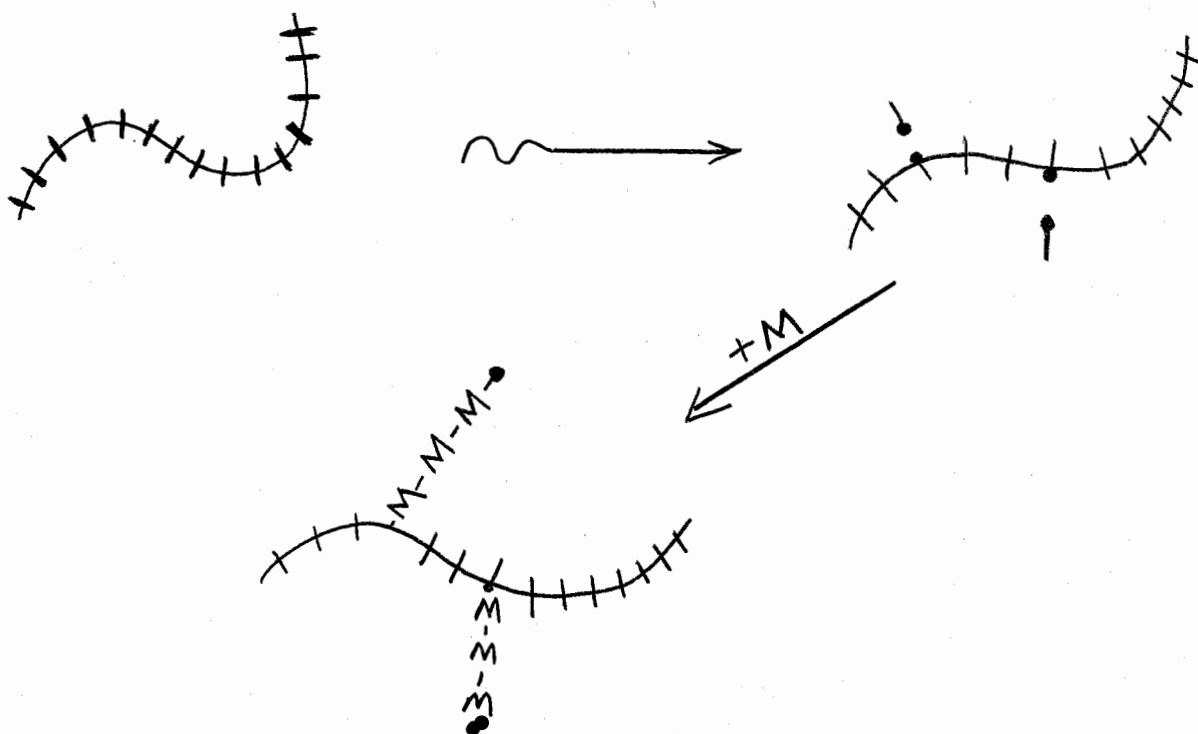
As previously mentioned, lignin exhibits a high stability to radiation. Hachihama (12) showed that the molecular weight and amounts of functional groups of various lignins remained reasonably constant after exposure to various doses of gamma radiation. Although Steelink (13), and later Kringstad (14), have shown that kraft lignin has a fairly high concentration of native free radicals ( $\sim 10^{17}$  spins/gram), Sofue and Ueno (15) and Koshijima (16) found that various lignins had very low  $G_R$  values (the  $G_R$  value being the number of radicals formed per 100eV of radiation).

From the above discussion it is possible to make some speculations concerning the behavior of lignin as a polymer backbone in a grafting system. As shown in Fig. 2, irradiated polymers may undergo scission in the main chain, or in a substituent group; in the former case, a block copolymer might be obtained, while in the latter instance, the possibility for graft copolymerization exists. From earlier remarks, lignin would predominantly form radicals of the second type, but their number would be small.

In addition to the problem of radical formation, the accessibility of the monomer to the radicals must be considered. That is, the lignin must be swollen, either by the monomer, or by the addition of a good solvent for the polymer. Recently, Hansen (17, 18) proposed that the swelling or solubility of polymers may be characterized by a volume of interaction with the polar, dispersion, and hydrogen bonding components of the solubility parameter. The method is a more detailed representation of the Hildebrand solubility parameter (19), or any of its subsequent modifications. Hansen has published extensive tables of these parameters for solvents, which have been plotted in Fig. 3, along with the corresponding solubility behavior of kraft softwood



A. Formation of block copolymers by radiation



B. Formation of graft copolymers by radiation

Figure 2. Formation of graft and block copolymers

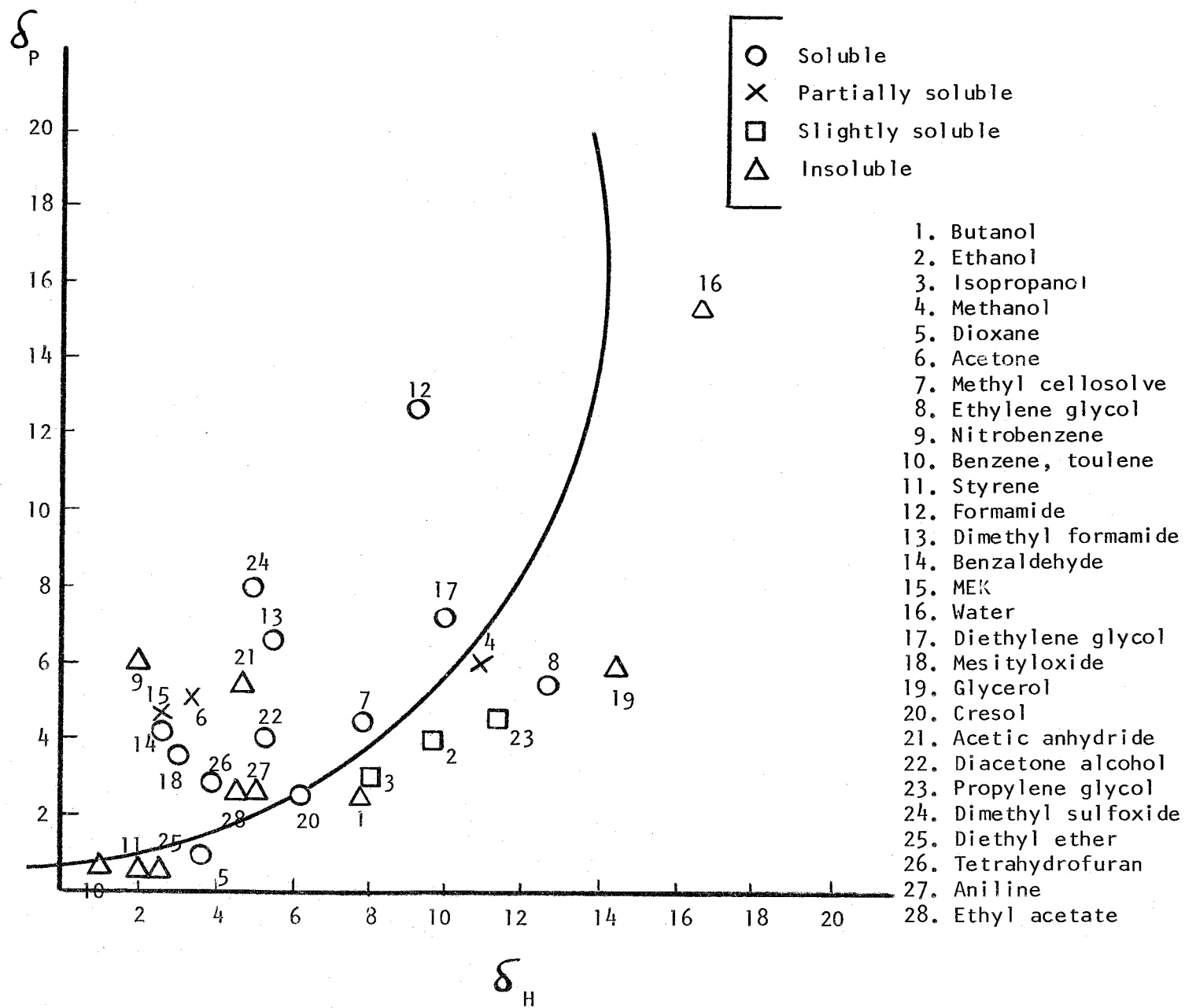


Figure 3. Solubility of kraft softwood lignin

lignin (20). Non-polar compounds such as styrene and benzene are poor solvents for kraft lignin, while more highly hydrogen bonded and polar materials such as methanol, dioxane and dimethyl formamide are better. Water, on the other hand, is found to be a non-solvent.

Earlier, a Japanese researcher, Koshijima, studied the radiation-induced graft copolymerization of methyl methacrylate (16, 21) and styrene (22-27) to hydrochloric acid lignin, a highly condensed form of lignin, formerly a by-product of a Japanese process for isolating cellulose from wood. The important findings of Koshijima were: (1) The grafting reaction is a free radical process; (2) grafting with styrene occurs on approximately 60% of the guaiacyl units, probably on one of the free aromatic carbons; (3) when no solvent is added, methyl methacrylate grafted more efficiently than styrene; (4) when the phenolic hydroxy groups were fully methylated, grafting increased from 25% to 40% maximum with styrene as monomer; (5) when 2% methanol was added, the grafting ratio of styrene increased from a maximum of 40% to 430%; (6) up to 100% graft the molecular weights of the grafted chains were constant at about 5,000; after 100% graft these molecular weights steadily increased.

The purpose of this research was to: (1) clarify the factors influencing the graft copolymerization of styrene and hydrochloric acid lignin; and (2) to apply this knowledge to the more practical problem of grafting to kraft softwood lignin. While characterization of the graft copolymer was not one of the goals of the research, some work in this area was conducted in order to prove that grafting did take place.

## 11-2 Experimental

### 11-2-1 Materials

Hydrochloric Acid Softwood Lignin was kindly provided by Dr. T. Koshijima of the Government Industrial Research Institute, Osaka, Japan. The lignin was prepared from *Pinus densiflora* according to the procedure described in (16), and was identical to the (unmethylated) lignin used in Koshijima's studies.

Kraft Lignin: The softwood kraft lignin was a commercial product, known as Reax 20, of the Polychemicals Division of West Virginia Pulp and Paper Company, North Charleston, South Carolina, and was donated by Dr. S. I. Falkehag of that organization.

Styrene, stabilized with tert-butyl pyrocatechol, was obtained from Eastman Organic Chemicals. The monomer was distilled in a packed column at approximately 45° and 20 mm Hg to remove inhibitor and other non-volatile contaminants. The styrene was stored with Drierite in a refrigerator until the day of use. A final cold distillation was made on the day of use to remove any polymer which may have formed.

Solvents: All solvents were reagent grade materials, obtained from Baker and Adamson. Methanol, N, N' - dimethyl formamide, and p-dioxane were used after distillation. Benzene and cyclohexane, used for Soxhlet extraction purposes, were used without purification.

#### 11-2-2 Grafting Procedure

Approximately 0.5 g of lignin, dried at 60° under vacuum, was placed in a 15- or 25-mm diameter glass ampoule connected to a 24/40 ground glass joint which could be attached to a high-vacuum system. In most experiments 10 ml of monomer-solvent mixture were pipetted into the ampoule. The ampoule was attached to the vacuum system capable of maintaining a pressure of less than  $10^{-5}$  mm Hg. The sample was degassed by repeated freeze-thaw cycles, taking approximately 30 minutes to evacuate the ampoule during each freezing. After the fifth freezing, the samples were sealed, and placed in the  $\gamma$ -radiation facility. The source used was Co-60 "gammacell 220" manufactured by Atomic Energy of Canada. Samples remained in the cell for a length of time sufficient to receive a given dose. The source had been previously calibrated, and the intensity was measured from a dose rate decay diagram. The dose rate was approximately  $0.14 \times 10^6$  rad/hr during most of the experiments.

#### 11-2-3 Measurement of Conversion

After irradiation, the ampoules were broken open, and the contents transferred, using benzene, to a tared beaker. After addition of 0.5 ml

alcoholic solution of 3% benzoquinone, the samples were air-dried in a hood. Finally, the beakers were placed in a vacuum oven, heated to 60° and remained until dried to constant weight. Per cent conversion was calculated as the weight increase due to polymer, divided by the weight of monomer initially present.

#### 11-2-4 Measurement of Per Cent Graft

For the hydrochloric acid lignin runs, the dried polymer-lignin mixture was soaked overnight in benzene. Afterwards, the contents of the beaker were transferred to a tared Whatman extraction thimble; the thimble was placed in a Soxhlet extraction apparatus, where the sample was extracted with benzene until no more polystyrene could be removed. Afterwards, the thimble and contents were dried under vacuum at 80°C. Per cent graft was calculated as follows:

$$\% \text{ Graft} = 100 \times \frac{\text{weight of material insoluble in benzene-weight of lignin}}{\text{weight of lignin}}$$

When kraft lignin was used, a different procedure described later in detail was used.

### 11-3 Results and Discussion

#### 11-3-1 Grafting to Hydrochloric Acid Lignin

Several experiments with HCl lignin, used in Koshijima's work, were conducted in order to gain experience with the lignin-styrene system, and to clarify several puzzling aspects of Koshijima's interpretation of his data.

As mentioned earlier, Koshijima reported an increase in grafting when: (1) phenolic hydroxyls were methylated; and (2) when methanol was added. Koshijima attributed the first increase to the prevention of formation of phenoxy radicals, which he believed too stable to participate in a grafting reaction. The second increase was thought to be a result of the methanol swelling the lignin.

Our results indicate that methanol plays a more important role than simply swelling the lignin. Fig. 4 shows the per cent graft of HCl lignin as function of dose, when no methanol is present. The grafting that occurs is almost negligible, even though the conversion

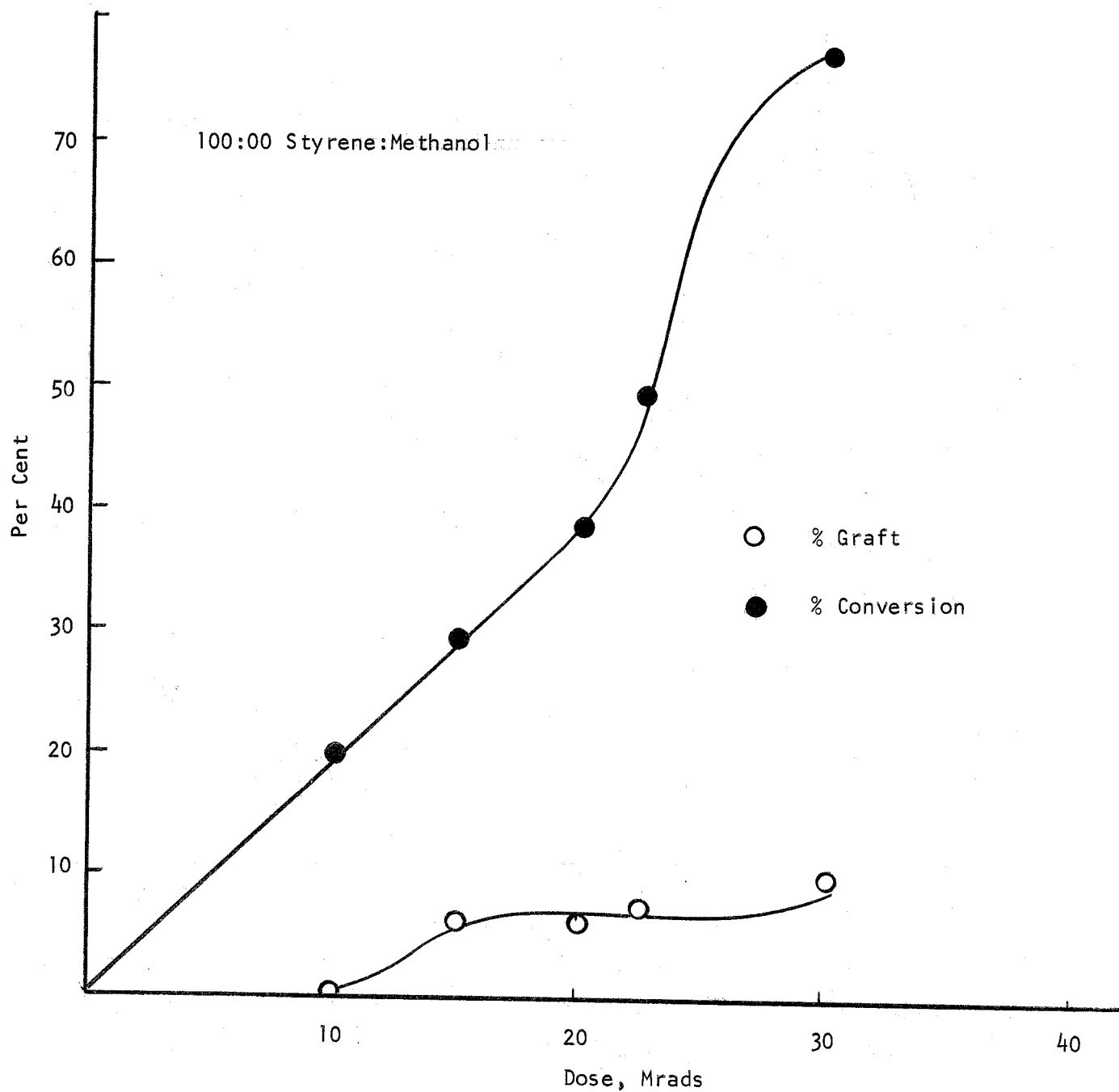


Figure 4. Grafting of HCl lignin with pure styrene

of styrene to polymer is quite high. Fig. 5 shows the same quantities when 2% methanol was added. Initially, the grafting is low, even though the lignin is presumably somewhat swollen. At a dose of 7 megarads, however, the grafting ratio begins to accelerate, at the same time that the conversion of monomer to polymer accelerates. This indicates that the "gel effect" does exist. Thus, there must be two factors affecting the grafting of styrene to unmethylated hydrochloric acid lignin: (1) swelling of the lignin; and (2) rate of radical termination.

