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DEVELOPMENT OF IMPROVED POLYPHENYLENE CURE PROCESSES

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TECHNICAL REPORT AFML TR 67-60
APRIL 1967

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Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

50th Anniversary
1917 1967
Materials Research in the Air Force

NOTICES

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OF
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FOREWORD

This contract was initiated under USAF Contract 33(615)-3479, Project No. 7340 "Nonmetallic and Composite Materials," Task Number 734001, "Thermally Protective Plastics and Composites." It is administered under the Air Force Materials Laboratory, Research and Technology Division, with Mr. Paul Pirrung serving as Project Engineer.

The principal investigator on the program is Dr. Norman Bilow, Hughes Senior Staff Chemist. Professional assistance was received from Dr. Richard I. Akawie and Dr. Leroy J. Miller and technical assistance was received from Joseph Madden, Kenneth Rose, and Raymond E. Lawrence.

The manuscript was released by the authors in February 1967 for publication as a technical report.

This technical report has been reviewed and is approved.

R. G. Spain

R. G. SPAIN, Acting Chief
Plastics and Composites Branch
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ABSTRACT

The object of this program was to obtain crosslinked polyphenylene resins through the identification of chemical curing agents and the development of curing processes. Improved resinous matrices of this type were expected to have improved ablative performance characteristics, mechanical properties, and processability.

Nitration, carboxylation, and sulfonation of polyphenylene polymers were accomplished in an effort to introduce reactive sites on the polymer for subsequent copolymerization or polymerization. Only the latter process yielded a useful product. Suitable cures were obtained with a trifunctional sulfonyl chloride and a disulfonic acid.

A polyphenylene thermosetting resin was prepared by dissolving the aromatic trisulfonyl chloride in chloroform lacquers of polyphenylene. The resin was then applied to carbon and high silica fabric, dried to a tacky state, plies cut and stacked in a mold, and then transformed into a hard composite by the application of heat and pressure. Ablative characteristics of the composite were determined. The benzene trisulfonylchloride cured polyphenylene was superior to the state-of-the-art phenol formaldehyde resin.

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I. SUMMARY

Three major approaches to the curing of polyphenylene were undertaken. In one approach the polymer was nitrated with the intention of reducing the nitro groups subsequently to amino groups. The aminated polymer was desired for curing with pyromellitic dianhydride, which would produce pyromellitimide bridges, or with epoxyphenolics, diisocyanates, or phthaloyl chloride. The major problem encountered in this investigation was the loss of tractability of the polyphenylene during nitration. In only two cases was completely fusible nitrated polyphenylene obtained. In one of these cases the polyphenylene had only 2 percent of the rings nitrated and in the other case the nitrated polymer was derived from a polyphenylene having a molecular weight below 500.

A second approach involved the preparation of carboxylated polyphenylene and the corresponding acid amides. Modified polyphenylene of this type was expected to be curable with tetraamines such as 3, 3'-diaminobenzidine producing benzimidazole bridges. Carboxylation was attempted by treating the polymer with phosgene but was accomplished by acetylation followed by oxidation. This approach also proved unsatisfactory because the polyphenylene acid amides were all intractable.

The third major approach involved cures via sulfonic acid groups and sulfonyl halides and was undertaken as a result of several promising experiments carried out at Hughes several years previously. Although little success was obtained when the polyphenylenes were sulfonated directly, suitable cures were achieved with di- and trifunctional sulfonic acids and sulfonyl halides such as 4,4'-biphenyldisulfonic acid and 1, 3, 5-benzenetrisulfonyl chloride. The latter compound, which was the best curing agent of this class, could be ball-milled with high molecular weight polymer to produce thermosetting resin or could be dissolved in chloroform lacquers of lower molecular weight polyphenylenes (1000 ±500). Lacquers of this type produced the best composite structures and also showed the best hyperthermal performance.

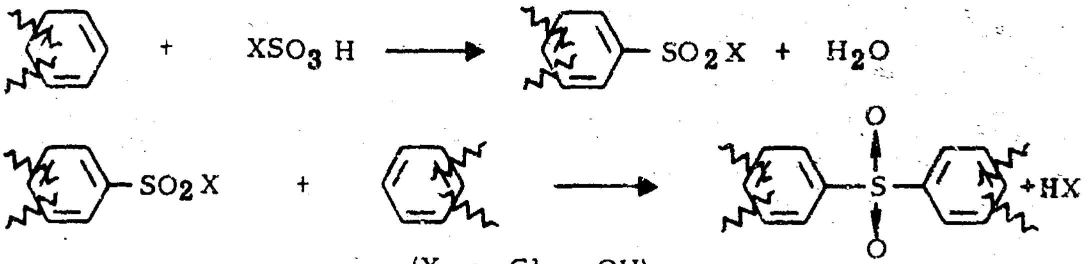
Resin evaluation consisted of fabricating composite structures using carbon or glass fabrics and exposing these composites to a 550 BTU/ft^2-sec. plasma composed of reconstituted air. The best hyperthermal performance was observed on the lacquer forming 1000 m.w. polyphenylenes cured with benzenetrisulfonylchloride.

II. MATERIALS SYNTHESIS

A. DISCUSSION

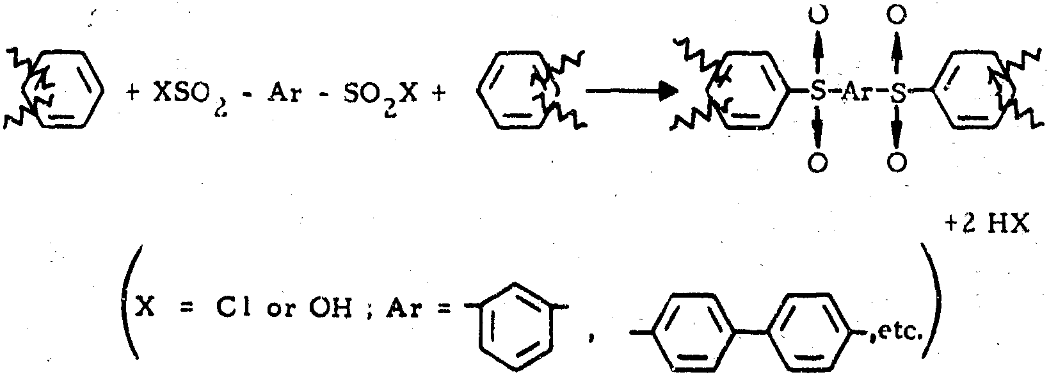
1. Sulfone and Phenylene Crosslinks

Some preliminary experiments carried out at Hughes during 1963 and 1964 indicated that a promising method of curing polyphenylenes would be through the introduction of sulfone crosslinks.[1,2] Two general approaches were considered. In one approach sulfonic acid or chlorosulfonyl groups were introduced first as substituents on the polyphenylene chain. The substituents were expected to react with other polymer chains to form crosslinks as follows:



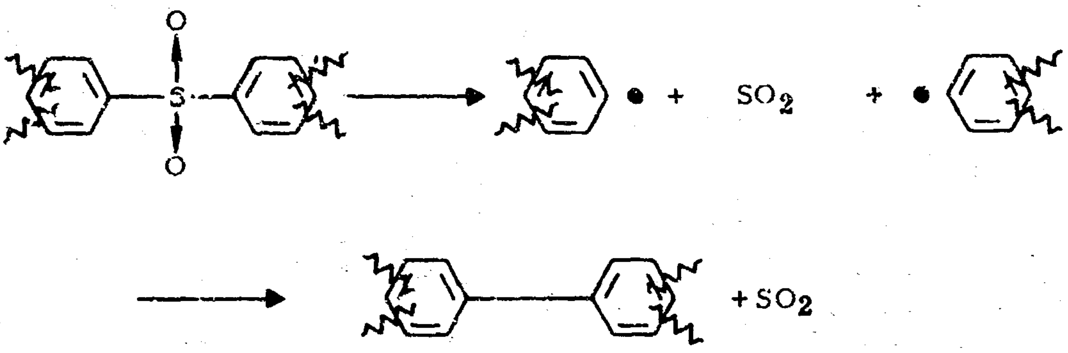
(X = Cl or OH)

The second approach was to utilize difunctional curing agents which would insert two sulfone groups per crosslink as illustrated below.

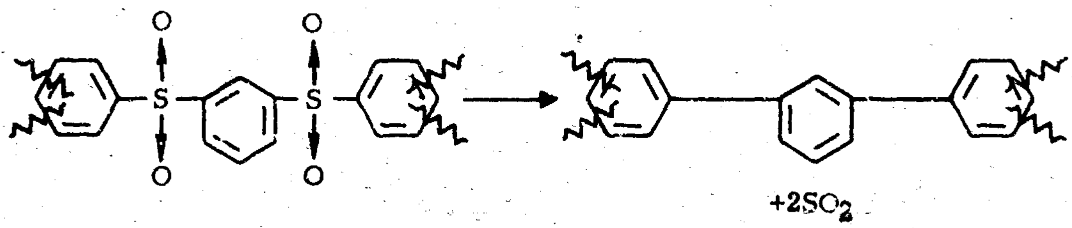


The first approach appeared to be preferable, since it would form only one sulfone group per crosslink and since the sulfone linkages were undoubtedly less stable thermally than the remainder of the polymer.

