# The Structure of Polymers Obtained from Arbuzov–Michaelis Reactions Involving Cyclic Phosphonites[1]

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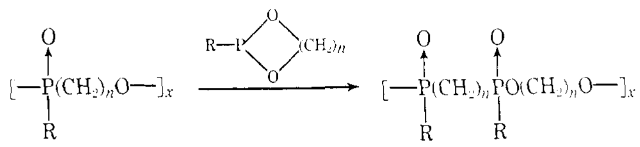
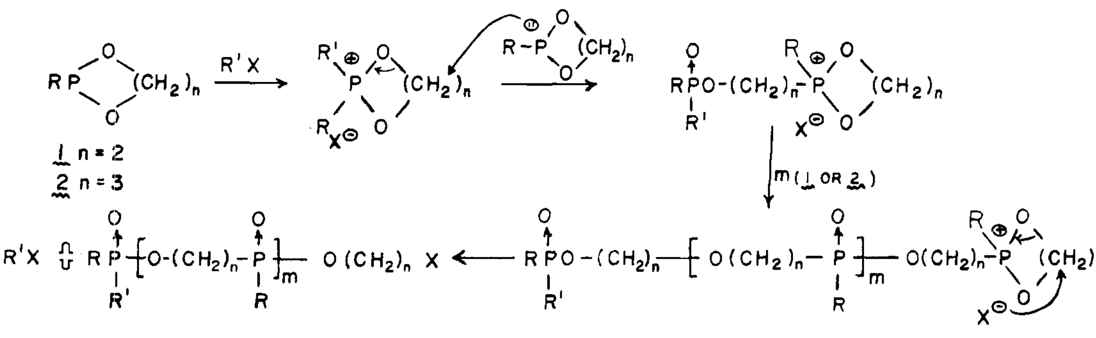
ABSTRACT: Polymers obtained by heating cyclic phosphonites with alkyl halides or Lewis acids were shown by degradation to contain alkylenebisphosphinate repeating units. Thus, polymers derived from 2-phenyl-1,3,2-dioxaphospholane, **1**, and 2-phenyl-1,3,2-dioxaphosphorinane, **2**, were hydrolyzed to obtain 1,2-ethylenebis(phenylphosphinic acid) and 1,3-propylenebis(phenylphosphinic acid), **3**, respectively. In addition, reaction of $PCl_5$ with the polymer derived from **2** yielded γ-chloropropylphenylphosphinic chloride and a material, presumably 1,3-propylenebis(phenylphosphinic chloride), which could be hydrolyzed to obtain **3**. To accommodate these results, previous formulations of the mechanism of cyclic phosphonite polymerizations must be modified to include the reaction



Many approaches have been taken in studies on the preparation of polymeric materials by the Arbuzov–Michaelis reaction.[2,3] Particularly interesting from the chemical standpoint are those studies[3] in which cyclic phosphite, phosphonite, or aminophosphonite esters are polymerized in the presence of alkyl halides or Lewis acids. In such polymerizations, an Arbuzov–Michaelis reaction, accompanied by ring opening, occurs during each propagation step and polymers containing carbon–phosphorus bonds in their backbones are formed. The mechanism[4,5] of such polymerizations can be formulated according to Scheme I.

The conclusion that polyphosphinates are obtained from the Arbuzov–Michaelis polymerization of cyclic phosphonites is based on studies of their infrared spectra and on studies of the degradation products obtained when the polymers are hydrolyzed or treated with $PCl_5$. For example, Mukaiyama and coworkers[3e] reported that the polymer derived from 2-phenyl-1,3,2-dioxaphospholane (**1**, R = $C_6H_5$) could be hydrolyzed to obtain the sodium salt of β-hydroxyethylphenylphosphinic acid in 55% yield. Similarly, reaction of $PCl_5$ with the polymer derived from 2-phenyl-1,3,2-dioxaphosphorinane (**2**, R = $C_6H_5$) was reported to

SCHEME I



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[1] Abstracted in part from the Ph.D. thesis submitted by N. K. Patel to the University of Akron, 1968.