Additional proof that the "gel effect" was in existence in Figs. 4 and 5 is given in Table III, which shows the intrinsic viscosities of the homopolymer extracted from the reaction mixture:

Table III  
Viscosity data for HCl lignin grafting

% MeOH	Dose (Mrads)	% Conversion	[ $\eta$ ]
0	15	29.4	0.419
0	20	38.7	0.406
0	30	77.5	0.528
2	5	24.1	0.388
2	7	33.7	0.392
2	8	40.5	0.416
2	9	53.2	0.516
2	10	93.4	0.641

These results might also explain Koshijima's data which showed a constant length of grafted chains up to 100% graft, and the subsequent increase; i.e. the "gel effect" was in existence in his system also.

The points raised above must cast some question on Koshijima's explanation of the effect of methylation. In a heterogeneous grafting system, as we are dealing with here, the nature of the polymer backbone should have little effect on the kinetics of the bulk polymerization of monomer. For graft polymerization, we must, however, consider both swelling and radical formation phenomena. The pertinent data are

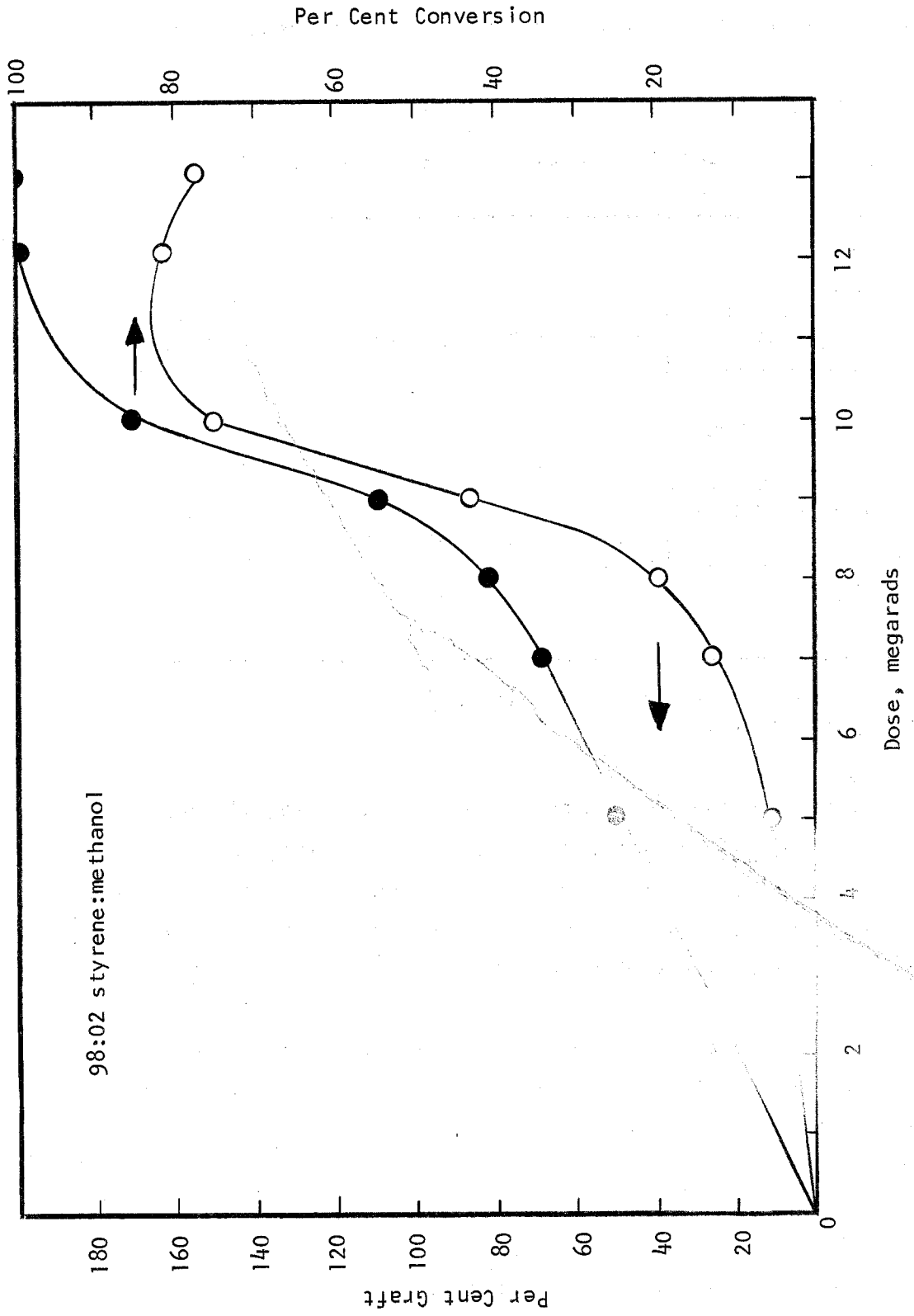
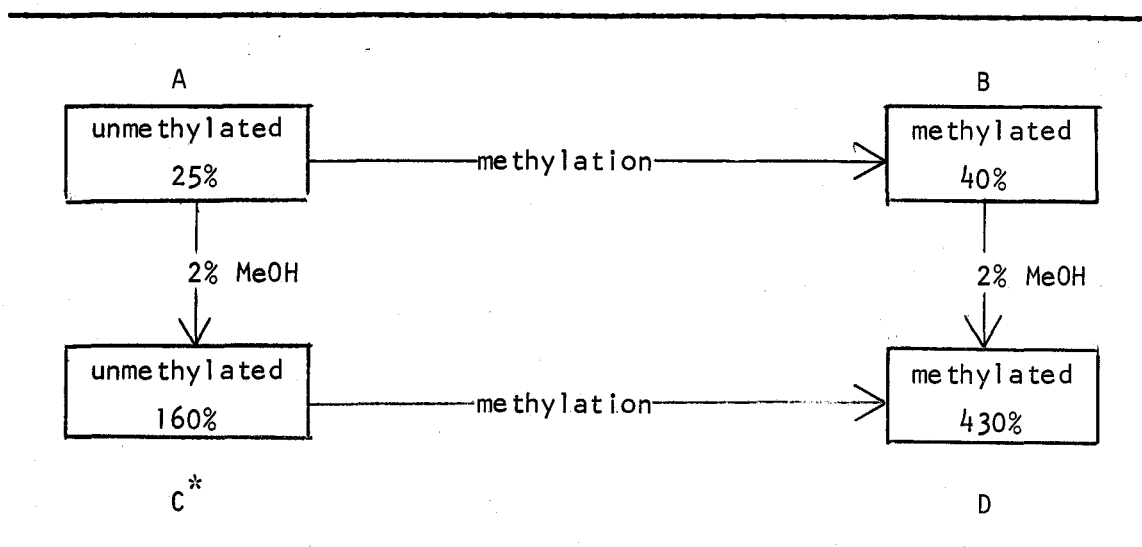


Figure 5. Grafting of HCl lignin with 98:02 styrene:MeOH

collected in Table IV, which reflect the effects of methylation and swelling with 2% methanol, on the maximum per cent graft obtainable:

Table IV  
Methylation and swelling of HCl lignin\*



\*Sample C is data from this report. All other data are from Koshijima's articles.

It is seen in the cases considered above that methylation causes an increase of ca. 2-3 times the unmethylated value, while addition of 2% methanol causes an increase in per cent graft of 8-10 times the value when methanol is absent. These considerations indicate that the main effect of methylation might simply be that methylated lignin swells more in styrene.

From an examination of structural features of both lignin and styrene, methylation of a phenolic substance would increase its swelling in a non-polar medium.

#### 11-3-2 Grafting to Kraft Softwood Lignin

For convenience, these experiments will be described in two sections: first, where the medium for the reaction is non-precipitating for the polystyrene, and second, where grafting takes place in a precipitating medium.

Non-precipitating Media. Earliest experiments showed that kraft lignin behaved quite differently from hydrochloric acid lignin; although the molecular weight of kraft lignin is much smaller than the other, swelling seemed to be the major problem. Table V shows the results of grafting experiments with styrene and small amounts of methanol.

In each case, the per cent graft is small, even when the "gel effect" exists. The last column of Table V shows that in some cases, a weight loss after extraction with benzene was recorded; these latter figures corresponded to samples where, from the color of the extractable portion in the Soxhlet apparatus, considerable amounts of lignin had either dissolved, or become extractable, in benzene. Unlike HCl lignin, which is completely inextractable with benzene, the lower molecular weight kraft lignin (by itself) is 3-4% extractable before irradiation, and 5-6% extractable after a dose of  $10^7$  rads.

Although some of the lignin dissolved in the reaction medium, depending on the amount of methanol present, the undissolved portion of the lignin appeared to be in a highly associated state, and, in some cases, a gel. Though methanol is probably the best solvent to use from a radiolysis standpoint (because of its high  $G_R$  value), both dioxane and DMF are better solvents for kraft lignin. Using these solvents, the phenomenon of increased extractability of the lignin became the predominant feature of the reaction.

The anomalous behavior of this grafting reaction required a new measure of per cent graft. In order to adequately explain the measure chosen, reference is made to Fig. 6, which reviews the experimental procedure with kraft lignin: the lignin-styrene-solvent mixtures were prepared, sealed, irradiated, and extracted as described above. At this point, kraft lignin departed from the behavior of HCl lignin. It seems likely that the kraft lignin became extractable with benzene because it was sufficiently grafted with polystyrene that the copolymer could demonstrate the solution properties of polystyrene more so than lignin. Thus, this reasoning allows the conclusion that the benzene extractable portion contains highly grafted lignin and homopolystyrene, and the inextractable portion contains only less grafted lignin and ungrafted lignin. It has been also found that there is no easy way to

Table V

## Grafting of lignin-styrene-methanol mixtures

Mixture <sup>1</sup> (Styr:MeOH)	Dose (Mrads)	Per Cent <sup>2</sup> Conversion	% Weight Gain or Weight Loss After Extraction W/Benzene
98:02	5	21.1	+ 2.3
	10	47.4	+ 2.0 (a)
	12	87.2	0.0
	12	88.0	+ 26.3 (b)
	12	88.2	1.7 (c)
97:03	5	26.6	- 4.8
	10	58.5	+ 11.6
95:05	5	23.0	- 5.9
	10	52.6	+ 4.0
90:10	5	14.9	+ 1.6
	10	46.0	+ 14.3

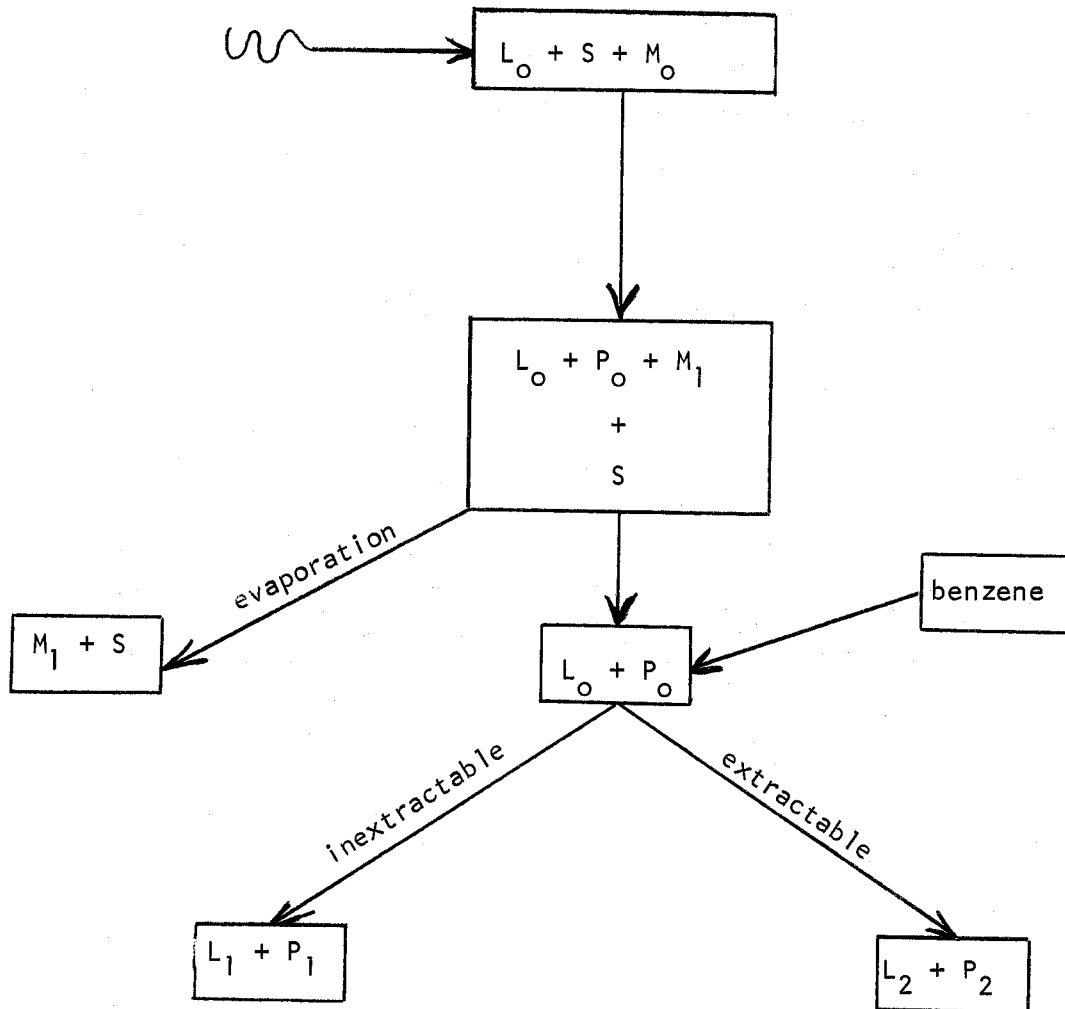
(a) Per cent graft by  $\text{OCH}_3$  content was + 5.7%.

(b) Lightly cross-linked with formaldehyde.

(c) Highly cross-linked.

<sup>1</sup> Styrene:solvent volume/volume ratio.

<sup>2</sup> 100 x ratio of polystyrene formed: weight of styrene monomer.



- $L_o$  = Original lignin  
 $M_o$  = Original monomer  
 $S$  = Solvent  
 $P_o$  = Polymerized monomer  
 $M_1$  = Unpolymerized monomer  
 $L_2$  = Lignin extractable with benzene  
 $P_2$  = Graft + homopolymer  
 $L_1$  = Grafted + ungrafted lignin  
 $P_1$  = Grafted polymer

Figure 6. Grafting procedure

separate homopolymer from the grafted lignin, because their solubility characteristics are so similar; hence, the adoption of a rather cumbersome method of reflecting the amount of grafting that has occurred has been necessary. From an independent chemical analysis, the exact amount of lignin present in any fraction of the product can be determined; hence, the calculation of the total amount of lignin which was extracted with benzene is possible. Since the lignin is extractable only because it is grafted, it is believed that this measure gives an adequate representation of the grafting which has occurred.

The results of grafting with dioxane and DMF may now be examined (Tables VI and VII):

Table VI

## Grafting of lignin-styrene-dioxane mixtures

Mixture (Styr:Diox.)	Dose (Mrads)	% Conv.	% Original Lignin Extrac. W/Benzene	% Graft of Inextract. Portion
80:30	5	15.6	17.9	9.1
	10	31.3	19.7	13.5
50:50	5	15.6	-21.0*	*
	10	30.7	-32.1*	*
20:80	5	25.7	28.9	18.6
	10	42.9	32.6	29.4

\*OCH<sub>3</sub> analysis not available; figure given is weight loss after extraction with benzene.

Table VII

## Grafting of lignin-styrene-DMF mixtures

Mixture (Styr:DMF)	Dose (Mrads)	% Conv.	% Original Lignin Extrac. W/Benzene	% Graft of Inextract. Portion
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*	*
	10	28.3	-16.0*	*
60:40	20	61.0	63.2	37.7
	25	100	45.4	38.3
50:50	(See Fig. 7)			
20:80	5	8.6	16.2	18.2
	10	30.4	20.8	23.9
	15	52.0	38.2	45.4
	16	57.6	25.4	35.7

\*OCH<sub>3</sub> analysis not available; figure given is weight loss after extraction with benzene.

In some of the cases shown in Tables VI and VII, the lignin contents of the fractions were not available, and simply the weight loss of lignin after extraction is shown. This figure is approximately equal in magnitude to the weight of lignin extracted with benzene. Where sufficient data are available, it appears that, within each composition examined, maximum grafting occurred at an intermediate dose. Also, there appears to be an optimum ratio of styrene to solvent for best grafting results.