The possibility of exploiting the relative weakness of the sulfone crosslinks was also considered. Thermal elimination of sulfur dioxide from the cured resin was expected to generate two aromatic free radicals held closely together in a rigid matrix. These radicals were then expected to react to form a bond directly linking the carbon atoms of two originally separate polyphenylene chains.



Correspondingly, if a bifunctional crosslinking agent is used, the cured product would contain phenylene crosslinks.

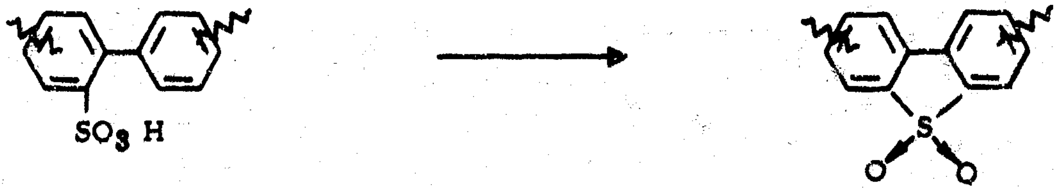


Since it has been reported[3] that a model compound, diphenylsulfone, decomposes at 800°F (427°C), elimination of sulfur dioxide would not be anticipated much below this temperature.

a. <u>Attempted Curing of Sulfonated Polyphenylene.</u> The possibility of curing by heating a directly sulfonated polyphenylene was first investigated. A 1,2,4-trichlorobenzene-soluble, chlorobenzene-insoluble polyphenylene fraction (with an average molecular weight of 2000-3000) was used in these experiments. [In the experimental section of this report this type of polyphenylene is designated as: ϕCl (-),ϕCl_3 (+).] One sample was sulfonated with concentrated sulfuric acid at 250°C over a period of 24 hours. The black product was soluble in water but infusible at temperatures up to 400°C.

Three other samples of the same polyphenylene were sulfonated with chlorosulfonic acid. The products weighed 9 percent, 24 percent, and 44 percent more than the starting polyphenylene. Only the first of these products was still partially fusible; however, it could not be cured by heating. Nevertheless, there was some evidence of reaction in all three products when they were heated. At 105-120°C a small quantity of volatile material was lost, and above 375°C the samples changed in color from greenish-black to chocolate brown. Elemental analyses were used to compare the initial polyphenylene, the sulfonated polymer which had gained 24 percent in weight, and the products which were obtained by heating this sulfonated material at 110-130°C and at 375-380°C. (Table I.) The results indicated that sulfonic acid groups were introduced rather than chlorosulfonyl groups. Apparently the sulfonated product was not entirely homogeneous and the analytical results were therefore not entirely self-consistent. Heating to 380°C removed about 40-50 percent of the sulfur and raised the carbon:(hydrogen + chlorine) atom ratio to 1.78.

Obviously no difficulty was encountered in preparing the sulfonated polyphenylene. However, sulfonation raised the melting point rapidly, so that even lightly sulfonated products were infusible and unsuitable for molding. Furthermore, there was no indication that the sulfonic acid groups could be utilized for crosslinking, and heating the fusible sulfonated products did not effect a cure. It seems likely that the sulfonic acid groups preferentially react internally whenever they are situated ortho to another aromatic ring[4].



Atom % or Atomic Ratio	Initial Polyphenylene (D1081-1-1)	After Reaction With $ClSO_3H$ (D1081-2-5)	After Heating To 110-130°C (C3004-56-1-B)	After Heating To 375-380°C (C3004-56-1-A)
%C	90.00	72.13	69.04	83.91
%H	4.80	4.36	4.10	3.95
%Cl	1.60	1.28	0.75	0.45
%S	-	6.08	6.98	4.42
%ash	3.47	-	-	-
C/ (H + Cl)	1.56	1.38	1.40	1.78
C/Cl	166	166	271	549
C/S	-	31.7	26.4	50.7
% O	-	9.10% O as SO_3H; 4.08% O as H_2O*	10.47% O as SO_3H; 3.04% O as H_2O*	4.41% O as $-SO_2-$
Total % without O	99.87	83.85	80.87	92.73
Total % with Calculated O	99.87	97.03	94.38	97.14
% of Material not Accounted For	-	2.97	5.62	2.86
% C/% Not Accounted For	-	24.3	12.3	29.3
Calculated Weight Gain	-	24.8**	-	-
Probable Formula	$[C_6H_{3.81}Cl_{0.04}]_n$	$[C_6H_{3.62}Cl_{0.04}(SO_3H)_{0.19}\cdot 0.35\ H_2O]_n$	$[C_6H_{3.58}Cl_{0.02}(SO_3H)_{0.23}\cdot 0.34\ H_2O]_n$	$[C_6H_{3.37}Cl_{0.01}(SO_2)_{0.12}]_n$

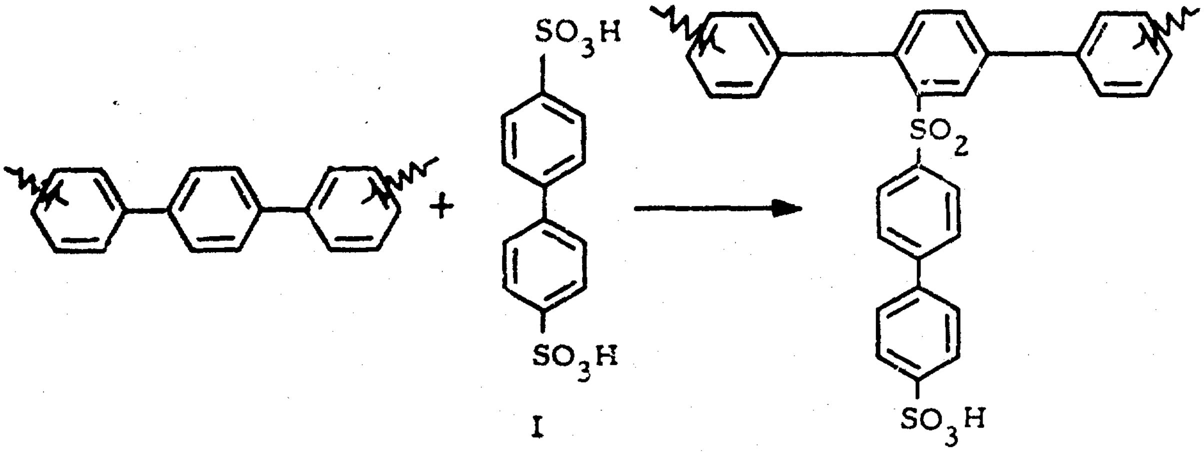
*Calculation based on the assumption that the C/H ratio should be the same as in the initial polyphenylene, and that the excess must be due to water bound to the sulfonic acid groups.

**Calculation based on decrease in the percentage of the total weight represented by carbon.

Table I. Analyses of various sulfonated polyphenylenes.

Since there is a high probability that substituents on the polyphenylene chain are located ortho to other aromatic rings, the probability that the sulfonic acid groups react to form crosslinks may indeed be quite low. This would explain the failure of the sulfonated polyphenylenes to cure to produce a continuous resin matrix. The formation of a number of dibenzothiophene dioxide units in the polymer chain by intramolecular reaction may be sufficient to make the polymer infusible, but without crosslinks the material would obviously lack structural integrity.

b. Cures With 4,4'-Biphenyldisulfonic Acid. Since attempts to cure polyphenylenes through sulfonic acid groups attached to the polymer chain failed, it was decided to turn to the investigation of crosslinking agents such as 4,4'-biphenyldisulfonic acid, 1,3-benzenedisulfonic acid, and the corresponding sulfonyl chlorides. The reaction of one sulfonic acid group of 4,4'-biphenyldisulfonic acid (I), for example, would introduce a substituent with a sulfonic acid group which is not ortho to another aromatic ring and which is remote from the original polyphenylene chain.



This remoteness would favor greatly a reaction with a second, separate polyphenylene chain and consequently intramolecular cyclization would be minimized and intermolecular reaction maximized.

4,4'-Biphenyldisulfonic acid was found to undergo polymerization to a black infusible resin when it was heated alone. In this respect it is similar to p-xylylene glycol, which is already being used to cure polyphenylenes[1,2,5] (although the xylylene glycol reaction requires the addition of an acid catalyst). Polymerization of the disulfonic acid takes place, with fuming, at temperatures over 250°C. The reactions involved in this polymerization are not known, but if the polymerization involves the formation of sulfones, the reaction should proceed far more rapidly with the aromatic ring of a polyphenylene chain than with aromatic rings of the curing agent itself. The benzene rings of 4,4'-biphenyldisulfonic acid already bear the electron-withdrawing sulfonic acid substituent, which deactivates the ring toward further electrophilic substitution. Consequently, reaction of the crosslinking agent with polyphenylene would predominate over reaction with itself.