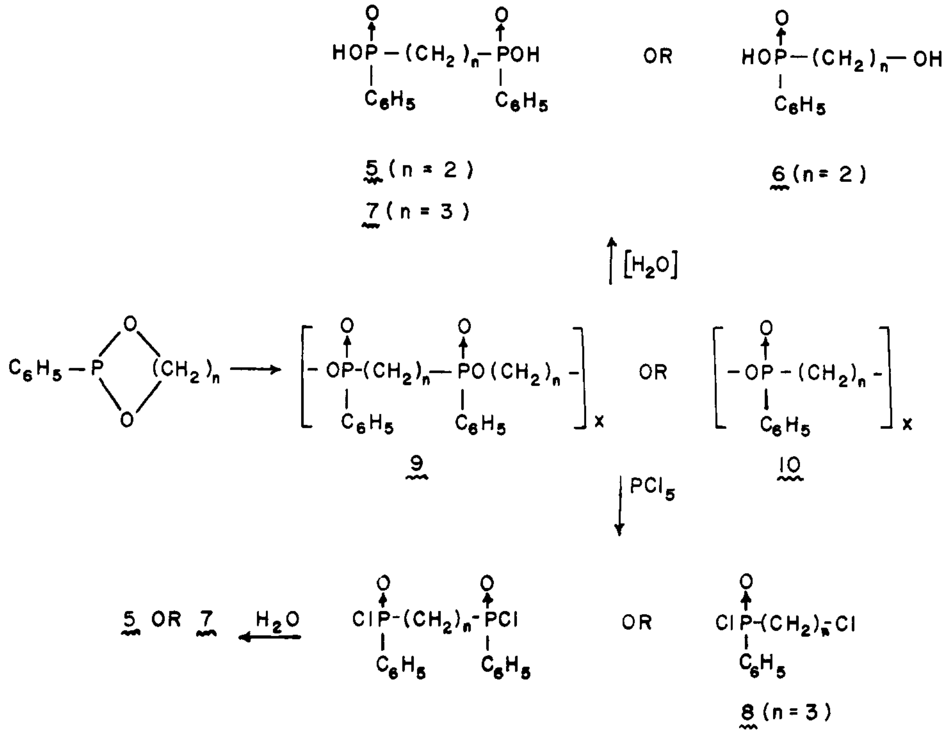
[2] (a) M. Sander and E. Steininger, *J. Macromol. Sci.*, C1, 1, 7, 91 (1967); (b) A. F. Childs and H. Coates, *Kunstoffe*, **54**, 501 (1964); (c) E. Steininger and M. Sander, *ibid.*, **54**, 507 (1964); (d) B. P. Stark, A. J. Duke, and R. J. Martin, *J. Appl. Chem.*, **17**, 127 (1967); (e) D. Grant, J. R. Van Wazer, and C. H. Dungan, *J. Polym. Sci., Part A-1*, **5**, 57 (1967); and references cited in the above papers.

[3] (a) R. J. McManimie, U. S. Patent 2,893,961 (1959); *Chem. Abstr.*, **53**, 20908 (1959); (b) K. A. Petrov, E. E. Nifantév, and I. I. Sopikova, *Vysokomol. Soedin.*, **2**, 685 (1960); *Chem. Abstr.*, **55**, 9935 (1961); (c) K. A. Petrov, E. E. Nifantév, and L. K. Khorkhoyanu, *Vysokomol. Soedin.*, **4**, 246 (1962); *Chem. Abstr.*, **56**, 15669*b* (1962); (d) T. Shimizu, T. Hakozaki, T. Kagiya, and K. Fukii, *Bull. Chem. Soc. Jap.*, **39** ,562 (1966); *J. Polym. Sci., Part B*, **3**, 871 (1965); (e) T. Mikaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964); (f) T. Fujisawa, Y. Yokota, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **40**, 147 (1967).

[4] This mechanism differs somewhat from that proposed by Mukaiyama[3e] and coworkers, who assume that the propagation reaction involves free carbonium ions. It seems more reasonable to assume that the mechanism of the alkylation step is analogous to that which is generally accepted for the polymerization of cyclic ethers.[5]

[5] P. Dreyfuss and M. P. Dreyfuss, *Advan. Polym. Sci.*, **4**, 528 (1967).

Scheme II



yield γ-chloropropylphenylphosphinic chloride in 39% yield. Similar results were reported by Petrov and coworkers[3c] in studies on the polymer derived from 2-phenyl-4-methyl-1,3,2-dioxaphosphorinane.