This first effect is shown rather vividly in Fig. 7, where grafting with a 50:50 styrene:DMF mixture was a maximum at about 16 megarads. There are two possible explanations for the decrease in extractability with increasing dose: either the graft copolymer degrades, or the grafted chains cross-link. Since polystyrene is known as a polymer of the cross-linking type, the second explanation seems most plausible on

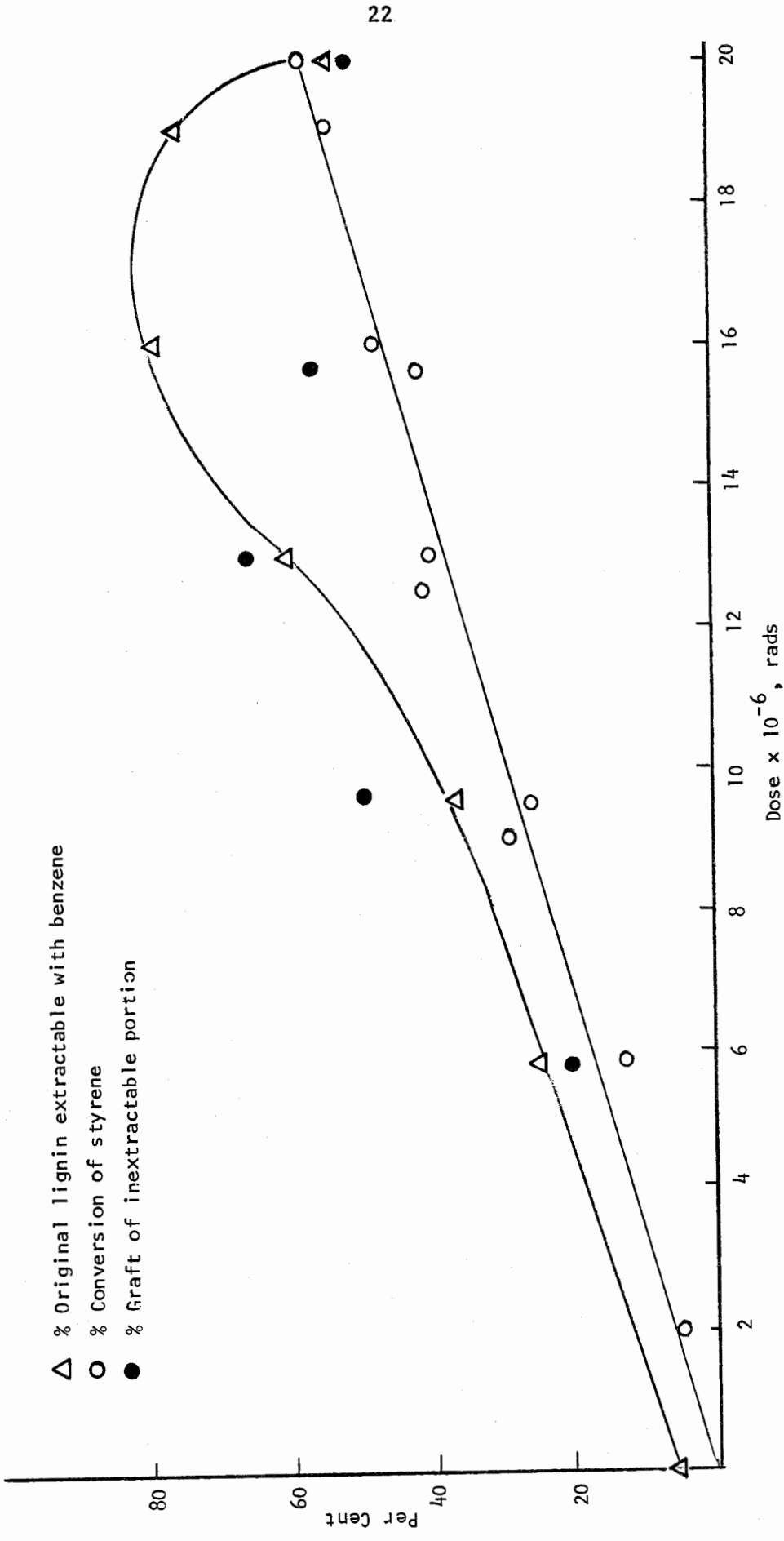


Figure 7. Grafting of kraft softwood lignin with 50:50 styrene:DMF

the surface. However, close examination of Fig. 7 reveals that the per cent graft to the inextractable portion also decreased in a similar manner. If the chains did cross-link, this value should steadily increase. This same trend is readily apparent with 20:80 styrene:DMF, shown in Table VI. Since polystyrene does not normally degrade, this might mean that degradation occurs exactly at the lignin-polystyrene linkage. In all of the cases here, and those to be presented later, the degradation occurred at a slower rate than the grafting; and since both processes require interaction with radiation at the aromatic portion of the graft copolymer, it seems reasonable to believe that grafting and degradation occur simultaneously throughout the entire reaction; it is only at the latter stages that degradation predominates. The degradation of the graft copolymer was also noted with HCL lignin (see Fig. 5).

The maximum that occurred for intermediate solvent compositions is more readily explicable. Once a grafted chain begins to grow, it behaves no differently from any other polystyrene chain radical. This means that chain transfer can become a limiting factor to the length of the grafted chains, particularly at high solvent concentrations. Thus, although the number of grafted chains might be large, their length must be small, and hence the graft copolymer is not extractable.

Though the solvents DMF and dioxane apparently can give a highly grafted product, the expense of the radiation involved is quite large. For this reason, the next area of investigation was that of grafting with large amounts of methanol as solvent.

Precipitating Medium. If the results of Chapiro's study (28-30) of the radiation-induced polymerization of styrene in the presence of methanol can be applied to the lignin-styrene-methanol grafting system, then some of the difficulties in swelling, and slow rate of grafting, should be overcome. Chapiro found that small amounts of methanol increased the rate of polymerization of styrene, because the solvent is much more sensitive to radiation, and hence the rate of initiation increased. At very high contents of methanol the medium became a precipitant for the polymer; between 10-40 volume % methanol, the chains merely coalesced, causing a reduction in the rate of polymerization; at methanol concentrations greater than 40%, the polymer precipitated as a

fine powder, causing the chain radicals to repulse one another, hence reducing the rate of termination of radicals, and causing an increase in the rate of polymerization. The latter mechanism is similar to the "gel" or Trommsdorff effect mentioned earlier, and has been equated to the Trommsdorff effect by Odian, *et al.* (31, 32). The description by Chapiro of the styrene-methanol behavior has been recently extended by Huang (33), and by workers in this laboratory (34).

Applying these results to grafting, it would seem that using large proportions of methanol would offer several advantages: first, the overall reaction would occur at much higher rate than before; secondly, the presence of large quantities of methanol would swell the lignin better; finally, the molecular weight of the chains would be large, and benzene extractability would be assured.

Figs. 8-11 show that these expectations were somewhat confirmed; first, with 50:50 styrene:methanol, almost 80% extractability was obtained after only 4 megarads (80% was the maximum obtained with DMF as solvent after 16 megarads). It is also seen that the per cent graft to the benzene inextractable portion followed a similar curve. With 25:75 styrene:methanol, again excellent grafting occurred at low doses. Also it was found that degradation of the graft copolymer occurred, both in the extractable and inextractable portions. Similar behavior was found with a 20:80 mixture (Fig. 11).

It is interesting to compare the factors affecting the grafting with DMF as solvent, and with high concentrations of methanol. DMF is a good enough solvent for lignin that a 20:80 styrene:DMF mixture gave a homogeneous grafting medium; all styrene:methanol:lignin samples were heterogeneous. DMF is so much less sensitive to radiation than methanol, that the rate of polymerization of styrene is far slower in the presence of DMF than in methanol (compare Figs. 7 and 8). Finally, DMF is a solvent for polystyrene, and cannot create the same rate-accelerating effects as methanol can.

### 11-3-3 Proof of Grafting

Normally, a mixture of two homopolymers can be separated by a series of solvent-non-solvent operations. This is particularly true