Ordinarily in polymer chemistry monomer purity is a critical requirement. In the preliminary investigation of new curing agents, however, it seemed safe to overlook the presence of impurities because of the extremely high functionality of the polyphenylene prepolymer. For example, a polyphenylene chain with a degree of polymerization of 26 and a molecular weight of about 2000 would theoretically have about 106 reactive sites available for crosslinking. Wasting some of these sites by reaction with impurities – such as a monosulfonic acid – might adversely affect the thermal stability of the cured product, but it would not preclude curing with the bulk of the di- or trifunctional curing agent. Therefore, commercial 4,4'-biphenyldisulfonic acid was used in the form it was received for the first experiments.

When polyphenylene was mixed intimately with a melt of commercial 4,4'-biphenyldisulfonic acid at 160-200°C, the soft, fluid mass changed to a gray-green powder within 5-10 minutes. Continued heating caused no apparent further changes until the mixture melted at 250°C. Above this temperature the melt reacted rapidly to become a black, plastic mass which then cured to a hard, infusible polymer.

Polyphenylene-biphenyldisulfonic acid mixtures with 2:1, 1:1, and 1:2 weight ratios were heated to obtain experimental molding powders. Powders advanced only to the gray-green powder stage (160-200°C) underwent excessive flow in a mold under pressure. The black products obtained by heating the mixtures above 250°C had a consistency suitable for molding if heating was limited to a short period of time. Some advancement of the resin also occurred, although at a slower rate, when the powder was heated at temperatures below 250°C. A further improvement was realized by drying the advanced resin for one hour at 110°C under vacuum. When the molding powder was not vacuum dried, the cured pellets contained cracks, whereas these cracks did not develop when the resin was vacuum dried prior to cure.

A sample of commercial 4,4'-biphenyldisulfonic acid began melting at 48°C and melted completely, when heated rapidly, at temperatures as low as 138°C. Continued heating caused it to resolidify, followed by melting at ~250°C. The melting point reported in Beilstein is 72°C, but a more recent reference[6] gives 240°C as the decomposition point for 4,4'-biphenyldisulfonic acid dihydrate. It was desirable, therefore, to investigate the use of purified disulfonic acid. The acid could be crystallized from a concentrated aqueous solution to which concentrated hydrochloric acid had been added. After being dried in a desiccator over anhydrous calcium sulfate and sodium hydroxide pellets, it melted at 260-265°C, with traces of partial melting at lower temperatures, probably due to the rapid absorption of moisture from the air. It seems obvious that the low melting point of the commercial acid was primarily the result of absorbed water.

The molten commercial acid, therefore, was actually a highly concentrated aqueous solution of the acid, and the mixture of acid and polyphenylene became a dry powder when all the water was driven off. While the extent of reaction between the acid and the polymer at this stage was not determined, the dry powder probably was little more than a mixture of the dried reactants, except in those cases in which the powder was heated further.

A study was carried out to determine the optimum mixing and advancement or "B" staging procedure using the recrystallized acid. An intimate mixture of the acid and the polyphenylene apparently advanced slightly when heated as a dry powder at 180°C. When the mixture was heated to temperatures at which the entire mixture melted and the ingredients could be mixed intimately (~260° or more), the curing reaction in an open container was very rapid. While satisfactory advancement could be realized at this temperature, the reaction was so rapid that it was extremely difficult to duplicate in large quantities.

Heating the mixture at 220°C — approximately the lower end of the polymer melting range — advanced the resin at a controllable rate, even though the mixture appeared to melt scarcely at all at this temperature. Heating for 15 minutes at this temperature produced a molding compound which had optimum flow properties when subsequently cured in a mold.

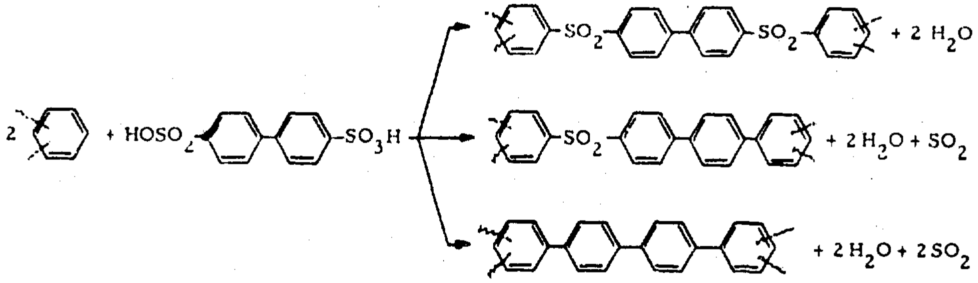
In order to obtain a more homogeneous mixture than could be obtained by mixing the solid reactants, one sample of the acid was first dissolved in water. The aqueous solution could then penetrate the polymer particles and coat all available surfaces. Water was removed from the resulting paste by drying in a desiccator. In a similar fashion, sufficient water was added to another sample to make the acid soluble at an elevated temperature, the polyphenylene particles being coated with acid and the water being driven off simultaneously. This procedure essentially duplicated the procedure previously used with the commercial disulfonic acid. Mixtures so obtained were then advanced at 220°C as before, but it was assumed that the advancement would be more uniform than that of the more heterogeneous mixtures derived by mixing the solid powders. The qualitative differences were small, but the resin prepared from the wet acid appeared to yield less brittle cured pellets.

It is believed that a major problem in effecting a cure is the removal of water from the advancing resin. Sulfonation is an equilibrium, with water being formed as one of the products, and in order for the reaction to proceed to completion water must be removed from the reaction. In an open container, where the water is readily lost to the atmosphere, the polyphenylene is cured quickly. In a mold, however, the reaction goes to completion more slowly, the rate controlling step probably being the diffusion of water out of the mold.

The best unreinforced resin pellet cured with biphenyldisulfonic acid and postcured to 316°C had a compressive strength of 2760 psi. While this is low compared to the values for fully developed resins, such as the phenolics, or for xylylene glycol-cured polyphenylene, it was considered promising at this stage of development.

A cured polyphenylene derived from a 1:1 mixture of prepolymer and 4,4'-biphenyldisulfonic acid by weight was found to contain only

3.0 percent sulfur whereas theoretically it should have contained about 10 percent. The fate of the remainder of the sulfur is unknown. Recent patents indicate, however, that sulfonic acids and sulfonyl chlorides can function as arylating agents when heated with aromatic hydrocarbons.[7] If arylation is taking place during the curing process, the crosslinks which are formed would consist exclusively of phenylene groups and the sulfur content of the cured polymer would be lowered correspondingly. The following equations describe reactions which would be occurring simultaneously.



While the low sulfur content lays the mechanism of the cure open to question, none of the above curing reactions would be undesirable. Originally it was intended that sulfur dioxide would be eliminated thermally from the sulfone-linked polymer to yield the phenylene-linked polymer anyway.

A portion of one cured specimen was heated under vacuum for 2 hours, with the temperature going as high as 460°C, to see if sulfur dioxide could be eliminated in a postcure treatment. The specimen decreased in weight by 28 percent due to the loss of volatile materials, but the residue still contained 8.5 percent sulfur. Apparently an even more drastic treatment is necessary to eliminate sulfur dioxide completely. The product was judged to be somewhat harder than the unheated sample.

Postcures of some cured pellets were carried out with a programmed heat cycle to a maximum temperature of 316°C (600°F). Continued heating of these postcured materials to about 400°C under vacuum removed an additional 12 percent of volatile material, some of which condensed as a solid in the cooler portions of the container. After the postcure cycle, one sulfur atom was present in the polymer for each 12.4 aromatic rings, and after an additional heat treatment at temperatures up to 475°C the sulfur content dropped to one atom for each 14.2 rings. While indeed a small percentage of the sulfur was lost and may have been eliminated as sulfur dioxide, one is impressed more with the tenacity of that sulfur which remained. The hydrogen content of the cured polymer scarcely changed during the heating, the number of hydrogen atoms per ring dropping only from 3.40 to 3.28.

Several reinforced discs were postcured to 450°C. Tiny surface cracks appeared during the postcure, indicating that the discs may have been subjected to too high a postcure temperature. Additional information on the behavior of the cured resins at elevated temperatures was obtained by thermogravimetric and differential thermal analyses of samples which had been postcured to only 316°C. Thermodifferential and thermogravimetric analysis curves are presented in Figures 1 through 4. An 18 percent weight loss was suffered by the sample in one reaction as it was heated to 565°C, and an additional 20 percent weight loss resulted on further heating to 850°C. An exotherm was apparent at temperatures above 364-390°C; consequently, cure or degradative processes occurring above ~400°C are different in nature from those which occur below ~400°C, and postcure temperatures above 400°C should be avoided. If allowance is made for the 12 percent which would have been lost in a postcure to 400°C, the weight loss of the postcured specimen in thermogravimetric analysis would have been about 30 percent. In subsequent experiments the specimens were generally postcured in a programmed heat cycle to 400°C.