These results are consistent with those expected if the polymers have the polyphosphinate structure **4**, and our present understanding of the Arbuzov–Michaelis reaction would lead to the expectation that polymers having such structures would be formed. Unfortunately, our own studies[6] on the structures of polymers obtained from the polymerization of cyclic phosphonites yielded results which differ from those reported by the other research groups. The purpose of this paper is to present our own results and to describe the results obtained when some of the work of Mukaiyama and coworkers[3e] was repeated.

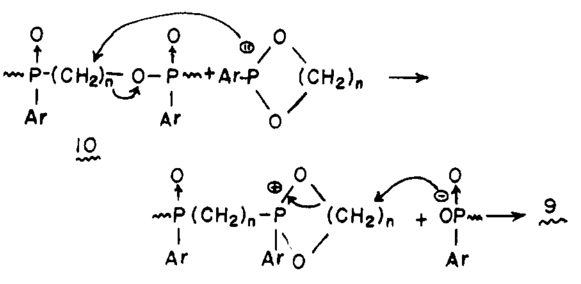
## Results and Discussion

When 2-phenyl-1,3,2-dioxaphospholane (**1**, R = $C_6H_5$) was heated with $AlCl_3$, $BF_3$ etherate or alkyl halides at 150–180°, it polymerized to form a colorless resin which softened at about 80°. Hydrolysis of the resin with dilute aqueous alkali, followed by acidification, afforded 1,2-ethylenebis(phenylphosphinic acid), **5**, in 61–67% yield. Mukaiyama and coworkers[3c] described the isolation of sodium β-hydroxyethylphenylphosphinate, **6**, when they hydrolyzed resin prepared under similar conditions, but we were not able to obtain this salt when their hydrolysis procedure was followed. We were able to obtain a high melting insoluble substance which resembles the material described by Mukaiyama, however, by treating **5** with 1 *N* NaOH or by hydrolyzing the resin in relatively concentrated alkali (Scheme II).

Similarly, when 2-phenyl-1,3,2-dioxaphosphorinane (**2**, R = $C_6H_5$) was heated for 24 hr at 160–180° in the presence of $BF_3$ etherate, it polymerized to form a hard colorless resin. Hydrolysis of the resin yielded 1,3-propylenebis(phenylphosphinic acid), **7**, in 33% yield. The resin was also treated with $PCl_5$ to obtain γ-chloropropylphenylphosphinic chloride, **8**, in 30% yield, in addition to a substance that could not be distilled easily. This latter material yielded **7** on hydrolysis. Mukaiyama and coworkers[3e] obtained only **8** when they reacted $PCl_5$ with polymers derived from 2-phenyl-1,3,2-dioxaphosphorinane, although the yield of **8** obtained by them was comparable to that realized in the present study. Apparently, they did not examine the high boiling product fraction obtained from this reaction.

The results obtained in the present study indicate that the polymerization of cyclic phosphonites yields polymers having not only phosphinate repeating groups, **10**, but also bisphosphinate repeating units, **9**. The formation of structures such as **10** is explicable in terms of the Arbuzov–Michaelis ring opening polymerization discussed above, but the formation of structures such as **9** requires explanation. It seems reasonable to believe that such structures arise from an Arbuzov–Michaelis reaction between polymer chain units and unreacted phosphonite, according to Scheme III.

Scheme III



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(6) (a) H. J. Harwood, U. S. Patent 3,157,694 (Nov 17, 1964); *Chem. Abstr.*, **62**, 4053 (1965); (b) H. J. Harwood, U. S. Patent 3,270,092 (Aug 30, 1966); *Chem. Abstr.*, **65**, 15425*d* (1966).

Thus, in the early stage of cyclic phosphonite polymerizations, the polymers formed are believed to contain repeating units of type **10**. As the concentration of such structures builds up, it might be expected that they would compete with chain ends for reaction with phosphonite. This will be particularly true when small amounts of catalyst or initiator are used and when units such as **10** are good alkylating agents. The presence of electronegative groups such as phenyl on phosphorus would favor this latter condition. When **10** type units react with the phosphonite ester, such units are converted into **9** type units as shown in the above scheme. However, reaction of a chain end or a **9** type unit wtih a phosphonite causes a new **10** type to be incorporated into the polymer. It is not surprising, therefore, that the polymers obtained in this study contained both phosphinate and bisphosphinate repeating units.