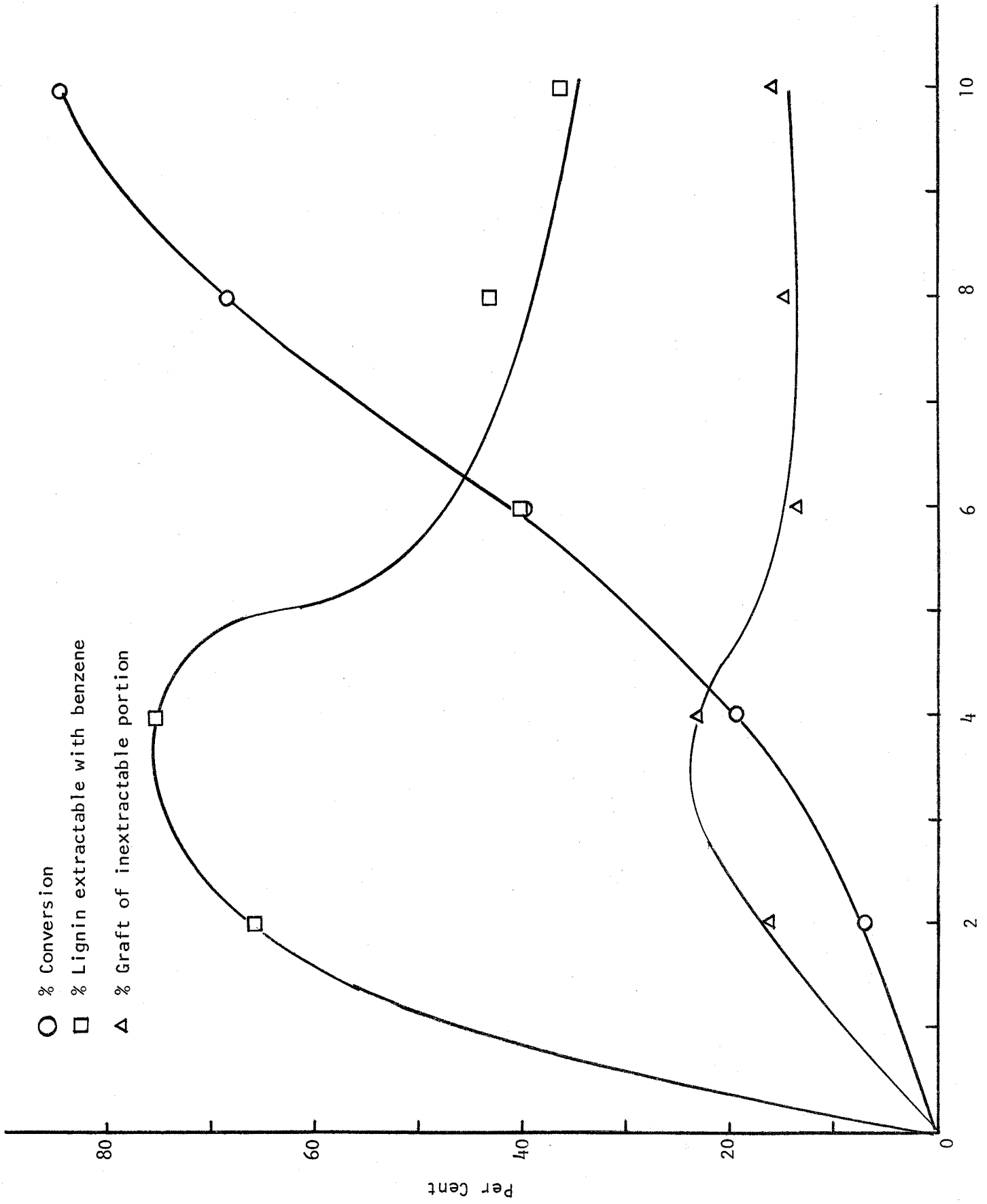


Figure 8. Grafting of kraft softwood lignin with 50:50 styrene:MeOH

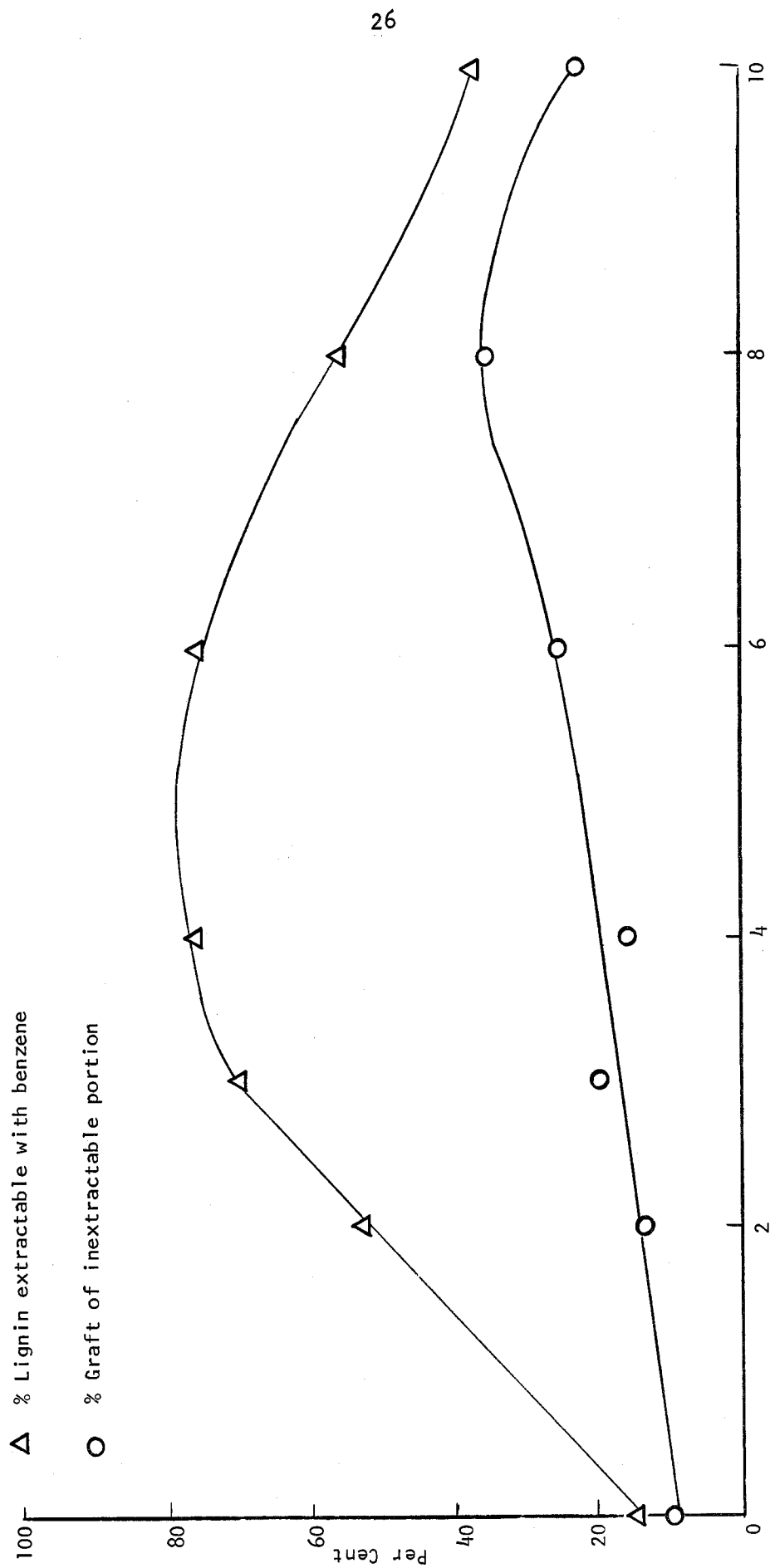


Figure 9. Grafting of kraft softwood lignin with 25:75 styrene:MeOH I

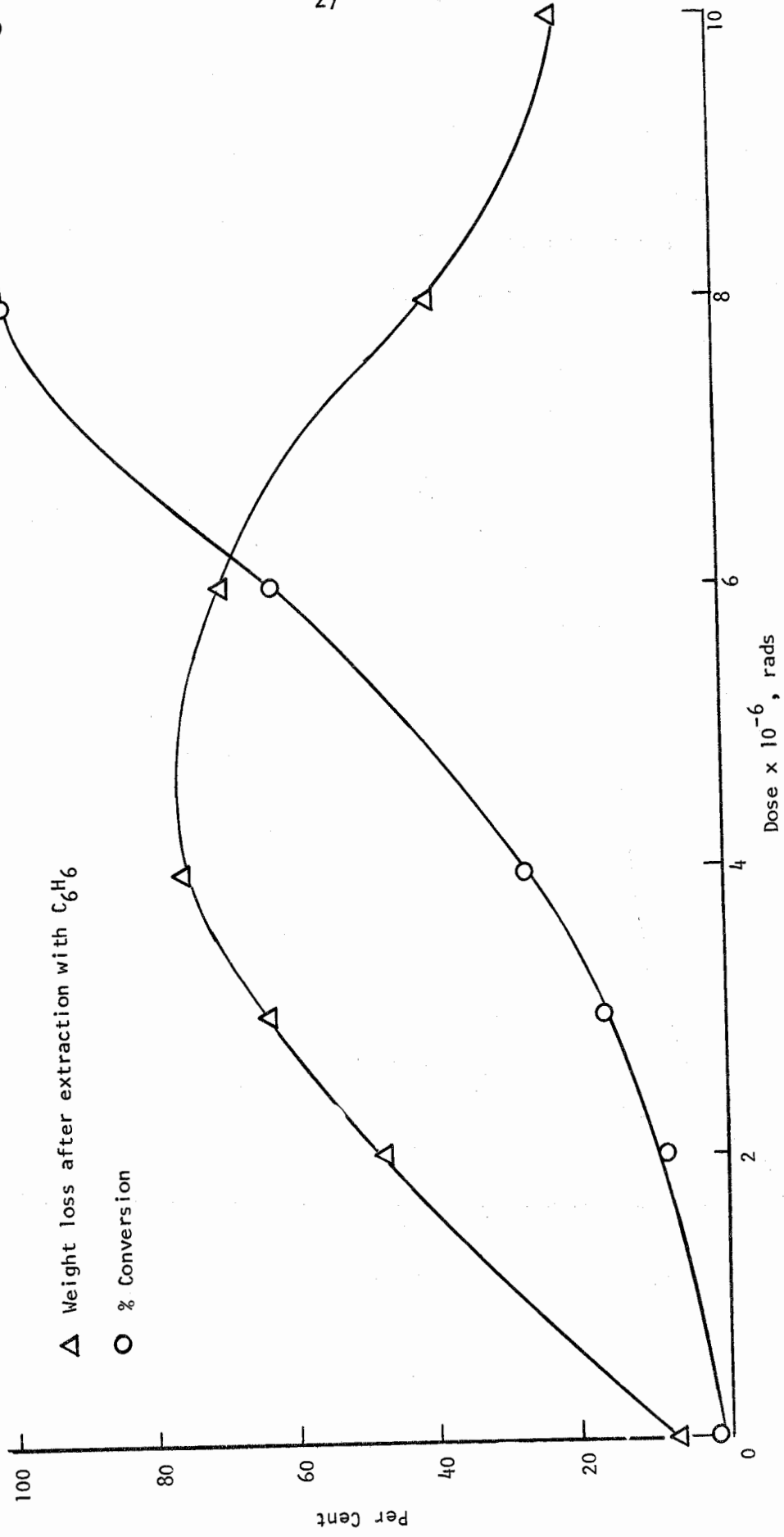


Figure 10. Grafting of kraft softwood lignin with 25:75 styrene:MeOH II

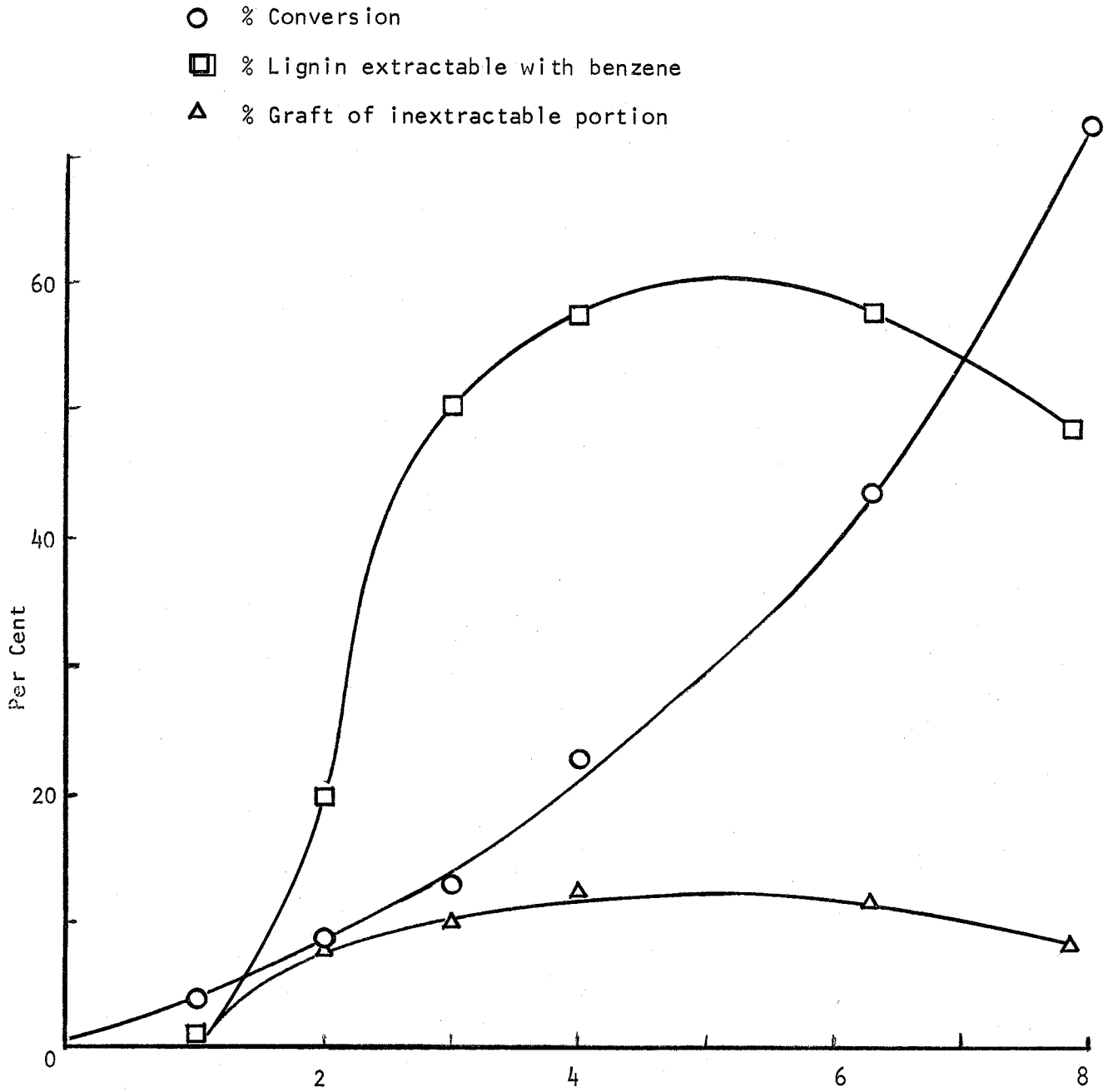


Figure 11. Grafting of kraft softwood lignin with 20:80 styrene:MeOH

if the two polymers differ widely in their solubility behavior, as do polystyrene and lignin.

A rather large-scale sample of grafted lignin was prepared, using a 25:75 styrene:methanol mixture, subjected to an extensive fractionation scheme as shown in Fig. 12. It would be useful to point out several of the features of the scheme; the reaction products, containing 33.2% lignin, were dissolved in a mixture of benzene and methanol. The addition of larger amounts of methanol caused precipitation of the polystyrene-rich material. This fraction, containing 13.0% lignin, was suspended in cyclohexane at various temperatures, and the insoluble material was collected. Perhaps the best proof of grafting is sample IIA, which is the material insoluble at 70° in cyclohexane. Polystyrene is soluble in cyclohexane above 36°; yet, IIA contained 69% polystyrene which was insoluble. Therefore, this polystyrene must be grafted, or chemically bonded, to the lignin, which is essentially insoluble in cyclohexane at all temperatures.

#### 11-4 Conclusions

The grafting of styrene and lignin is controlled by the following variables:

1. The swelling of the lignin backbone;
2. The rate of termination of chain radicals, including the decrease in rate because of the viscosity of the medium (the gel effect), or because of the precipitating nature of the medium; or an increase in rate of termination because of the concentration of a non-precipitating solvent (chain-transfer); and
3. The relative rates of formation of graft, and degradation of grafted chains.

Finally, it may be concluded that true grafting does occur, because it has been shown that polystyrene is insoluble in cyclohexane under conditions where, unless it is grafted, it would be insoluble.

Fractionation of S-109

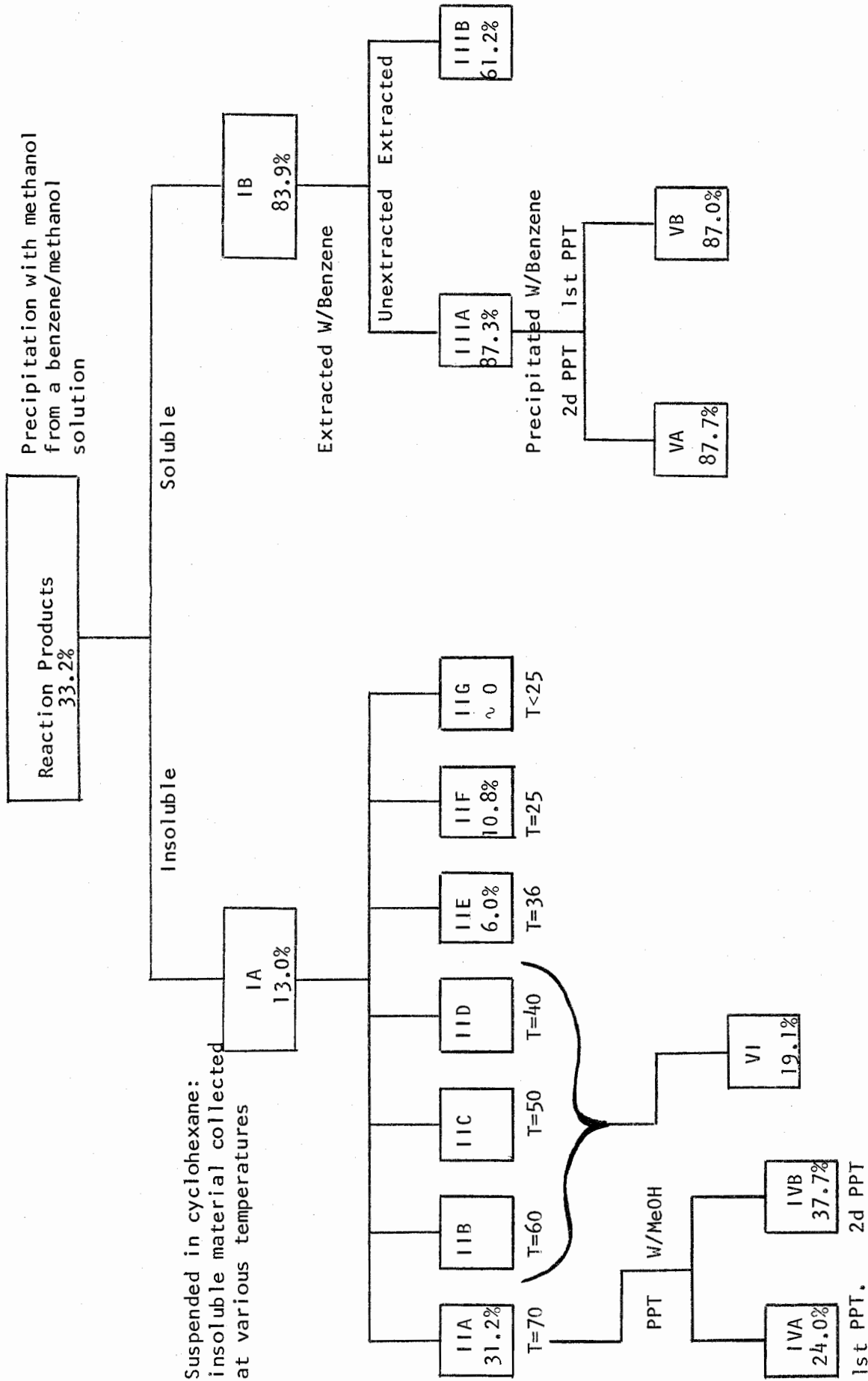


Figure 12. Fractionation of graft + homopolymer (numbers in boxes indicate the per cent lignin present in the fraction)

## III - GRAFTING TO PULPS

III - 1 Introduction

A large amount of successful research has been carried out on the grafting of a number of different polymers to cellulose. The results of this work have been adequately summarized in several recent reviews (1-4). Most of the work however has been accomplished with rather pure forms of cellulose such as cotton, rayon and regenerated viscose films. At the other end of the scale a great deal of work has been carried out on the modification of wood itself by grafting and more extensively by simple in-situ polymerization. The results of this work have also recently been well summarized (35). However grafting to wood pulp has been comparatively neglected and when studied usually cotton linter or high alpha cellulose pulps or paper sheets have been used as the grafting substrate. The second approach used in this program to reduce the presence of lignin as a water pollutant was to try to improve the properties of high lignin content pulps (high yield pulps) by grafting to them a highly hydrophilic polymer with good hydrogen bonding capacity. The acid amide group has one of the highest hydrogen bond strengths and polyacrylamide is known to impart excellent strength characteristics to paper sheets both by beater addition and by grafting (35). Acrylamide was thus chosen as the monomer to be studied in this grafting program. In some experiments styrene was also used to provide a direct comparison with the work on grafting to lignin itself discussed in the previous section of this report.

A variety of pulps were used ranging from pure alpha cellulose dissolving pulp and cotton linters to unbleached kraft pulps containing up to 24% of lignin. Radiation was chosen as the method of grafting since all the procedures and techniques are well established in these laboratories. The results, however, can readily be extended to chemical methods of grafting without major changes in the behavior of the grafted pulps.

There are three methods of radiation grafting; these are:

1. Mutual method (as used in the lignin work reported in the previous section). The pulp and monomer are irradiated together to form the graft copolymer.

If the monomer is rapidly polymerized by radiation then this method is not suitable since it leads to excessive formation of homopolymer. Acrylamide is in this category, whereas styrene is only slowly polymerized by radiation and is therefore ideally suited for the mutual method.

2. Pre-irradiation method. The pulp is irradiated in the absence of air and then deaerated monomer added. The graft polymerization is initiated by the trapped radicals. This method is very useful for monomers which are unsuitable for the mutual method, such as acrylamide.

3. Peroxide method. The pulp is irradiated in the presence of air forming peroxide compounds. These are then heated in de-aerated monomer in the absence of air. The grafting is initiated by the decomposition of the peroxides. With many polymers the diffusion of oxygen to the active centers formed by the irradiation is so slow that, in actuality, the grafting is brought about by a mixture of grafted radicals and peroxide decomposition (36).

All three methods were investigated in the present project.

### III - 2 Experimental

#### III-2-1 Materials

Kraft Pulps (KP). Three kraft pulps were prepared by the West Virginia Pulp and Paper Company, North Charleston, S. C., by cooking spruce wood to different degrees of delignification. The pertinent data on the pulps are collected in Table VIII:

Table VIII

#### Kraft softwood pulps

Cook No.	% Yield	Kappa No.	Lignin Content* (%)
612	73.16	174	24.24
616	54.96	96.9	12.63
620	45.40	26.3	4.00

\*Determined according to Tappi Standard T222-M-54.

Bleached Kraft Pulp (BKP) The kraft pulp containing 4% lignin was washed with alkali and then bleached with chlorine dioxide, followed by extensive washing with pure water. This procedure reduced lignin content to zero, by the 72%  $H_2SO_4$  method, but one might suspect that not all traces were removed (S.A. Rydholm, *Pulping Processes*, Interscience, 1965, New York).

Dissolving Pulp (DP) was furnished by the Rayonier Corp., Jessup, Ga. and was prepared by the sulfate process from Southern Pine wood. This pulp was identical to that used by LePoutre (37).

Cotton Linters were obtained from Hercules Powder Company, Wilmington, Delaware.

Monomers. Acrylamide was obtained from Eastman Organic Chemicals, and was recrystallized from water before use.

For details on styrene, see 11-2.

#### III-2-2 Preparation of Grafts

To a mixture of 70 ml water and 30 ml ethanol, 20 grams of dry crystalline acrylamide were added; for most experiments, 10 grams of the resulting solution were added to one gram (dry-basis) of air dried pulp.

In the pre-irradiation experiments, the pulp was degassed for 24 hours at  $10^{-6}$  mm Hg in a glass ampoule fitted with a break-seal as shown in Fig. 13a.

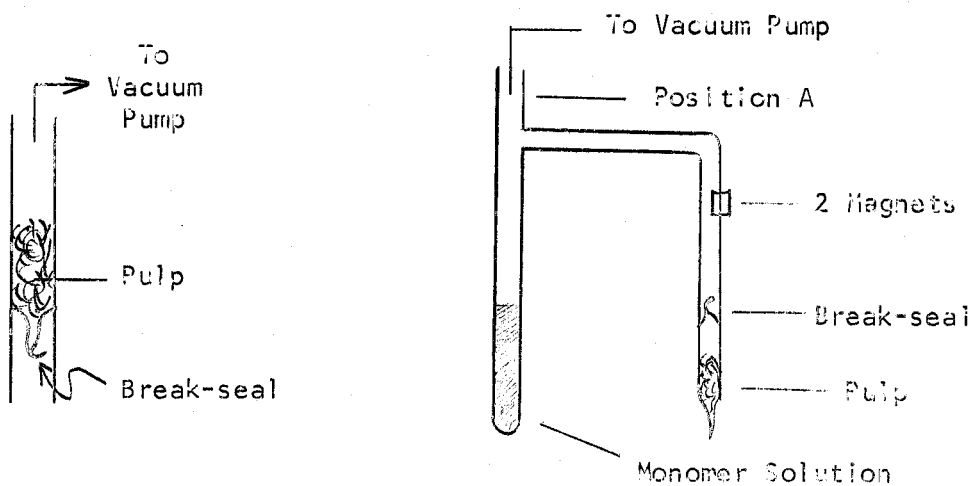


Figure 13. (a) Ampoule containing pulp; (b) Apparatus for adding solution

After sealing, the ampoules were placed in a Co-60 radiation source (Gammacell, Atomic Energy of Canada, Ltd.), with an intensity of 1 megarad per hour, for the desired dose. After removal from the source, the ampoules were sealed to an apparatus as shown in Fig. 13b. This configuration allowed the monomer solution to be degassed, and kept at a pressure of  $10^{-6}$  mm Hg, while the apparatus was sealed at position A. After sealing, the break-seal was smashed with a magnet as shown in the figure. Then the apparatus was tipped, and the monomer solution allowed to flow into the ampoule containing the pulp. Finally, the ampoules were sealed while frozen, and placed in a constant temperature bath of  $60^{\circ}$  for various lengths of time.

In the peroxide method, the pulp was placed in a beaker, and irradiated in air. After removal from the source, weighed amounts of the pulp were placed into simple ampoules, which could be fitted to the high vacuum system. Monomer solution was added directly to the pulp in the ampoules. The contents were then degassed with repeated freeze-thaw cycles, until a vacuum of greater than  $10^{-5}$  was achieved. The frozen ampoules were then sealed and placed in the water bath as before.

In the mutual method, weighed amounts of pulp were added directly to the ampoules and monomer solution added as above. The contents were degassed as in the peroxide method and sealed in the same fashion. Then the pulp and monomer solution were irradiated simultaneously.

In all three methods, separation of homopolymer was conducted in an identical manner: the reaction products were transferred to tared soxhlet extraction thimbles, and extracted for 72 hours with water at  $100^{\circ}$ . The thimbles were dried and weighed; the weight increase of the pulp due to grafting was calculated as the per cent graft.