In the first attempt to mold a carbon cloth-reinforced laminate it became apparent that the resin did not "wet" the cloth and therefore did not penetrate into the fabric as is necessary for the formation of a strong composite. Two different methods of preparing the surface of the reinforcement were used to solve this problem. In the first method the carbon cloth was treated with 4,4'-biphenyldisulfonic acid at temperatures over 250°C. This treatment undoubtedly caused reactions between the acid and the surface of the carbon fibers similar to the reactions between the acid and polyphenylene.

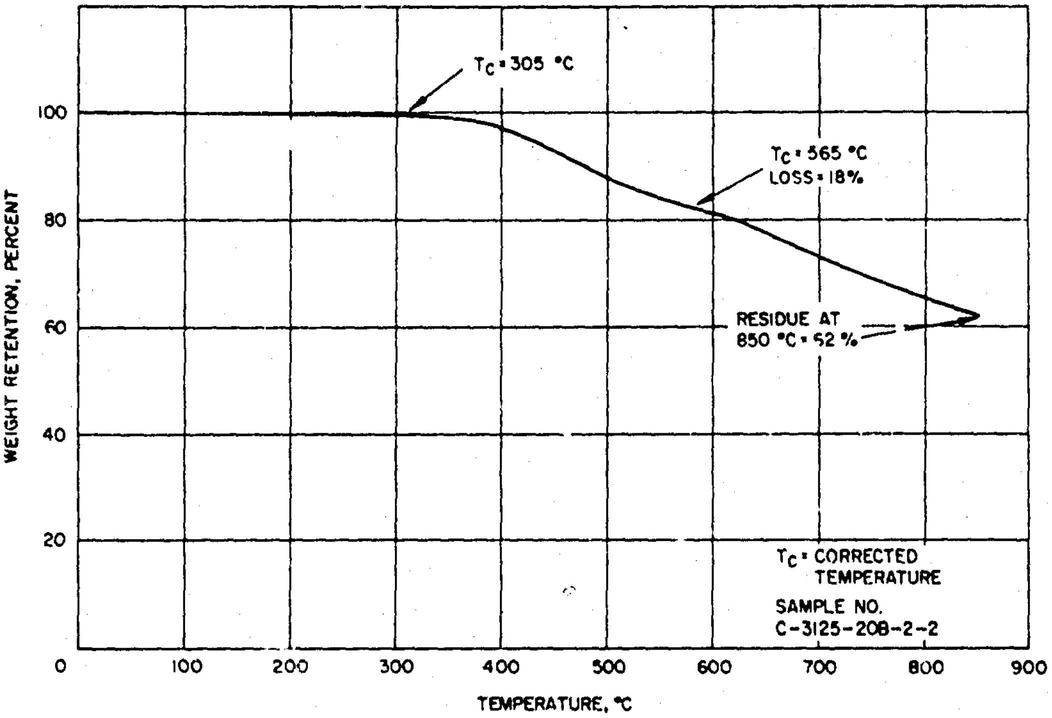


Figure 1. Thermogravimetric analysis of a 4, 4'-biphenyl-disulfonic acid-cured polyphenylene in nitrogen.

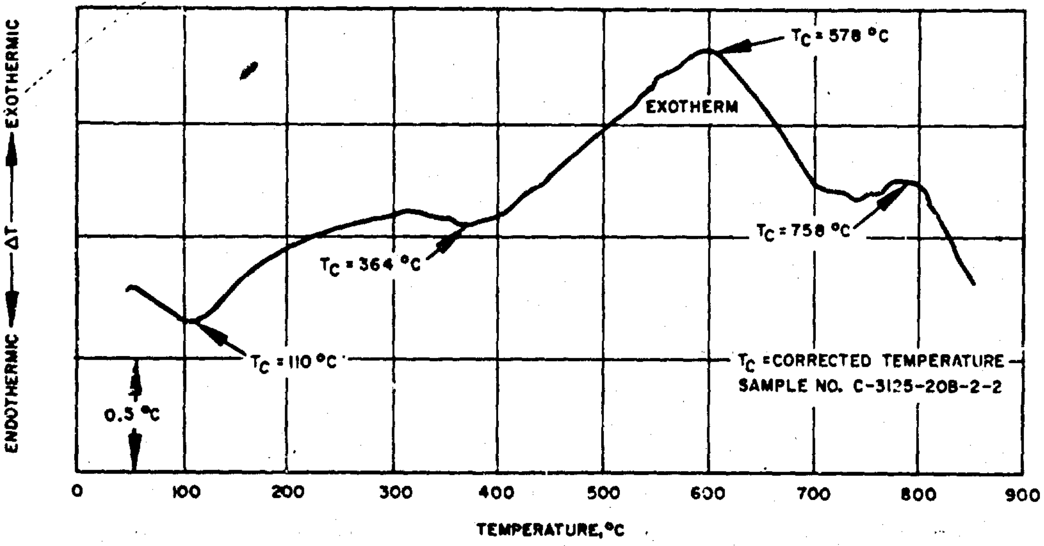


Figure 2. Differential thermal analysis of a 4, 4'-biphenyl-disulfonic acid-cured polyphenylene in nitrogen.

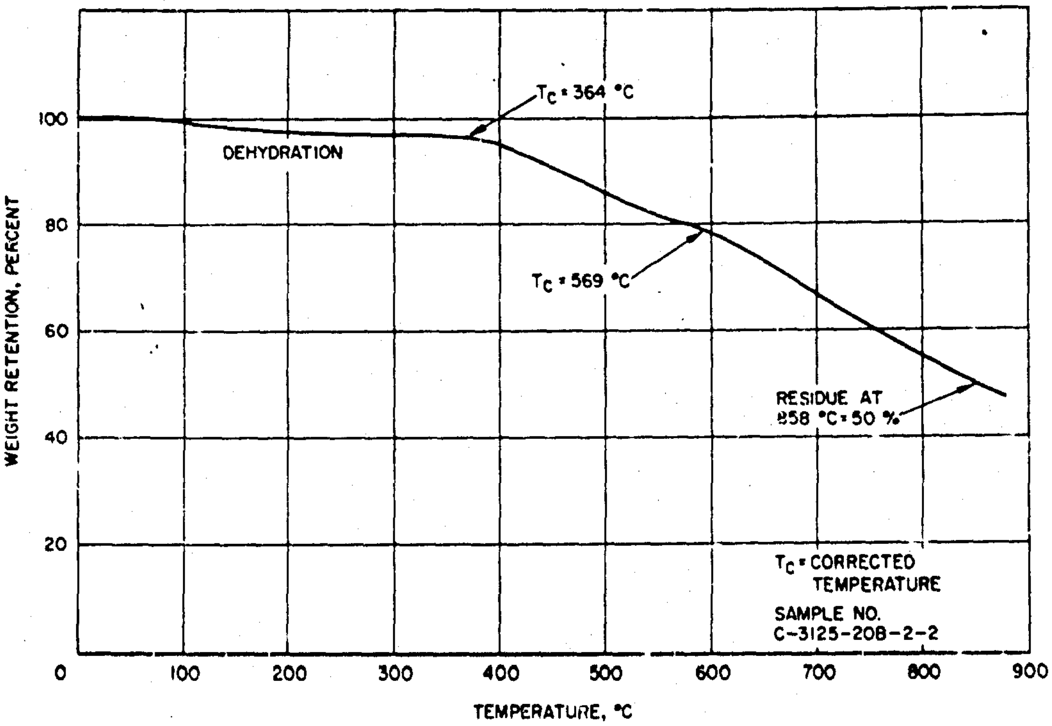


Figure 3. Thermogravimetric analysis of a 4, 4'-biphenyl-disulfonic acid-cured polyphenylene in static air.