## Experimental Section

**2-Phenyl-1,3,2-dioxaphospholane.** A solution of phenylphosphorus dichloride (17.9 g, 0.10 mol) in 100 ml of dry benzene was added dropwise over a 2-hr period to a stirred solution of carefully dried ethylene glycol (6.2 g, 0.10 mol) and freshly distilled triethylamine (20.2 g, 0.20 mol) in 100 ml of benzene. The reaction mixture was maintained at 5–10° during the addition and was heated for 45 min at 45° after addition was complete. The reaction mixture was then filtered to remove triethylamine hydrochloride. The filtrate was chilled in a refrigerator and was refiltered to remove additional quantities of triethylamine hydrochloride. The filtrate was concentrated *in vacuo* and distilled to obtain 2-phenyl-1,3,2-dioxaphospholane: yield 8.1 g (48%); bp 86–89° (1.6 mm); $n^{20}\text{D}$ 1.5656 (lit.[3d,7] bp 79–80° (0.8 mm), bp 88–89 (1 mm), $n^{20}\text{D}$ 1.5789).

*Anal.* Calcd for $C_8H_9O_2P$ (168): C, 57.14; H, 5.36; P, 18.50. Found: C, 56.94; H, 5.55; P, 18.46.

This compound is very hygroscopic and it has a great tendency to polymerize spontaneously when small amounts of water or other impurities are present. Thus, the viscosity of impure material increases considerably on storage and its refractive index changes to 1.598. Hydrolysis of a sample of the viscous product with dilute HCl yielded phenylphosphonous acid, mp and mmp 85–86°. The pure ester crystallizes to form long white needles when stored at low temperatures. The crystals melt at room temperature.

**2-Phenyl-1,3,2-dioxaphosphorinane** was prepared in 59% yield from 1,3-propanediol and phenylphosphorus dichloride using the same procedure employed for the preparation of 2-phenyl-1,3,2-dioxaphospholane: bp 96–98° (0.3 mm); $n^{25}\text{D}$ 1.5659 (lit.[3d] bp 72–74° (0.15 mm)).

*Anal.* Calcd for $C_9H_{11}O_2P$ (182): C, 59.40; H, 6.09; P, 17.01. Found: C, 59.20; H, 6.55; P, 16.97.

**Polymerization of 2-Phenyl-1,3,2-dioxaphospholane. A. $BF_3$ Etherate Catalyzed Polymerization.** Freshly distilled $BF_3$ etherate (2 drops) was added to an ice cold sample of 2-phenyl-1,3,2-dioxaphospholane (2.5 g, 0.015 mol) and the mixture was sealed under nitrogen in a glass tube. After being heated at 160–180° for 24 hr, the mixture had changed to a transparent resin.

The resin was hydrolyzed by stirring it with 15 ml of 0.5*N* NaOH at room temperature until all but a very small amount of the material dissolved. The solution was then refluxed for 5 hr, filtered, and acidified with dilute HCl. The precipitate which separated was filtered and dried. It was shown by its infrared spectrum to be 1,2-ethylenebis(phenylphosphinic acid),[8,9] 1.52 g (67%). The material was recrystallized from glacial acetic acid to obtain glistening plates, mp 271–273° (lit.[8] mp 266–267°).

*Anal.* Calcd for $C_{14}H_{16}P_2O_4$ (310.6): C, 54.10; H, 5.20; P, 20.00; neut equiv, 155.3. Found: C, 54.07; H, 5.16; P, 19.98; neut equiv, 153.5.

In an attempt to isolate β-hydroxyethylphenylphosphinic acid from the resin hydrolysate, a new sample (2.2 g) of resin was prepared and submitted to the hydrolysis procedure of Mukaiyama and coworkers.[3e] A mixture of the resin and 5.0 ml of 0.1 *N* NaOH in 30 ml of dioxane was refluxed for 5 hr and allowed to stand overnight. No solid precipitated. An additional 2.0 ml of 0.1 *N* NaOH was added to the reaction mixture and refluxing was continued for several more hours. The solution was then allowed to cool to room temperature and was then acidified with concentrated HCl. The semisolid precipitate which formed was allowed to harden over a 48-hr period. It was then recrystallized from glacial acetic acid to obtain 1,2-ethylenebis(phenylphosphinic acid), mp 271–273° (lit.[8] mp 266–267°). The yield was 0.95 g (38%).