### III-2-3 Characterization of Blends

As described later, BKP was grafted with 58% acrylamide, and DP was grafted with 98% acrylamide. These grafts, along with ungrafted BKP, were blended in various proportions with the high yield pulp from Cook #616. Handsheets of the blends were prepared according to Tappi Standard T 205 m-58, and subjected to the following physical tests:

- 1) Bursting strength (T 403 ts - 63)
- 2) Tensile Breaking Strength (T 404 ts - 66)
- 3) Stretch (T 457 m - 46)
- 4) Folding Endurance (T 511 su - 69)
- 5) Internal Tearing Resistance (T 414 ts - 65)

### III - 3 Results and Discussion

#### III-3-1 Grafting Experiments

A very pure sulfate dissolving pulp was investigated first. Since acrylamide polymerizes very rapidly with radiation, the pre-irradiation and the peroxide techniques were mainly used as described in the introduction to this section. The pulp was irradiated in air at a dose rate of 1.0 Mrad per hour at 30°C; then the air was removed and a de-aerated solution of 20% of acrylamide in a 70:30 water-ethanol mixture was added. The temperature was raised to 60°C and the reaction allowed to proceed. It was found that the grafting was complete in 15 hours; only negligible changes in yield were found on increasing the yield to 50 hours. The grafting yield as a function of the dose used is shown in Fig. 14. After 2 Megarads the plateau of radical concentration appears to have been reached and no further increase in grafting was found. At this point 130% grafting was achieved, i.e., the pulp had increased in weight 2.3 times. In Fig. 15, the effect of the water-ethanol ratio on the grafting yield at 3 Mrads is shown. Increasing the water content increases the yield presumably mainly due to the increased swelling of the pulp. However, above about 90% water, there is considerable gel formation in the monomer phase making it impossible to remove the grafted pulp in a clean manner.

After the success of these initial experiments a number of additional pulps were studied under the 3 Mrad pre-irradiation in air conditions described previously. Cotton linters and the pure alpha cellulose sulfate dissolving pulp both grafted easily to about 60%. The presence of even small amounts of lignin, however, caused a sharp drop in the grafting yield; even bleached kraft pulp (BKP), with close to zero lignin content, only grafted 20% and the unbleached kraft, with only 4.0% lignin, grafted essentially nothing. To see if dose

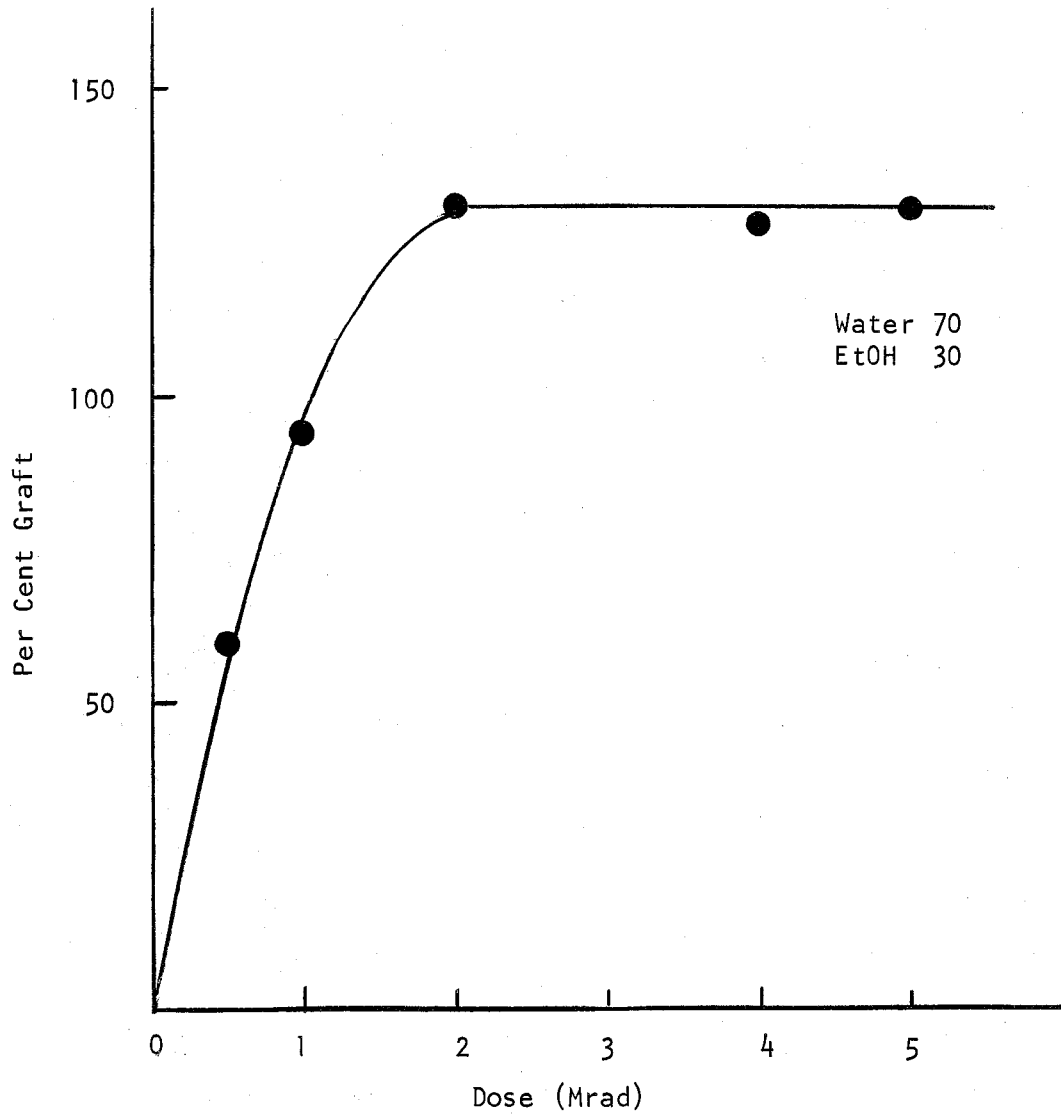


Figure 14. Grafting of DP with acrylamide vs. dose: pre-irradiation in air

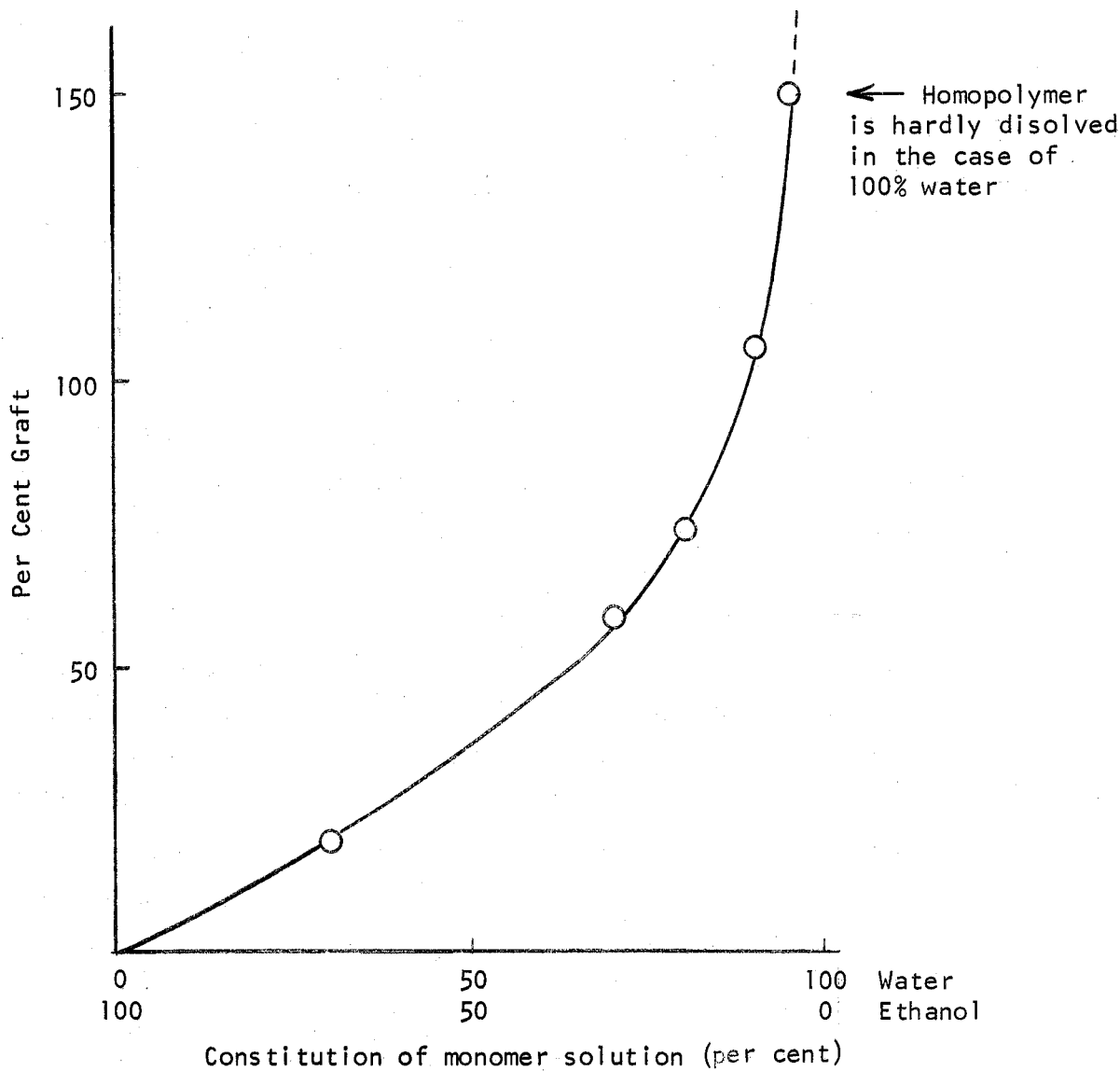


Figure 15. Grafting of DP with acrylamide vs. % H<sub>2</sub>O; pre-irradiation in air

was a factor, these pulps were irradiated with up to 47 Mrads; again no grafting of consequence was achieved. All these data are shown graphically in Fig. 16. These results were surprising, since earlier work in these laboratories showed that styrene could be readily grafted to unbleached kraft pulps using the mutual technique.

A number of the grafting experiments were conducted by irradiating the pulps under vacuum to see if oxygen had a deleterious effect on the grafting reaction. It was known that certain phenolic compounds, for example, only behaved as inhibitors in the presence of air. The results are shown in Fig. 17. It can be seen that cotton linters gave greatly increased grafting by pre-irradiation under vacuum compared with in air. The unbleached kraft pulp, however, continued to give disappointingly poor yields. The grafting was more effective, however, than those carried out in air. Thus, the highest lignin content pulp (24.2%) grafted about 7% in vacuum compared with only about 1% in air at 3 Mrads. These samples were irradiated at room temperature. On irradiating the samples in vacuum at  $-78^{\circ}\text{C}$  yields up to 19% were obtained. This was presumably due to the more efficient production of radicals in the frozen system.

Since the mutual method worked so effectively with grafting styrene to unbleached kraft, it was tried with acrylamide as the monomers. The results, shown in Fig. 18, confirmed that some grafting took place when the lignin content was zero, although only about 17% even in the case of cotton linters. The kraft pulp, however, even with only 4% lignin, grafted to only 5% in the best case. To check, if acrylamide or the pre-irradiation technique was responsible for the poor results with the lignin pulps, the experiments were repeated using styrene as the monomer.

Considering first the mutual results with styrene shown in Fig. 19, it can be seen that the lignin containing pulps actually grafted more than the pure cellulose pulps especially in the aqueous methanol solvent system. This is in agreement with the results previously obtained by Lepoutre (37). The pre-irradiation method, however, using the same solvent system, gave essentially zero grafting with the lignin-containing pulps, in line with the results obtained with acrylamide. Again excellent