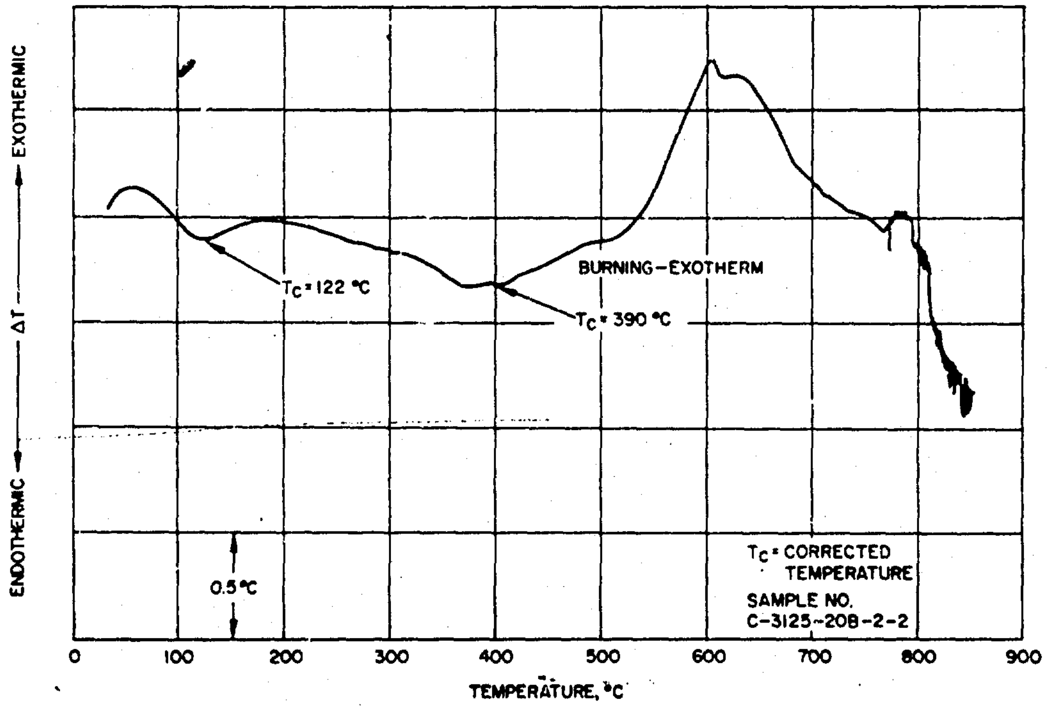
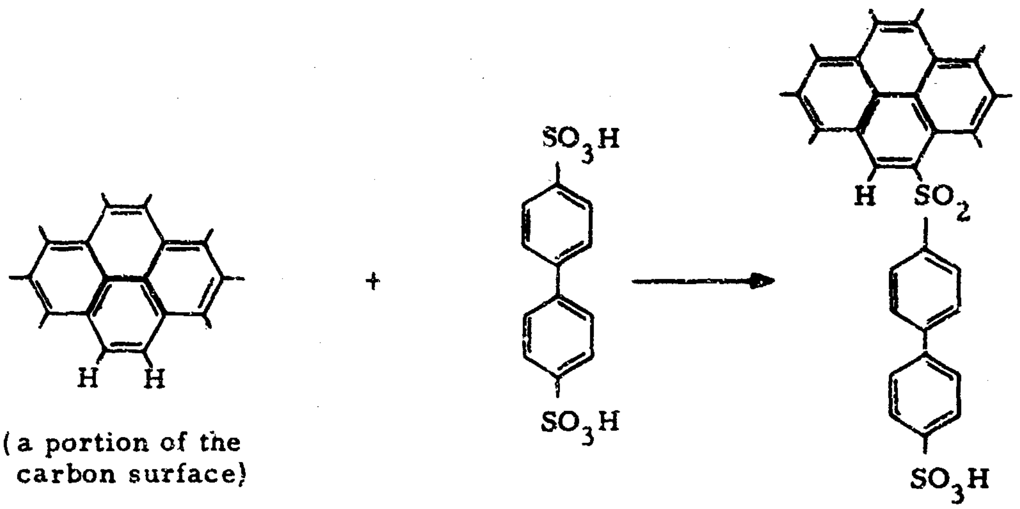


Figure 4. Differential thermal analysis of a 4, 4'-biphenyl-disulfonic acid-cured polyphenylene in static air.

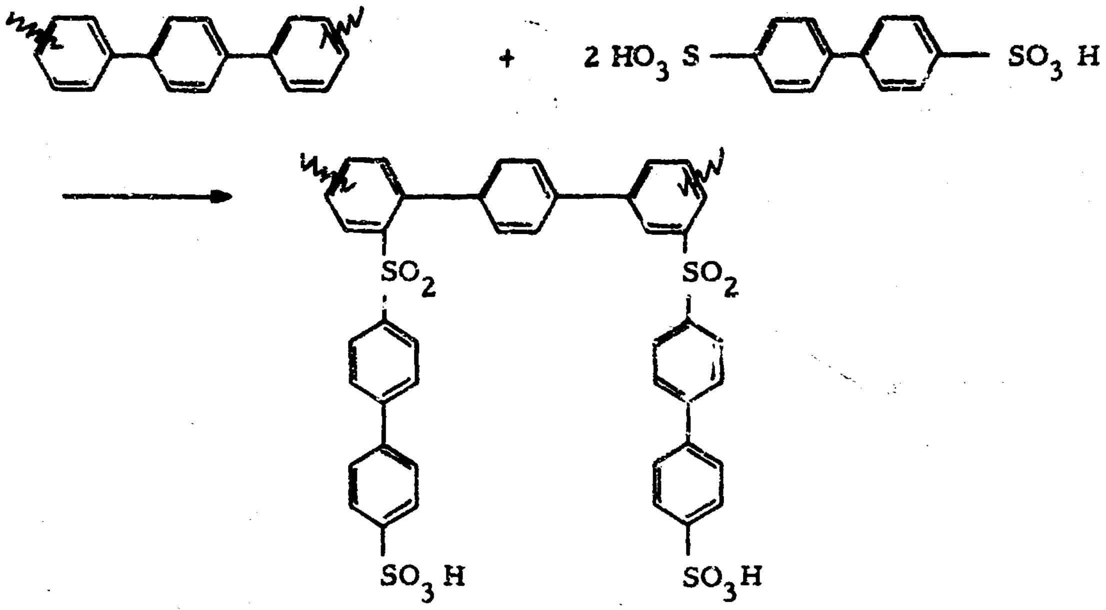


This treatment permitted adequate wetting of the surface to be achieved. The attached sulfonic acid substituents were available for reaction with the polyphenylene to tie the aromatic polymer to the carbon surface. Most of the composites prepared on this program were fabricated from cloth which was treated with biphenyldisulfonic acid. Several different treatment procedures were employed and are described in the experimental section.

A second method of preparing the cloth consisted of heating the carbon fabric with molten polyphenylene at 220-230°C for 3-1/2 hours. Reinforced parts were fabricated with this fabric, and this treatment also succeeded in permitting adequate wetting of the reinforcement.

Another factor which was found to be involved in wetting was the melting range of the polyphenylene. Molding compound prepared from polyphenylene melting at 255-320°C failed to wet the carbon cloth well, while a molding compound prepared from a polyphenylene melting at 215-255°C wet the fabric effectively and yielded an excellent part.

An effort was made to find a method of incorporating the polyphenylene-biphenyldisulfonic acid resin in a lacquer. Polyphenylene was therefore heated with a large excess of the acid in a melt with the intention of introducing 4'-sulfo-4-biphenylsulfonyl groups. This reaction is illustrated below.

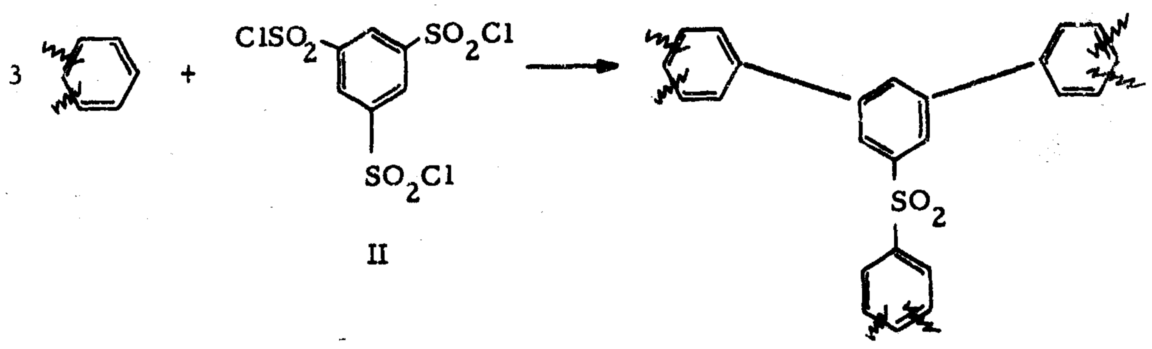


With a large excess of biphenyldisulfonic acid present there was a high probability that the pendant sulfonic acid groups would not react further. It was assumed that all of the polyphenylene had reacted with acid to some extent and that the substituted polyphenylene would be less soluble in aqueous acids than the unreacted biphenyldisulfonic acid. In one small-scale experiment two fractions were isolated corresponding to 46 percent and 92 percent of the weight of the original polyphenylene. The first of these was only partially soluble in water, but the second was completely soluble. The first softened only partially on heating, but the second softened completely and then proceeded to cure. The soluble fraction contained 16.2 percent sulfur, however, corresponding to almost one substitution per benzene ring. Nevertheless, it appeared that this would be a route, although an inefficient one, to a soluble polyphenylene prepolymer which could subsequently be cured by heating to form sulfone crosslinks. An acid : polyphenylene weight ratio of about 10:1 was necessary to bring about sufficient reaction to achieve a soluble polymer without promoting crosslinking and curing the material.