**B. Methyl Iodide Initiated Polymerization.** Methyl iodide (2 drops) was mixed with 13.6 g of 2-phenyl-1,3,2-dioxaphospholane and the mixture was heated in a nitrogen atmosphere at 150° for 1.5 hr. No change was observed so a few additional drops of methyl iodide were added to the hot mixture and a vigorous reaction took place. The mixture was heated at 150° for an additional 1.5 hr and was then treated with 2 drops of 1,6-dibromohexane. Heating was continued at 150° for an additional 3 hr. The product was a brown, tacky but hard resin. On standing exposed to the atmosphere, it slowly crystallized. A solid acid, 4.3 g, mp 220–240°, was isolated by partially dissolving the resin in acetone or ethanol. Additional material, 3.3 g, mp 220–237°, was obtained by refluxing the alcohol or acetone extracts with dilute NaOH for several hours followed by acidification. The total yield of the crude acid, which was shown by its infrared spectrum to be 1,2-ethylenebis(phenylphosphinic acid), was 7.6 g (61%). After recrystallization from glacial acetic acid, the acid was obtained as glistening plates, mp 266–267°.

**C. Aluminum Chloride Catalyzed Polymerization.** A mixture of 2-phenyl-1,3,2-dioxaphospholane (9.5 g, 0.052 mol) and aluminum chloride (110 mg, 0.82 mmol) was sealed in a Carius tube and heated at 160° for 65 hr. The resulting product was a clear, hard resin which was soluble in chloroform, but not soluble in benzene. A Rast determination indicated the molecular weight of the resin to be about 700. The product became soft, oily and acidic when exposed overnight to water. Hydrolysis of a portion of the resin with 0.5 *N* NaOH, followed by acidification, yielded 1,2-ethylenebis(phenylphosphinic acid), mp 255–258° dec. The infrared spectrum of this acid corresponded with that of authentic[5] material.

**Polymerization of 2-Phenyl-1,3,2-dioxaphosphorinane with $BF_3$ Etherate.** A mixture of 2-phenyl-1,3,2-dioxaphosphorinane and a small amount of $BF_3$ ethereate was sealed under nitrogen in a glass tube and the mixture was heated for 24 hr at 160–180°. The resulting product was a colorless, hard resin.

**Hydrolysis of Resin Obtained from 2-Phenyl-1,3,2-dioxaphosphorinane.** A sample (2.5 g) of the resin was added to 20 ml of 0.5 *N* NaOH and the mixture was stirred until a slightly turbid solution was obtained. The mixture was then refluxed for 6 hr, cooled, and acidified with concentrated HCl to obtain an oily solid. The solid hardened after standing exposed to the atmosphere. It was filtered, washed wit

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(7) A. N. Pudovik and G. I. Yeustafyev, *Vysokomol. Soedin.*, **6**, 2139 (1964); *Polym. Sci. USSR*, **6**, 2367 (1964).

(8) H. J. Harwood and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **82**, 423 (1960).

(9) P. Mastalerz, *Rocz. Chem.*, **33**, 985 (1965).

water, and recrystallized from an acetic acid–acetone mixture to obtain 1,3-propylenebis(phenylphosphinic acid), mp 153–155° (lit.[10] mp 157–159°).

*Anal.* Calcd for $C_{15}H_{18}P_2O_4$ (324.2): C, 55.61; H, 5.61; P, 19.14; neut equiv, 162.1. Found: C, 55.79; H, 5.81; P, 19.91; neut equiv, 166.5.

The yield of diacid was 0.82 g (33%). When the acid is recrystallized from ethanol, an alcoholate which decomposes at about 120° is obtained.

**Reaction of $PCl_5$ with Resin Obtained from 2-Phenyl-1,3,2-dioxaphosphorinane.** The resin obtained from the polymerization of 2-phenyl-1,3,2-dioxaphosphorinane with $BF_3$ etherate (4 g) was mixed with $PCl_5$ (3.5 g) and the mixture was heated in a sealed tube for 5 hr. The reaction mixture was distilled to obtain $POCl_3$, bp 101°, 1.6 g (48%), γ-chloropropylphenylphosphinic chloride, 1.5 g (30%), bp 150° (0.3 mm) (lit.[3d] bp 125–127° (0.05 mm), and a distillation residue of 2.20 g.