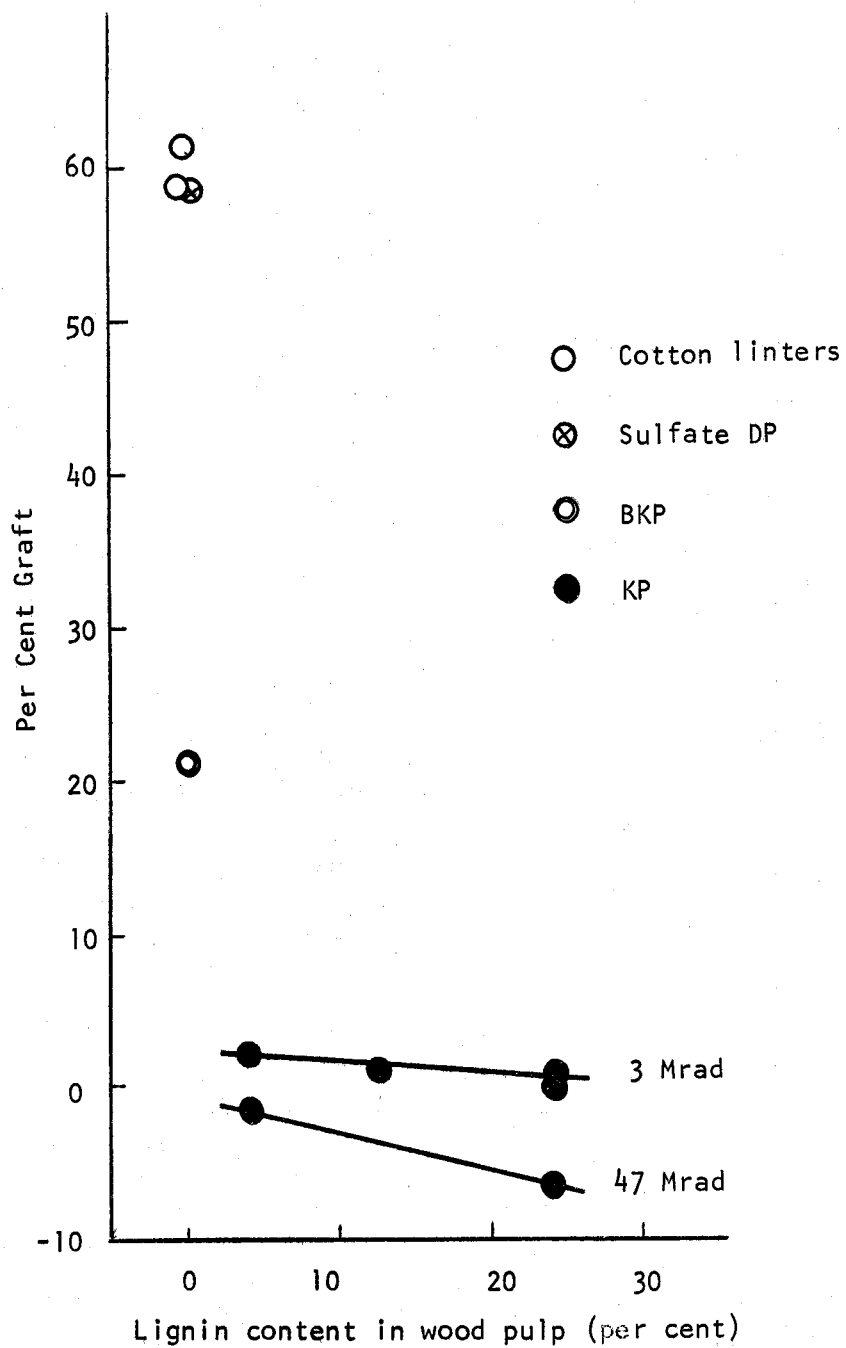


Figure 16. Grafting of wood pulp with acrylamide:pre-irradiation in air

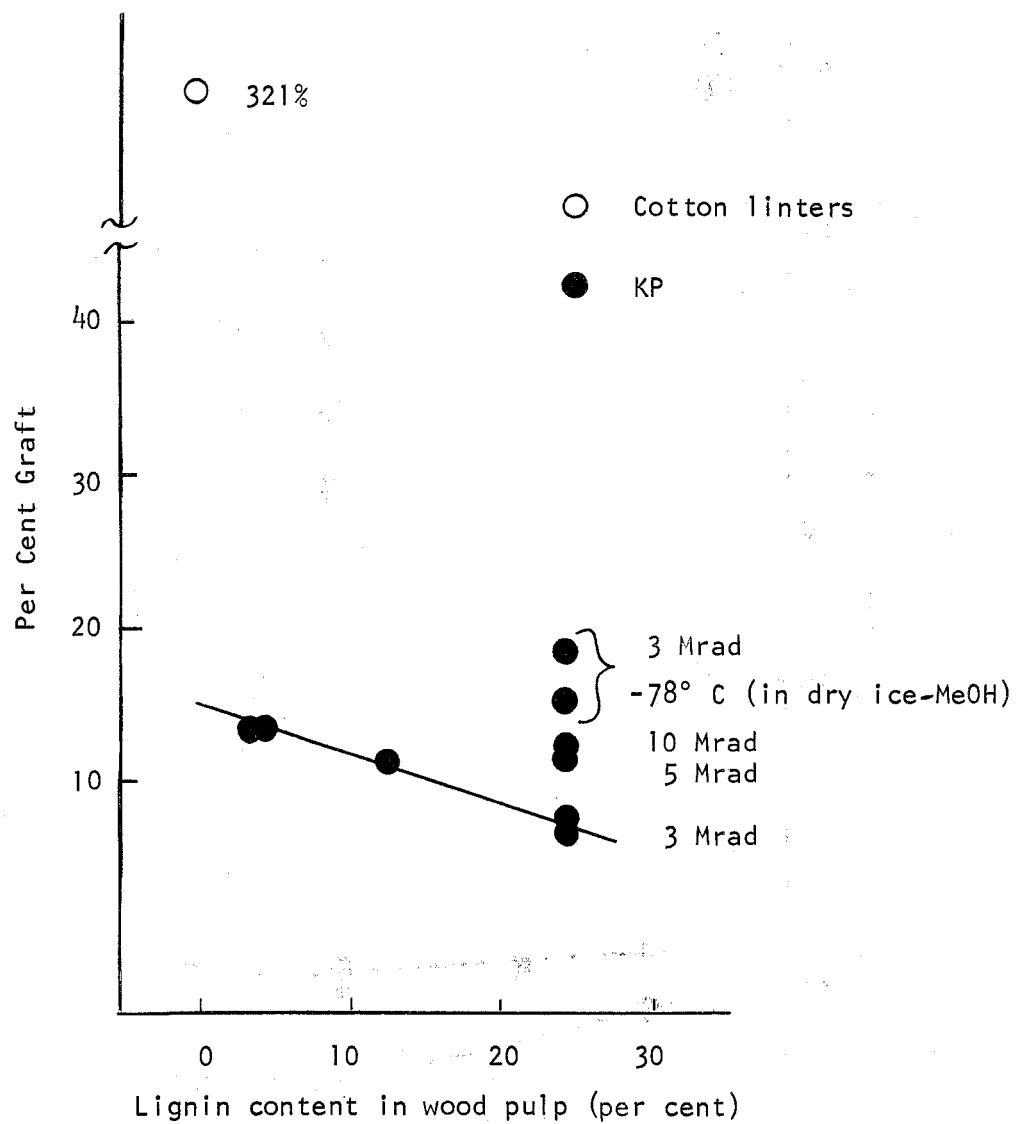


Figure 17. Grafting of wood pulp with acrylamide:pre-irradiation in vacuum

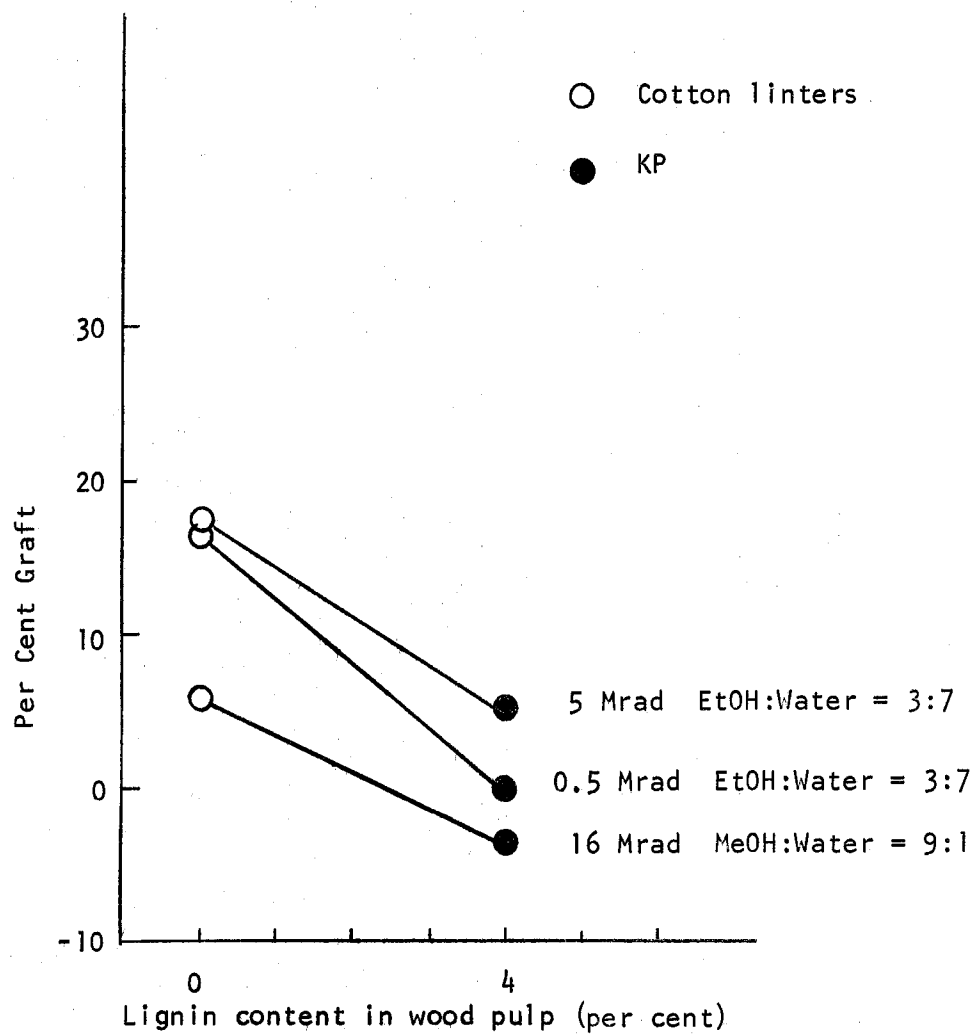


Figure 18. Grafting of wood pulp with acrylamide:mutual irradiation

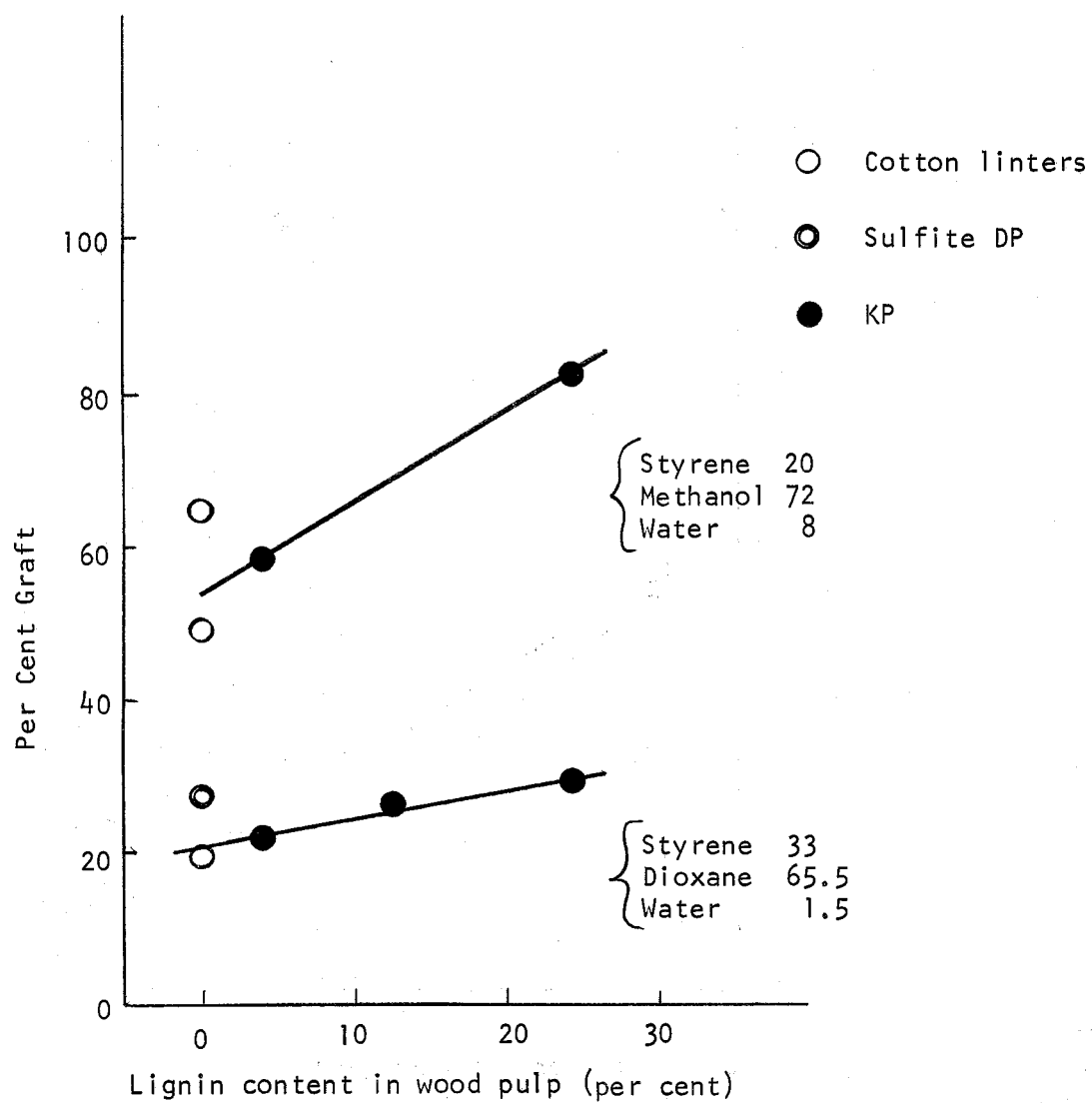


Figure 19. Grafting of wood pulp with styrene:mutual irradiation

grafting yields were obtained under identical conditions with the pure cellulose pulps (Fig. 20).

In an attempt to find the reason for the deleterious effect of lignin on the grafting yield, cotton linters were coated with a known amount of lignin from solution. These cotton linters were then subjected to the various grafting treatments studied previously. The results are shown in Figs. 21-22. It can be seen that in every case the lignin caused a huge decrease in the grafting yield. Even in the case of the mutual grafting of styrene, Fig. 24, the yields dropped from about 60% to 36% at 3 Mrads. It was thought that the lignin would reduce the swelling of the paper sheets made from the treated cotton linters but experiments showed that this effect was only minor and not sufficient to account for the drastic decrease in grafting.

The effect of beating the pulp on the grafting yield was also studied, with the bleached kraft pulp and the unbleached kraft containing 4.0% lignin. The results, presented in Fig. 25, showed that beating actually caused a small decrease in the grafting yield, the reason for this is not clear and was quite unexpected.

Finally, electron spin resonance (ESR) spectroscopy was used to study the production of pure radicals in the various pulps during the pre-irradiation technique. The results are summarized in graphical form in Fig. 26. It is clearly seen from these results that the lignin had zero or only minor effects on the yield of radicals. Furthermore, the shape of the spectrum itself showed simply an additive effect on the spectrum of the lignin plus that of the cellulose. The inhibition of the pre-irradiation grafting of both styrene and acrylamide to cellulose pulps by the lignin is quite puzzling and certainly needs further investigation. From the practical viewpoint, however, it is clear that it is not possible with the present techniques of radiation grafting to successfully graft acrylamide to high yield pulps. Accordingly, another approach was used. That is, lignin-free pulps were heavily grafted with acrylamide and these were then used as additives to boost the strength properties of high yield pulps. The results of these studies will be described in the following section.

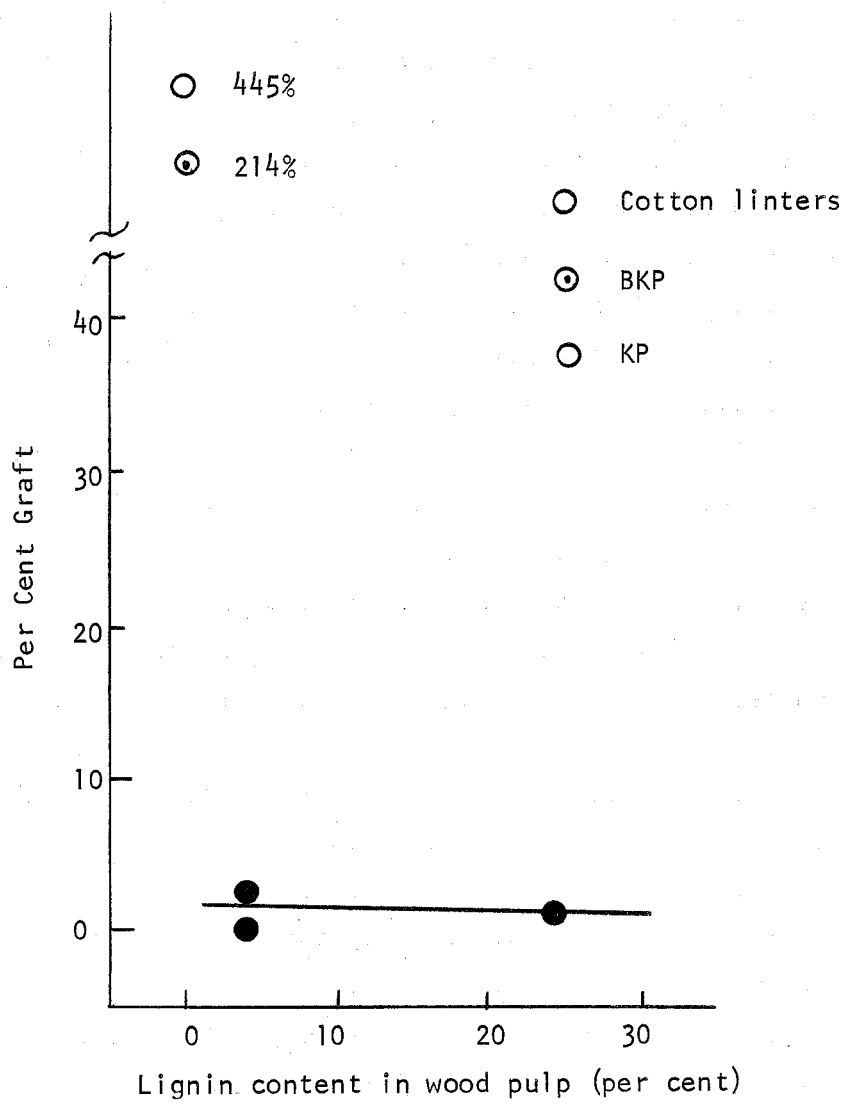


Figure 20. Grafting of wood pulp with styrene:pre-irradiation in air

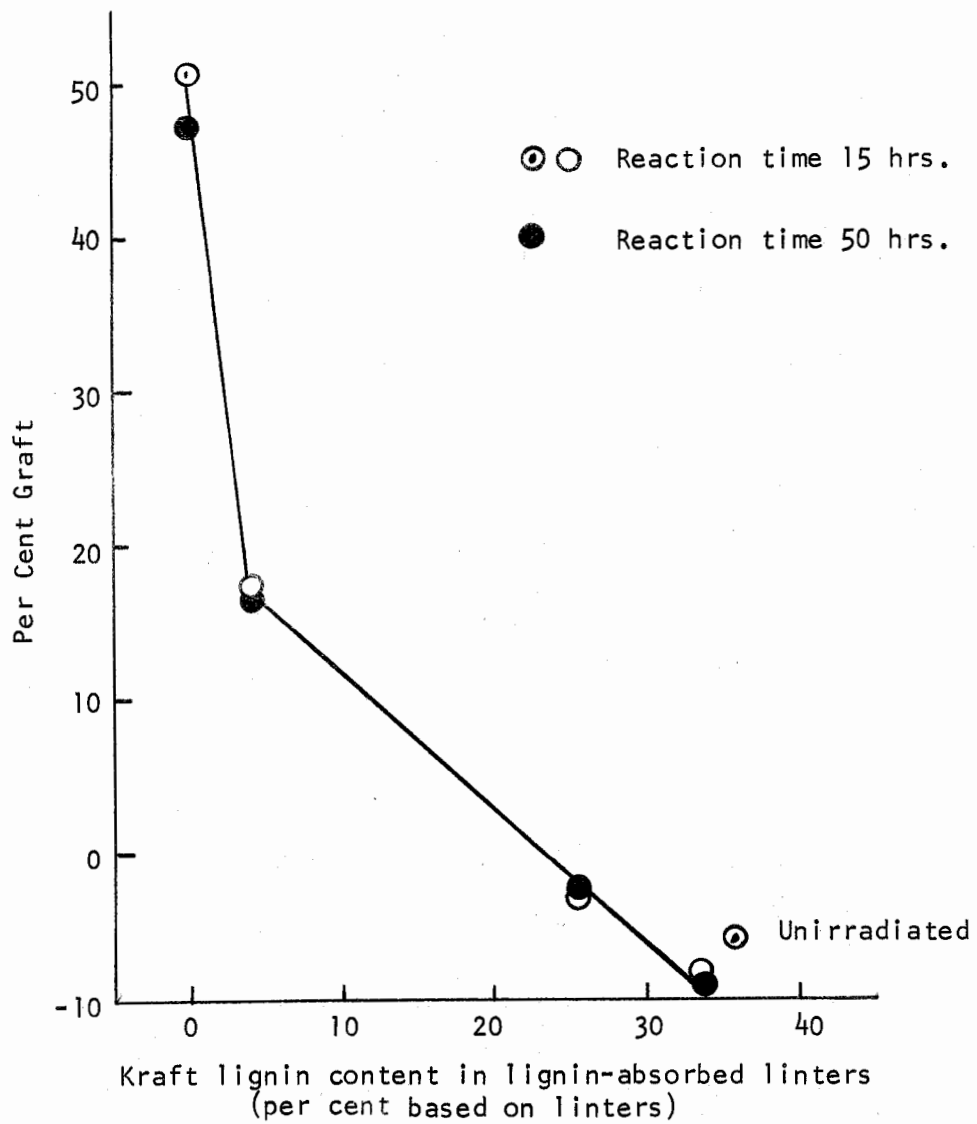


Figure 21. Grafting of linters-lignin mixture with acrylamide: pre-irradiation in air