A water-soluble prepolymer was prepared by the above method from 10g of polyphenylene and 100g of 4,4'-biphenyldisulfonic acid. From this mixture were obtained 8.8g of insoluble polymer and 9.5g of polymer which was the least soluble portion of the soluble fraction.

The distribution of the original polyphenylene in these two fractions was unknown; however, if one assumes that at least one out of every three rings of the original polyphenylene reacted with a molecule of biphenyldisulfonic acid, the weight of polymer was at least doubled by the reaction. The conditions of the reaction were quite strenuous (1-1/2 hours at 270-280°C); therefore, the reaction very probably proceeded to such an extent. Under these conditions biphenyldisulfonic acid also polymerizes by itself, but only a water-soluble product is obtained. Consequently it seems reasonable that the reacted polyphenylene would be represented by the insoluble and infusible fraction, which results from crosslinking, and by the least soluble portion of the soluble fraction. Furthermore, since the weight of polymer derived from the polyphenylene was very likely at least double that of the original polyphenylene, the soluble fraction which was isolated probably consisted entirely of polyphenylene-based polymer. This polymer could be cured by further heating. However, when the preparation of reinforced pellets was attempted, the resin did not wet the fabric during cure, and consequently there was very poor interlaminar adhesion. It seemed unprofitable to pursue this line of investigation further.

c. <u>Cures With 1,3,5-Benzenetrisulfonyl Chloride</u>. The curing agent which was utilized most successfully was 1,3,5-benzenetrisulfonyl chloride (II). The anticipated curing reaction is illustrated below.



II

Curing took place very rapidly at temperatures above the melting point of the trisulfonyl chloride (189-192°C). When mixtures of this compound and high-melting polyphenylene were heated in open containers, curing was completed before the softening temperature of the polyphenylene was reached. One of the major problems in curing high-melting polyphenylenes with this curing agent was achieving adequate flow. Nevertheless, good laminated parts of this type were obtained from mixtures of the prepolymer and curing agent which either were not advanced prior to molding or which were advanced for no more than 3 minutes at 195°C. Advancement in a solution would have been extremely difficult because of the very limited solubility of the high melting (>250°C), high molecular weight (≈2000) polyphenylene.

In most of the experiments with this high molecular weight polyphenylene, a 2:1 weight ratio of polyphenylene to benzenetrisulfonyl chloride was used. Plasma arc test data indicate, however, that a 2.67:1 ratio was preferable. Higher ratios were tested only with a lower molecular weight fraction of polymer. For polyphenylene with a mean molecular weight of 2000, the theoretical maximum of this ratio would be 8:1 if the resin were to be completely cured with one crosslink per prepolymer molecule.

Whenever the high-melting polyphenylene was cured with benzenetrisulfonyl chloride and no reinforcement was used, there was a strong tendency for the molded part to crack. A microscopic examination of the cured matrix revealed that it was not homogeneous and that there were small, shiny regions associated with the cracks. This appearance and behavior may have been due to small crystals of curing agent present in the molding compound. Because of the extremely high reactivity of the trisulfonyl chloride, these crystals probably reacted with the surrounding polymer immediately upon melting to form a region with a high crosslink density. It is likely that the resulting unequal distribution of crosslinks introduced strains and caused cracking, and that the shiny areas observed with a microscope corresponded to the position of small crystals of trisulfonyl chloride.

A method of distributing this curing agent more uniformly was therefore required. To improve the efficiency of mixing, the polyphenylene and benzenetrisulfonyl chloride were ground together in a ball mill for several days, and the powder was then passed through a 100 mesh screen. This method of preparation permitted the molding of an unreinforced pellet without cracking. During postcure, however, small cracks again appeared in the cured part. A photograph of the postcured disc is shown in Figure 5.

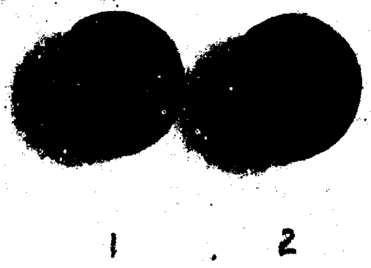


Figure 5. Photograph of exposed faces of a bisected, unreinforced polyphenylene disc cured with 1, 3, 5-benzenetrisulfonyl chloride (resin C2943-65B; 1, postcured to 400°C; 2, postcured to 288°C).

Most of the unreinforced resin pellets were badly cracked and unsuitable for obtaining meaningful compressive strength data. However, the pellet shown in Figure 5 has a compressive strength of 12,600 psi in spite of the cracks it contained. Scratch tests indicated that the cured resin was harder than a cured phenolic.

One of the specimens prepared from a 2:1 mixture of prepolymer and 1, 3, 5-benzenetrisulfonyl chloride was postcured by heating in vacuum to 405°C. A thermogravimetric analysis of the product was performed, and a weight loss of 16.4 percent was observed as it was heated to 850°C (see Figure 6). A similar pellet which was postcured to 400°C in Argon with a standard programmed temperature postcure cycle exhibited the same stability in thermogravimetric analysis (Figure 7). Differential thermal analysis revealed that exothermic decomposition began above 436°C (Figure 8). These results are approximately the same as those obtained for the polyphenylenes cured with p-xylylene glycol.

The preparation of a lacquer in 1, 1, 2, 2-tetrachlorethane was attempted. However, a saturated solution of a 2:1 mixture of the high-melting polyphenylene and benzenetrisulfonyl chloride contained only 0.6g. of solids in 10 ml. Since the solubility was not enhanced by heating the mixture under reflux, attempts to prepare a lacquer in this manner were abandoned.

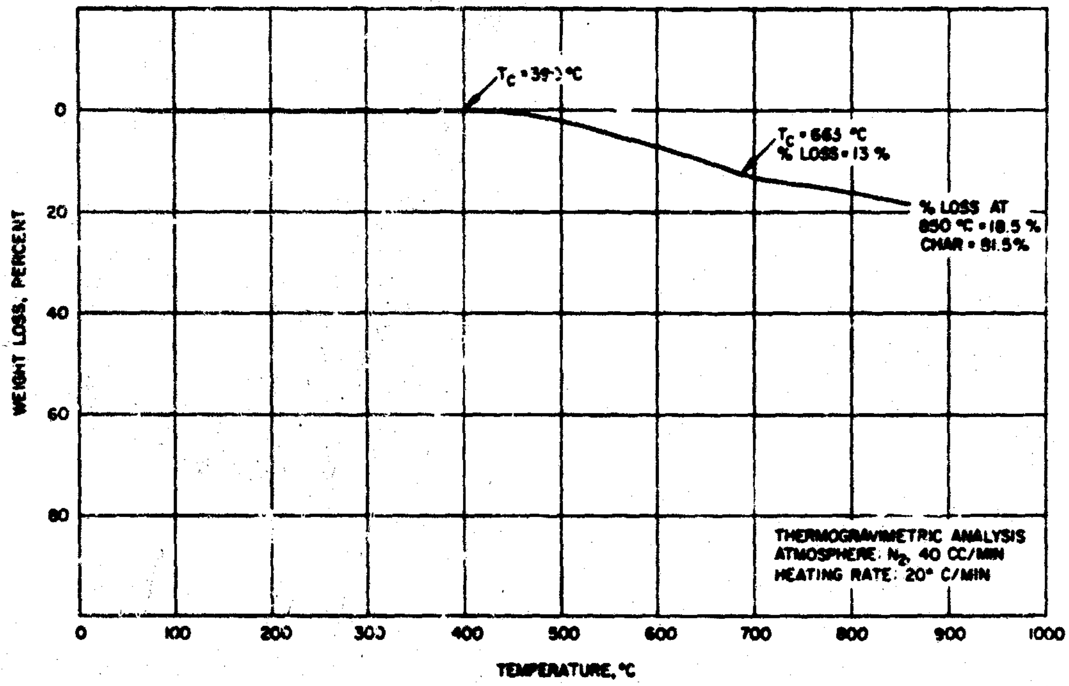


Figure 6. Thermogravimetric analysis of a 1, 3, 5-benzenetrisulfonyl chloride-cured polyphenylene in nitrogen.