The γ-chloropropylphenylphosphinic chloride was identified by hydrolysis to the corresponding acid, mp 82–84°.

*Anal.* Calcd for $C_9H_{12}ClPO_2$ (237.0): C, 45.65; H, 4.69; P, 13.10; Cl, 29.51; neut equiv, 218.5. Found: C, 45.17; H, 4.30; P, 13.32; Cl, 29.98; neut equiv, 218.2.

The distillation residue could not be rectified further. It was dissolved in saturated sodium carbonate solution. The resulting solution was filtered from a trace amount of insoluble material and was acidified with dilute HCl. The sticky precipitate which separated was dissolved in acetone and the resulting solution was evaporated to dryness *in vacuo*. The residue as triturated with acetone to obtain 1,3-propylenebis(phenylphosphinic acid), 0.64 g (20%), as a white powder, mp 153–155° (lit.[10] mp 157–159°). The infrared spectrum of this product was identical with that of the diacid recovered from the resin hydrolysate.

**Acknowledgments.** The authors are grateful to the Esso Research and Engineering Co. for support of this study.

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(10) P. Mastalerz, *Rocz. Chem.*, **39**, 1129 (1965).

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# Lignin. XIV. Gel Chromatography and the Distribution in Molecular Size of Lignin Sulfonates at Several Electrolyte Concentrations[1]

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ABSTRACT: Sodium lignin sulfonates, from gymnosperm woods, were fractionated using Sephadex G-50 gel columns and eluting with distilled water or with $10^{-1}$ to $10^{-4}$ *M* NaCl solutions. Molecular weights of certain lignin sulfonate fractions were estimated by ultracentrifuge sedimentation equilibrium and were found to range in an orderly manner from about 70,000 in the mostly excluded initial eluates down to several hundred in the final eluates. For approximately corresponding fractions in the several separations conducted, the elution curves and the estimated molecular weights were similar but not identical and the observed changes occurred sequentially with respect to the molarity of the eluent. The sizes of the lignin sulfonate polymer molecules in terms of equivalent Einstein spheres, $r_\eta$, were estimated from the measured molecular weights and from intrinsic viscosities calculated using relationships reported by Goring and coworkers. These ranged from about 7 to 70 Å. For a lignin sulfonate of a particular molecular weight, $r_\eta$ was estimated to be up to two times greater in water than in 0.1 *M* NaCl solution—behavior expected for an elastic network containing negative charge sites in an environment of varying ionic strength. Support for the concept of change in molecular size with electrolyte concentration is found in the fact that column functioning was correlated satisfactorily in terms of log $[\eta]M_w$ *vs.* $V_e$, the elution volume; $r_\eta$ *vs.* $K_d$, the fraction available of the volume of the gel liquid; and $r_\eta$ *vs.* the inverse error function complement of $K_d$.

Lignin is a phenylpropane type of polymer which exists in wood as a three-dimensional network probably chemically bound at some sites to cellulose and/or other carbohydrate materials.[3,4]

By treatment of woody tissue at elevated temperature with an aqueous solution containing bisulfite ions, at least some linkages in the lignin polymer network and lignin–carbohydrate attachments are hydrolyzed. Simultaneously, sulfonate groupings are added to the phenylpropane-type residues to yield soluble lignin sulfonate (LS) molecules which become dissolved in the aqueous solution along with other soluble components of the tissue.[4b]

Several investigators have shown that these soluble LS molecules and other lignin preparations manifest a

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(2) (a) Senior Research Associate, Department of Chemical Engineering, University of Washington, Seattle, Wash. (b) Professor of Chemical Engineering and Dean of Graduate School, University of Washington, Seattle, Wash.

(3) F. E. Brauns and D. A. Brauns, "The Chemistry of Lignin," Supplementary Volume, Academic Press Inc., New York, N. Y., 1960.

(4) (a) I. A. Pearl, "The Chemistry of Lignin," Marcel Dekker, Inc., New York, N. Y., 1967. (b) E. Nokihara, M. J. Tuttle, V. F. Felicetta, and J. L. McCarthy, *J. Amer. Chem. Soc.*, **79**, 4495 (1957).