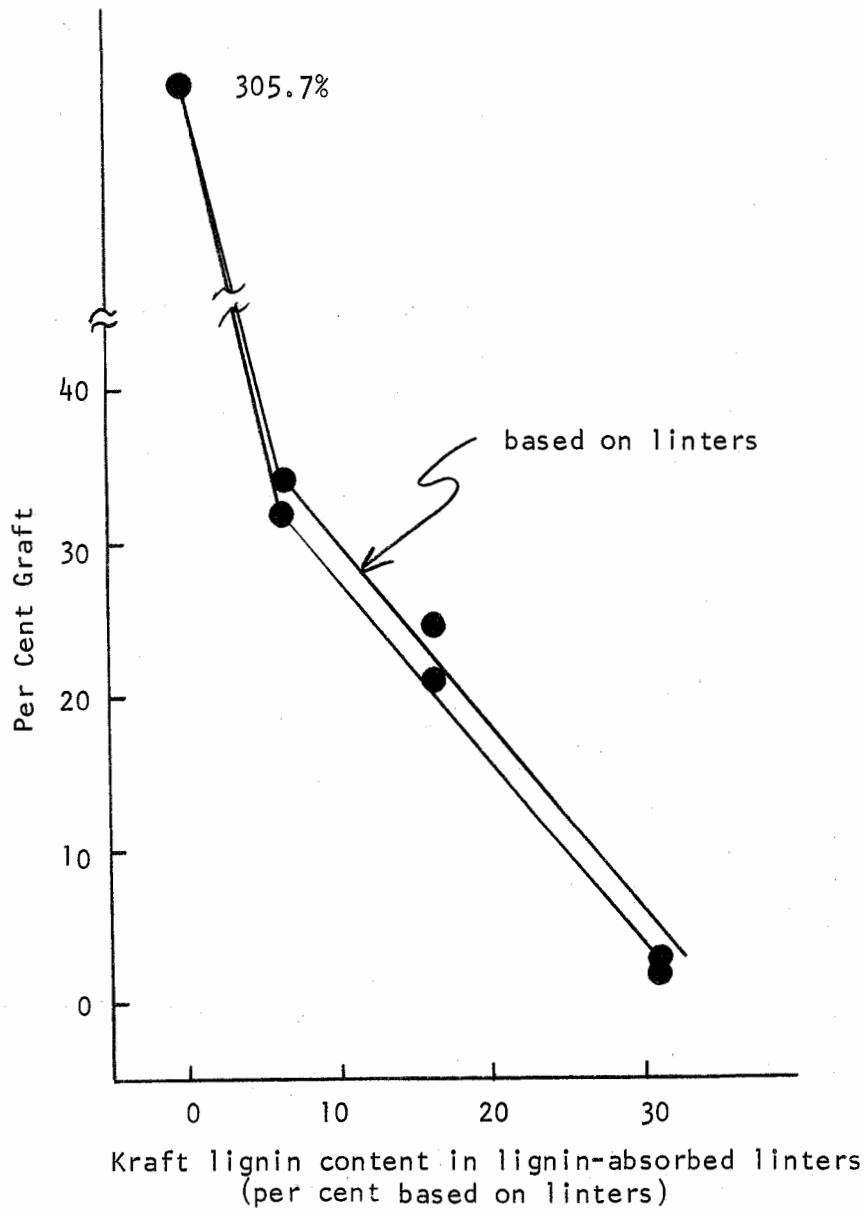


Figure 22. Grafting of linters-lignin mixture with acrylamide: pre-irradiation in vacuum

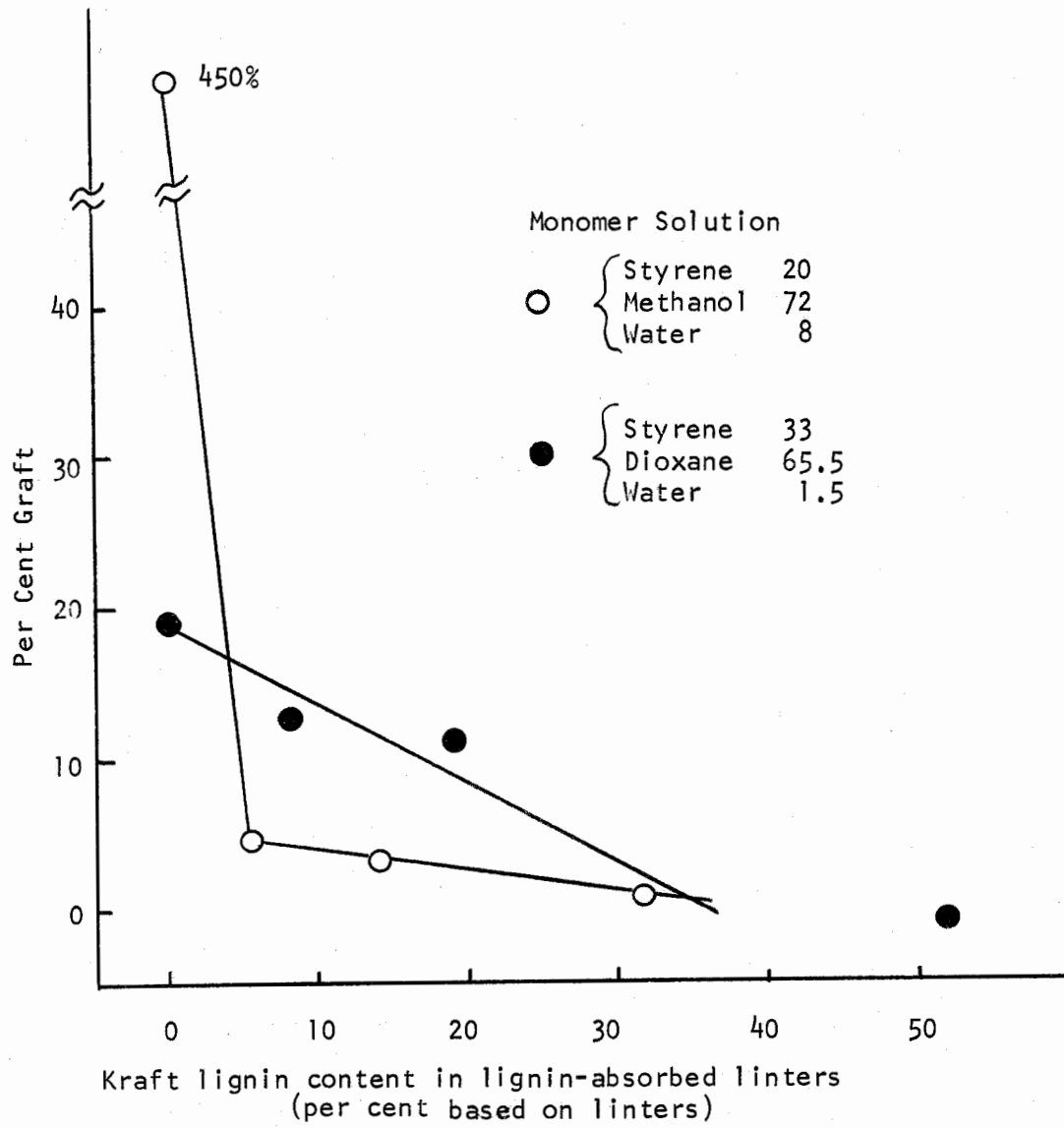


Figure 23. Grafting of linters-lignin mixture with styrene: pre-irradiation in air

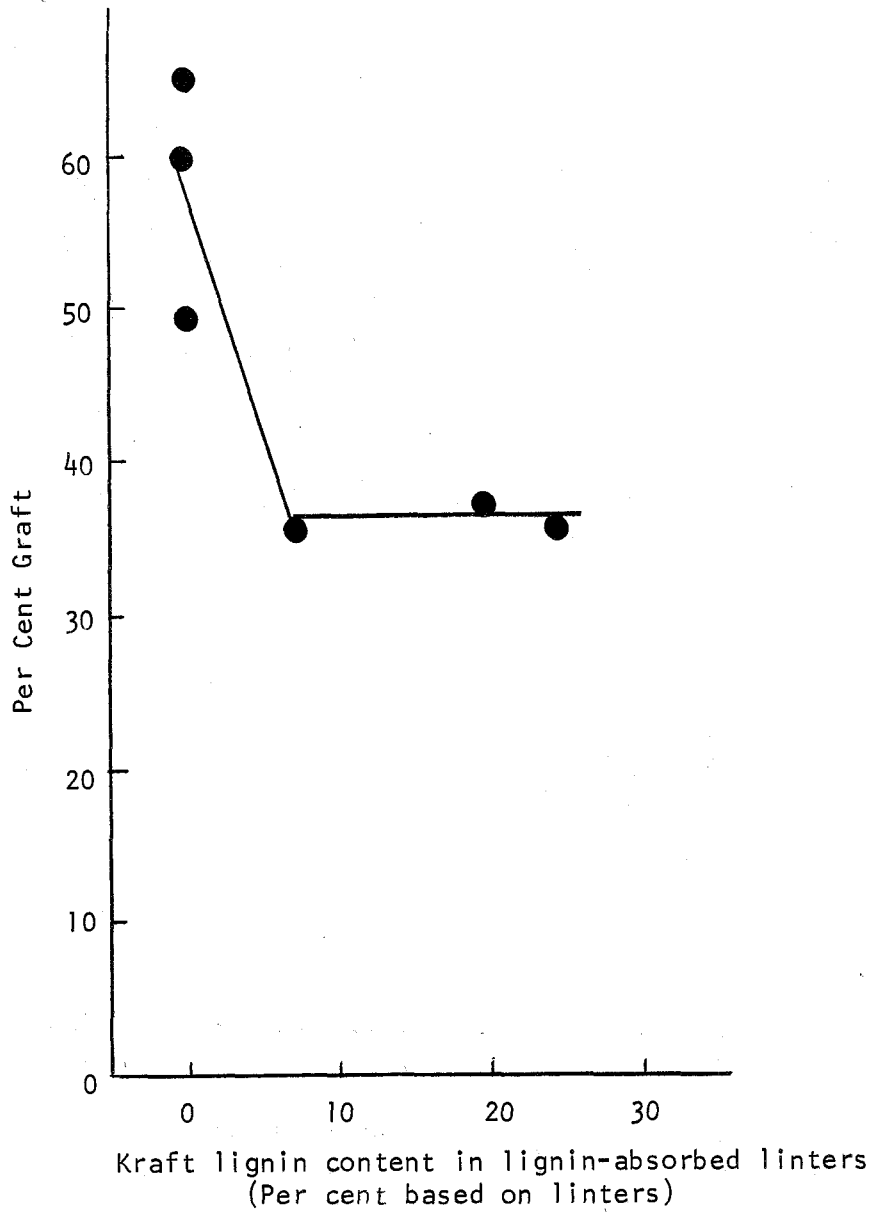


Figure 24. Grafting of linters-lignin mixture with styrene:mutual irradiation

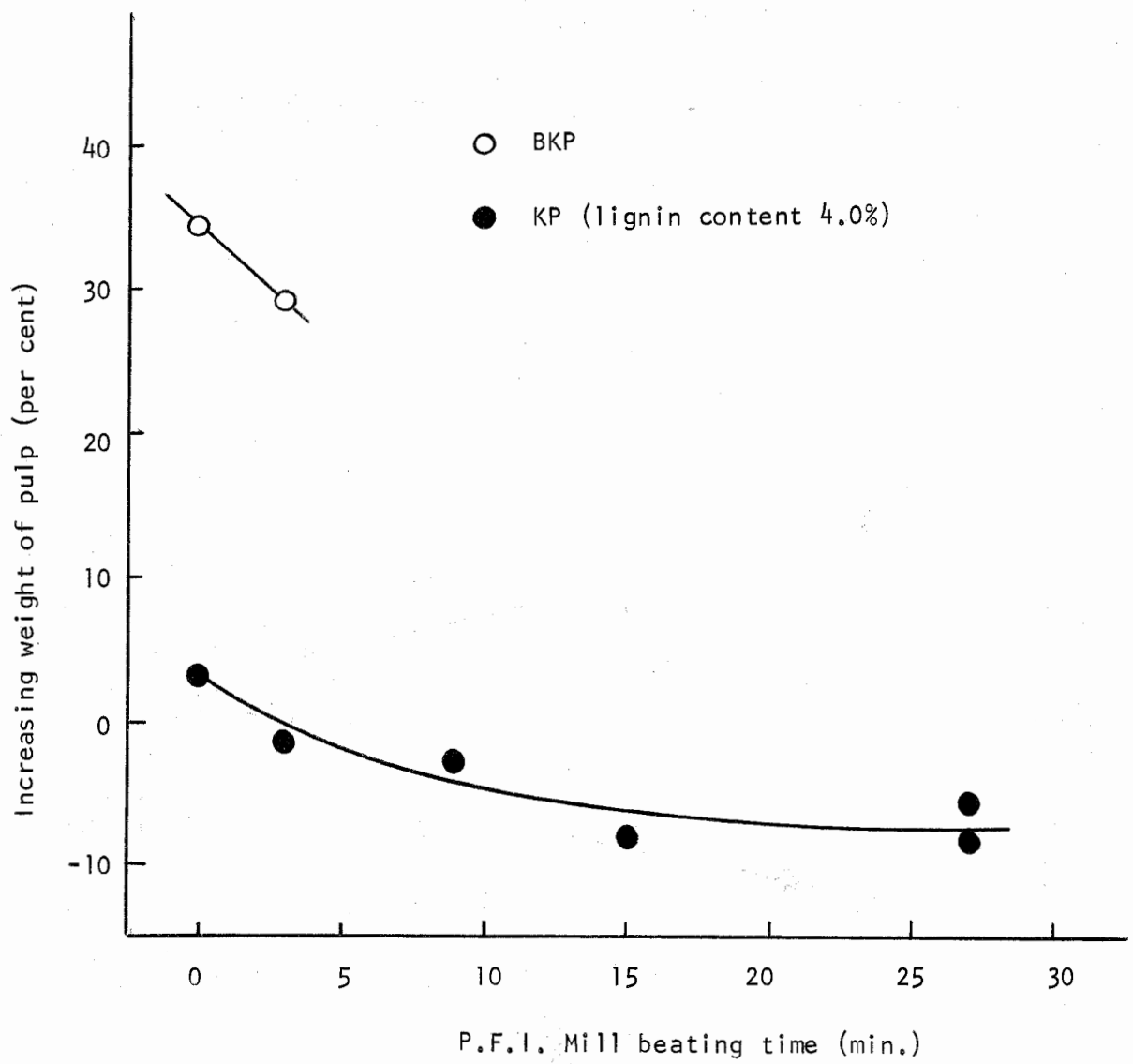


Figure 25. Effect of beating on grafting of wood pulp; pre-irradiation in air

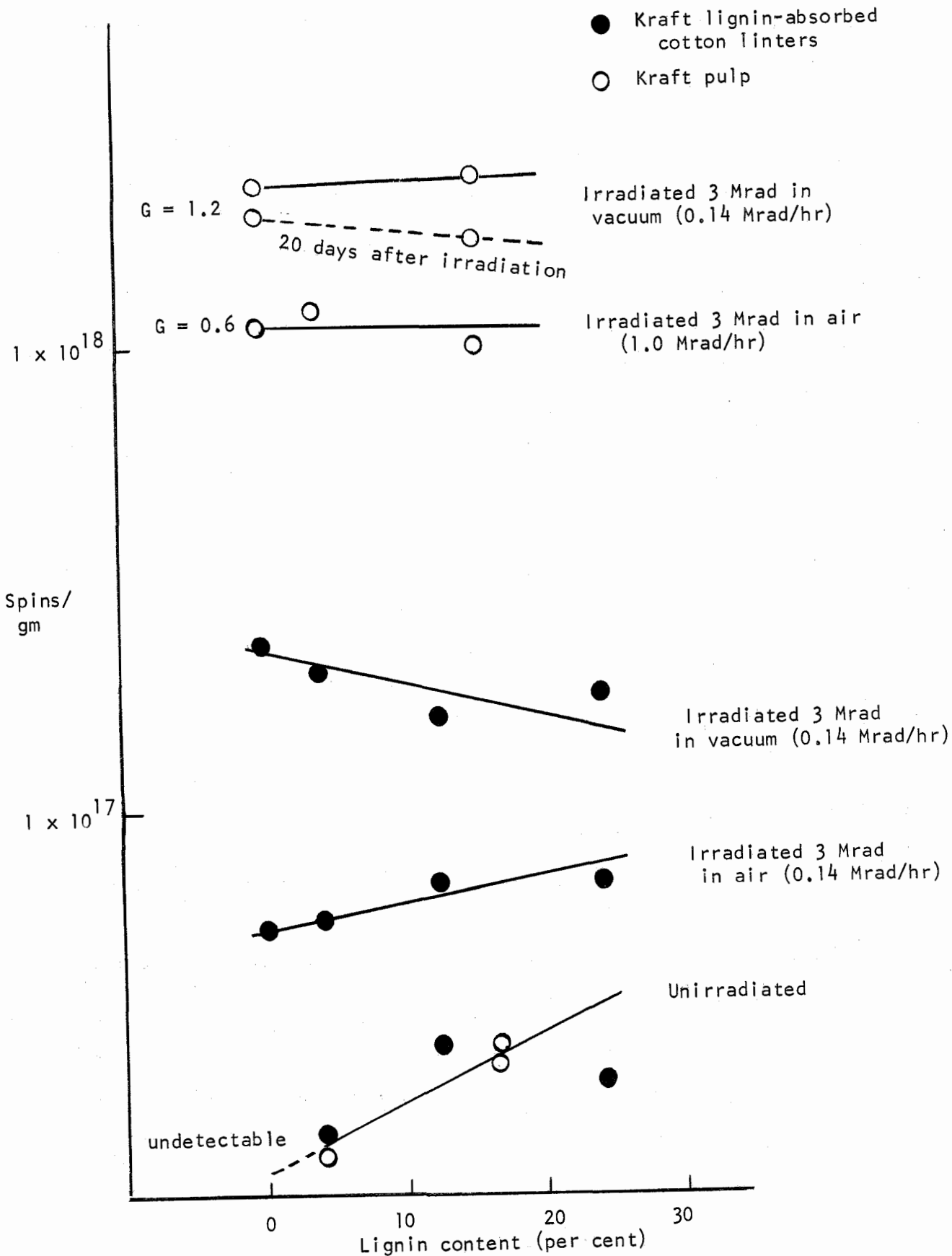


Figure 26. Concentrations of free radicals in irradiated pulps

### III-3-2 Strength of Blended Grafted Pulps With High Yield Pulps

Two highly grafted lignin free pulps were used for the blending studies. The first was a bleached kraft (softwood) pulp grafted with 58% of acrylamide designated BKPG and the second was a softwood dissolving pulp grafted with 98% of acrylamide (DPG). The high yield pulp was a softwood unbleached kraft (Cook No. 616, Table VIII) containing 12.6% lignin.