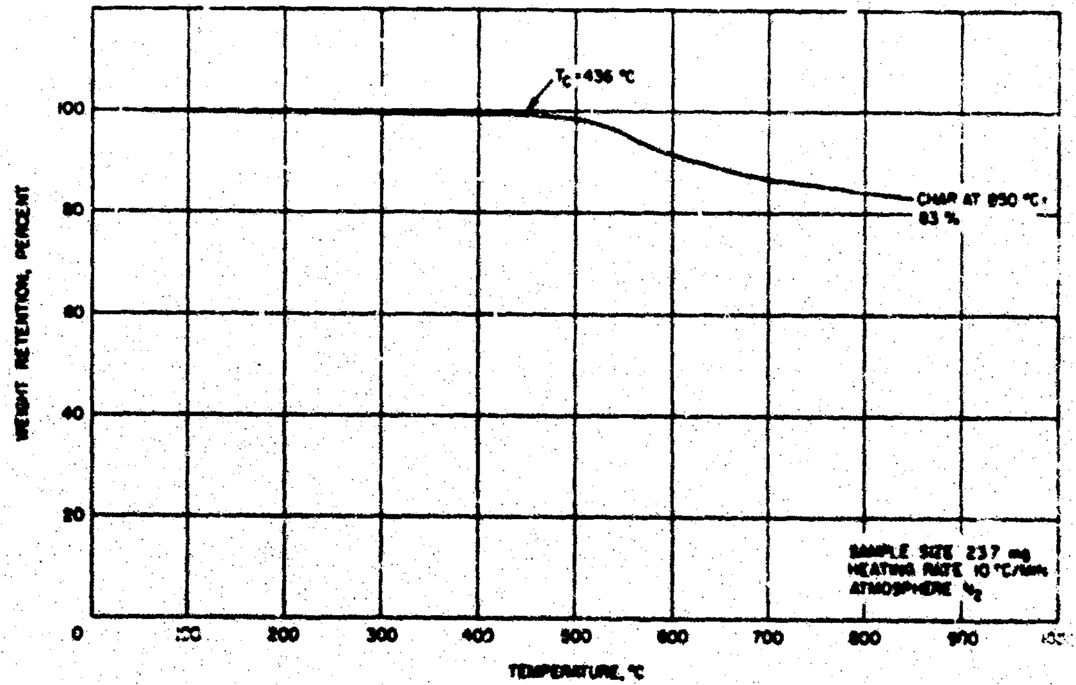


Figure 7. Thermogravimetric analysis of Benzenetrisulfonyl chloride cured polyphenylene (C2943-65B, high m. w.).

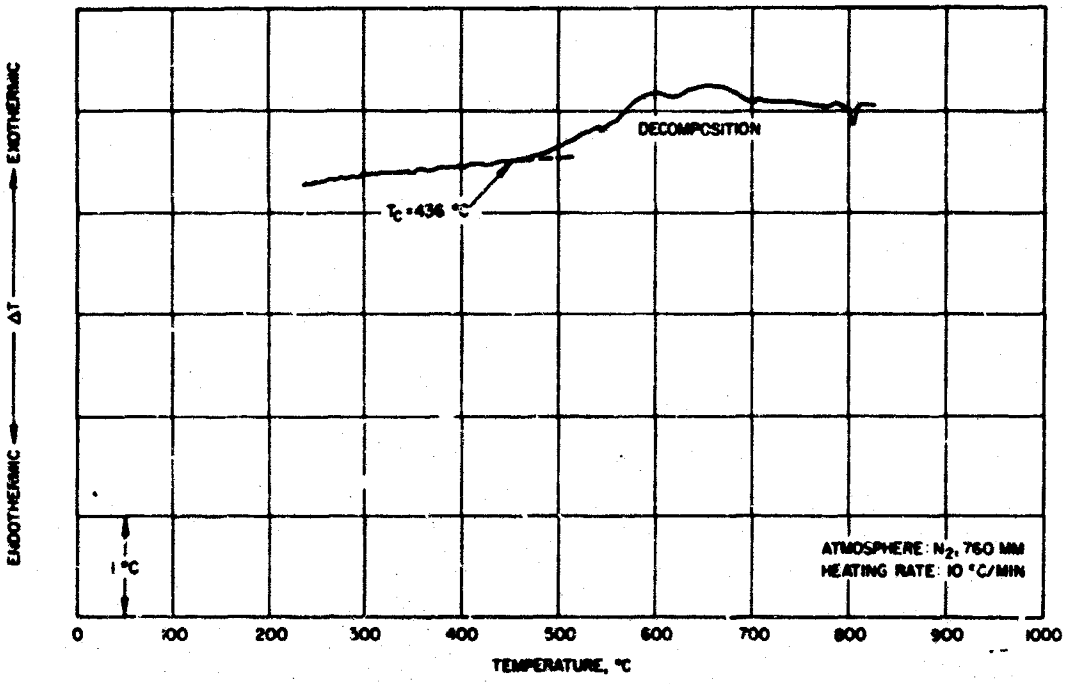


Figure 8. Thermodifferential analysis of Benzenetrisulfonyl chloride-cured polyphenylene (C2943-65B, high m.w.).

Athough satisfactory lacquers could not be prepared from the high molecular weight polyphenylene, stable thermosetting lacquers were readily prepared from the benzenetrisulfonyl chloride and polyphenylenes in the 1000 mean molecular weight range. Chloroform proved to be an excellent solvent for this system. Furthermore, carbon cloth laminates were easily fabricated from these lacquers and were cured readily at about 200°C. It should be noted here that this lower molecular weight polyphenylene fraction is the same as that currently used in the Hughes polyphenylene-xylylene glycol resins. The latter resins also are cured at about 200°C and are also prepared in chloroform solution.

Polyphenylene-benzenetrisulfonyl chloride-chloroform lacquers have been made using polyphenylene : benzenetrisulfonyl chloride weight ratios of 2:1, 3:1, and 4:1. Although the latter two appeared to be comparable in plasma arc tests, the 3:1 ratio appeared to be slightly superior. More extensive testing would be required to substantiate this since the differences were minor.

A thermogravimetric analysis and thermodifferential analysis of the 2:1 resin (C2943-66B) was carried out in nitrogen. In the former test the sample exhibited only 1/2 percent weight loss at 400°C and produced 86 percent char at 900°C; whereas, in the thermal differential analysis the first tract of decomposition was obserbed at 400°C with the maximum rate appearing at 530°C. Results of these analyses are shown in Figures 9 and 10.

Carbon cloth treated with 4,4'-biphenyldisulfonic acid was used in preparing laminates from the high molecular weight polyphenylene and benzenetrisulfonyl chloride. The necessity for this treatment was not established, however. Untreated carbon cloth was satisfactory for use with the lacquers.

The low melting range of the polyphenylene used in the lacquers also provided better flow characteristics during cure. These lacquers represent the most successful products derived from this program.

These studies on the curing of both high molecular weight fractions and low molecular weight fractions of polyphenylene illustrate a principle that is believed to have general application. This principle is that favorable physical properties of a molding compound will usually be more important than the chemical stability which may be derived by employing prepolymers with a high molecular weight at a sacrifice in desirable physical properties. Thus, if one has to choose between a readily soluble prepolymer with an acceptable melting or softening range and a low molecular weight on the one hand and a slightly soluble prepolymer with a relatively high melting or softening range and a high molecular weight on the other, the low molecular weight fraction will be favored to yield superior molded composites. Those resin properties which enable one to prepare dense molded parts are more important to the success of an ablative material than is chemical stability which may be imparted to the cured resin by using prepolymers with a high molecular weight. Inherent in this postulate is the assumption that the difference between the two prepolymer fractions lies only in their molecular weight and the attendant physical properties and not in their fundamental chemical structure. This principle was also borne out by the accumulated experience obtained by Hughes on the curing of polyphenylenes with p-xylylene glycol.

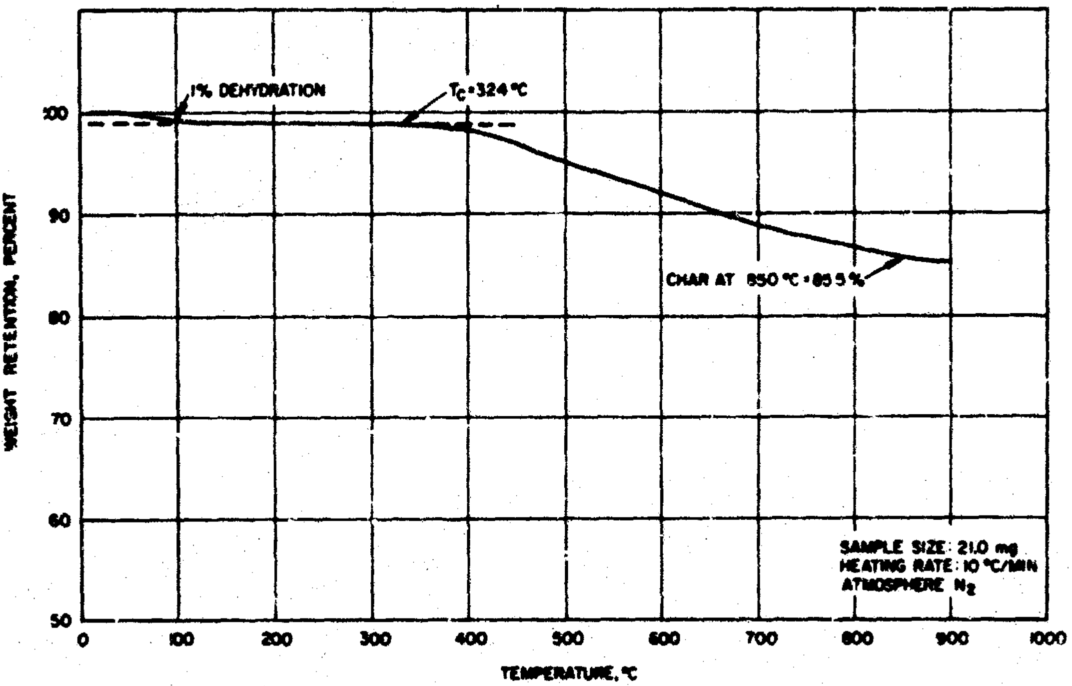


Figure 9. Thermogravimetric analysis of Benzenetrisulfonyl chloride-cured polyphenylene (C2943-66B, low m.w.).