The blends were all beaten for 3 minutes in a PFI mill. The pure grafts would not form good hard sheets, being too jelly-like for good formation. They blended, however, extremely well with the high yield pulp, forming good handsheets of good appearance. The strength of the sheets are presented at various blending ratios in Figs. 27-31. In addition to the blends with the grafted pulp, blends with a strong bleached kraft pulp (ungrafted) was also studied and these results are also included. The results may be summarized as follows: the bursting strength is greatly improved by the addition of the grafted pulp, increasing 2.5 times with a 25% addition of the grafted dissolving pulp, and 2.0 times with 25% of the grafted bleached kraft pulp. The pure bleached kraft pulp, on the other hand, was only 2.2 times as strong as the high yield pulp. The tensile breaking strengths were also encouraging, 25% blends reaching more than double the strength again higher than the bleached kraft pulp alone. The elongations were also higher but lower than those obtained with the pure bleached kraft pulp. The folding endurances were also high, increasing from only 20 to nearly 700 at 25% blends. Finally the internal tearing resistance was also found to increase but only 1.5 times at the 25% level.

### III - 4 Conclusions

The primary goal of this portion of the investigation could not be accomplished; it was not possible, using radiation, to graft significant amounts of acrylamide to the high yield pulps, regardless of the technique used. The reason for the failure is not clearly understood.

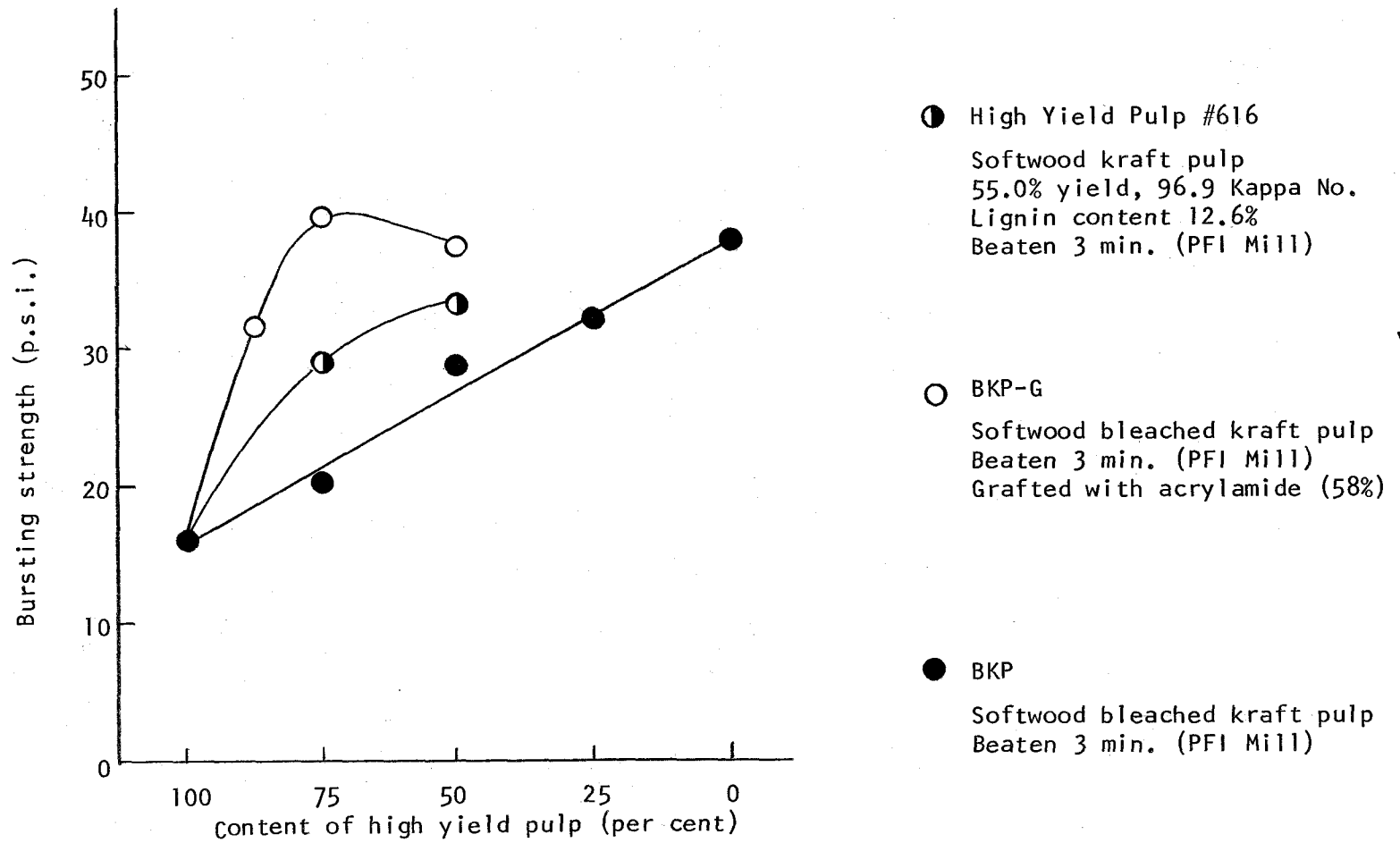


Figure 27. Bursting strength of blended pulps

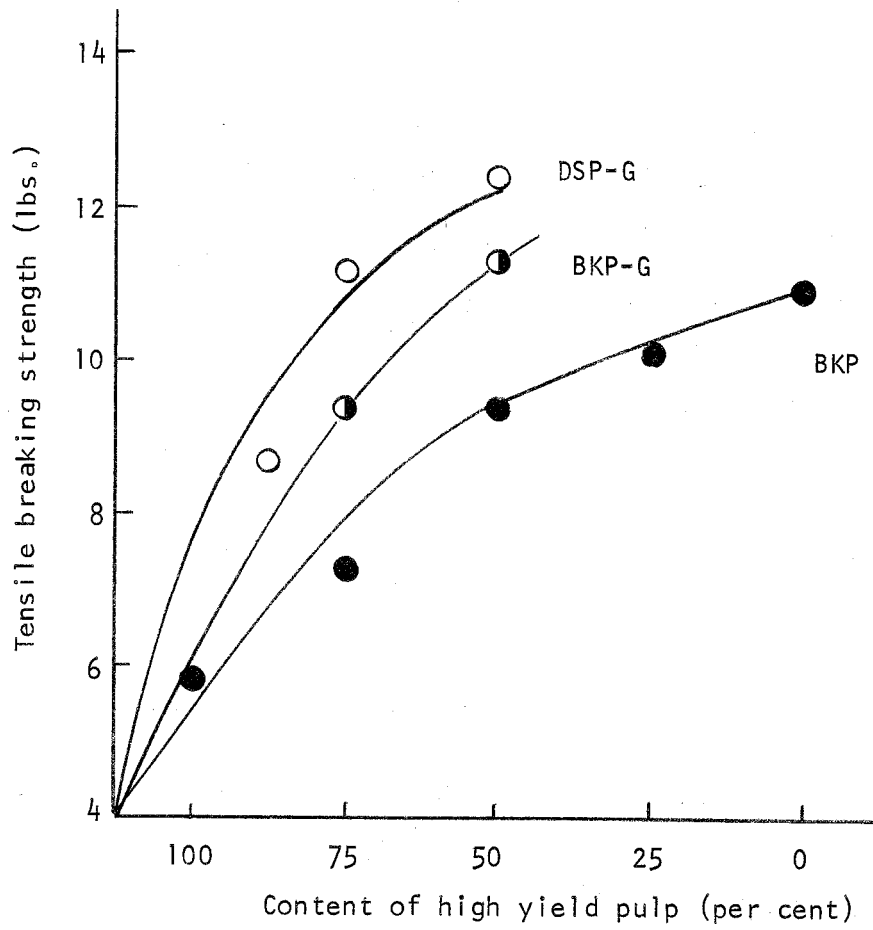


Figure 28. Tensile breaking strength of blended pulps

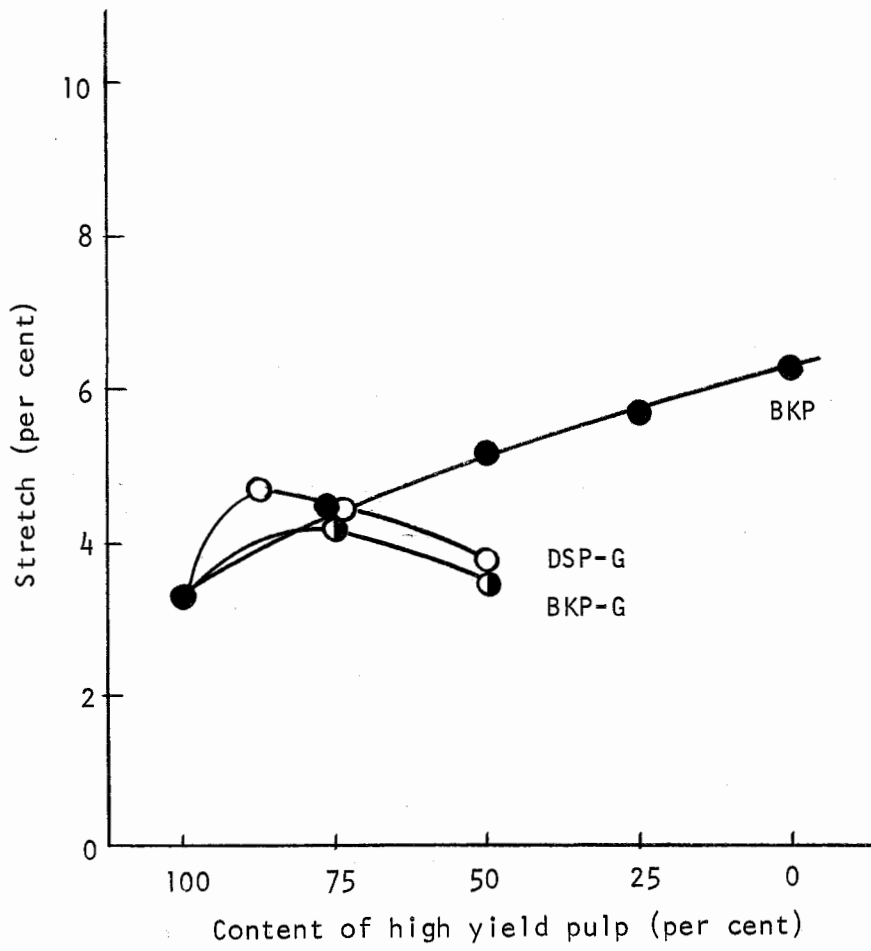


Figure 29. Stretch of blended pulps

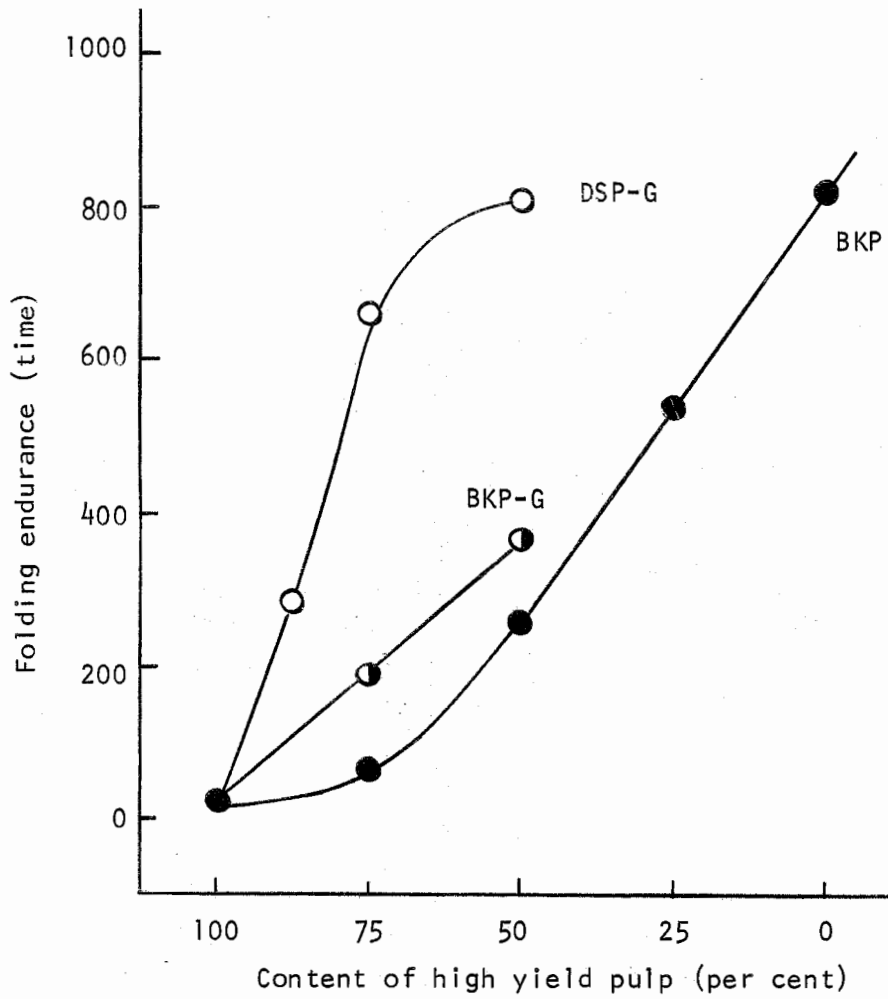


Figure 30. Folding endurance of blended pulps

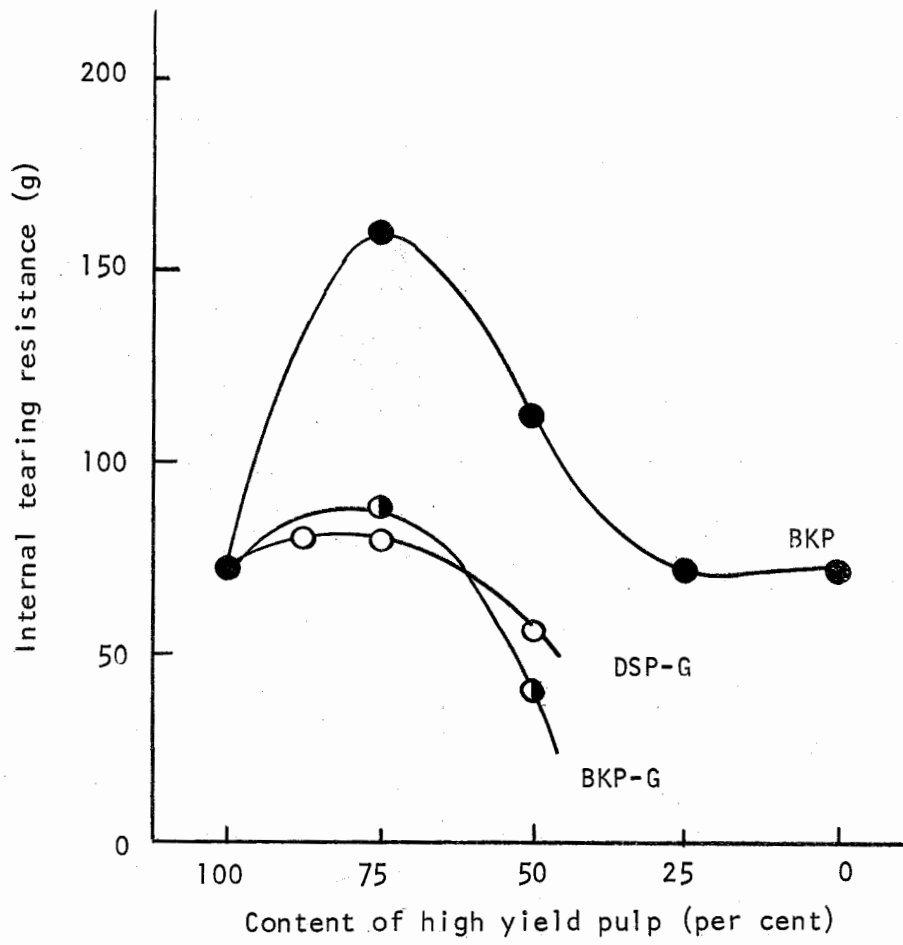


Figure 31. Internal tearing resistance of blended pulps

The blends of high yield pulp and highly-grafted cellulose pulps do give improved strength properties; the blends of grafted cellulose pulp and high yield pulp are stronger than high yield pulp alone, and also stronger than blends of ungrafted cellulose pulp and high yield pulp.

The more highly grafted dissolving pulp appears to be more effective in improving strength properties than the less-grafted bleached kraft pulp. It is not known whether the increased effectiveness is a function of the per cent graft, or a property of the cellulose pulp itself.

## IV - ACKNOWLEDGMENTS

The research described in this report will constitute a portion of the doctoral dissertation by R. B. Phillips. He initially conducted this research while an Eastman Kodak Fellow, and later as a Fellow of the Textile Research Institute, Princeton, New Jersey, a position he holds at present. He expresses appreciation to these organizations for supporting him, and to the Water Resources Research Institute for supporting the work.

Dr. A. Kobayashi was partially supported on a study grant from the Kokusaku Pulp and Paper Company, Tokyo, Japan, in addition to his support from the Water Resources Research Institute of the University of North Carolina.

The donation of materials and consultations by the West Virginia Pulp and Paper Company is gratefully acknowledged.

The authors wish to thank Dr. K. P. Kringstad for his assistance in obtaining the ESR spectra. A more complete study will be included in a forthcoming publication.

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