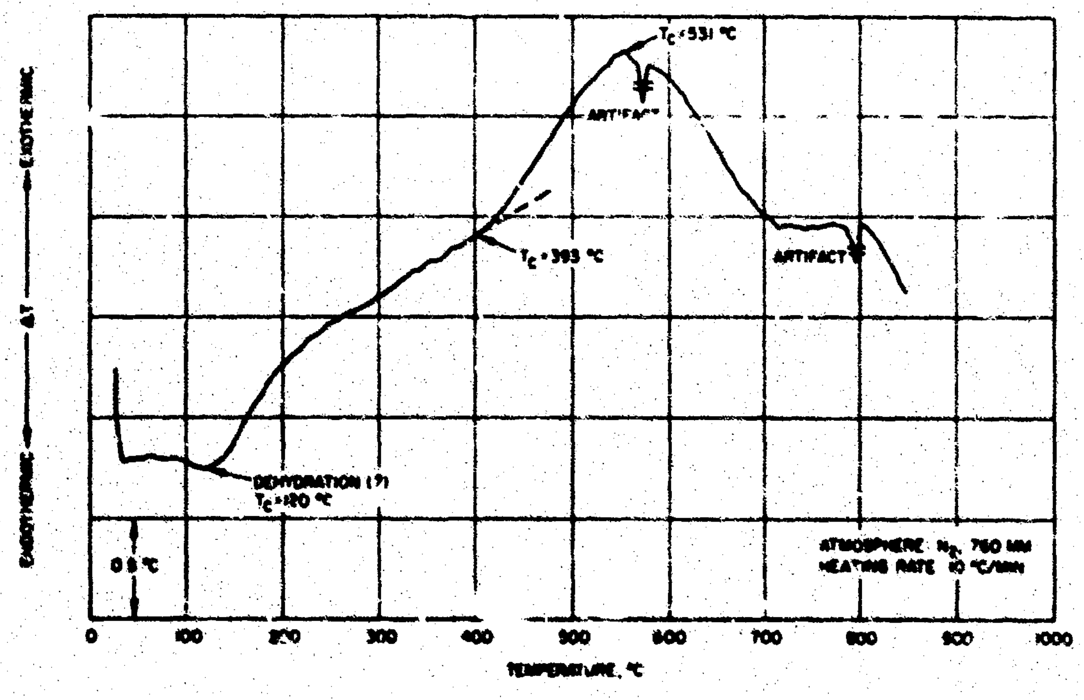


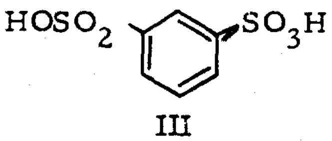
Figure 10. Differential thermal analysis of Benzenetrisulfonyl chloride-cured polyphenylene (C2943-66B, low m.w.).

d. Cures With Mixtures of 4,4'-Biphenyldisulfonic Acid and 1,3,5-Benzenetrisulfonyl Chloride. The use of mixtures of 4,4'-biphenyldisulfonic acid and 1,3,5-benzenetrisulfonyl chloride was also investigated. Experimentation with these mixtures was begun because very little flow occurred in cures with the trisulfonyl chloride, and the polyphenylene-disulfonic acid resins tended to flow more readily than desired. Mixtures with a polyphenylene: biphenyldisulfonic acid; benzenetrisulfonyl chloride weight ratio of 4:2:1 performed best in these experiments.

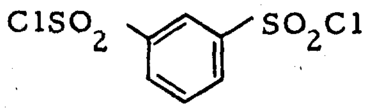
Three unreinforced pellets were prepared from such a molding compound. Two of them were molded after loading the powder into a hot mold and were badly cracked or broken. The third pellet, which was molded after loading the resin into a cold mold, appeared to be intact, but portions of the surface were somewhat friable and too many cracks were present in the interior to allow a meaningful measurement of the compressive strength.

Two carbon cloth-reinforced laminates were also fabricated for plasma arc testing. There was no apparent advantage, however, in the use of a mixture of the two curing agents over the use of each one separately.

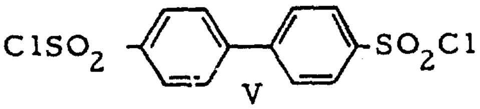
e. Cures With Other Sulfonic Acids and Sulfonyl Chlorides. Polyphenylene cures were also achieved with 1,3-benzenedisulfonic acid (III), 1,3-benzenedisulfonyl chloride (IV), 4,4'-biphenyldisulfonyl chloride (V), and diphenyl ether-4,4'-disulfonyl chloride (VI).



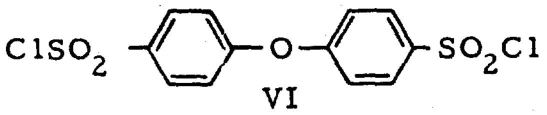
III



IV



V



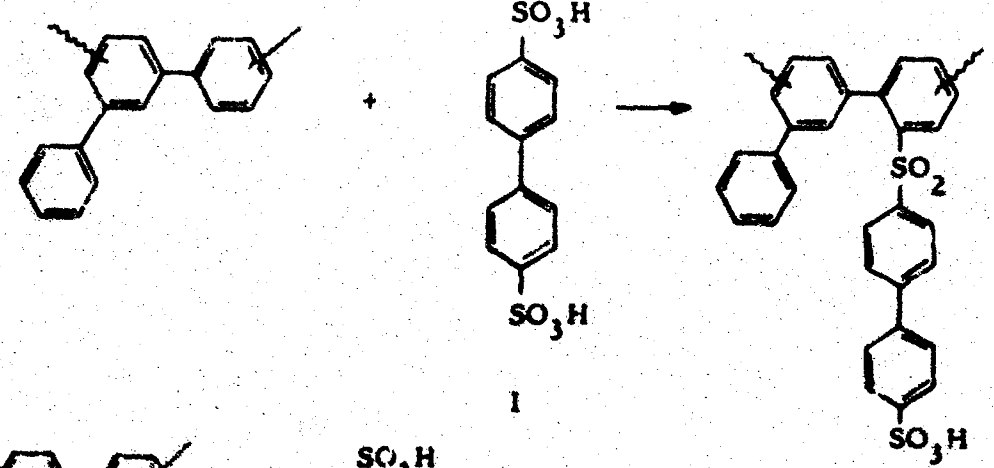
VI

Difficulties were encountered in the initial experiments with each of these curing agents, and consequently their study was given little emphasis.

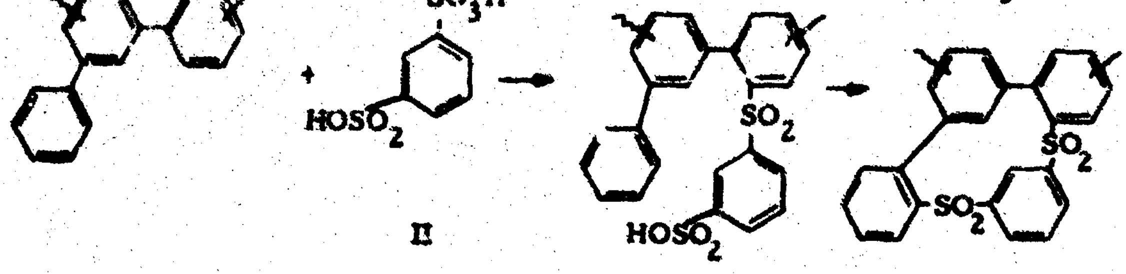
In a previous investigation[1] it was established that 1,3-benzenedisulfonic acid can cure polyphenylenes to a black, infusible product. While a molded pellet prepared during this program was fairly hard initially but after several weeks in contact with air it lost its physical integrity and became friable. The moist appearance that the sample acquired suggested that a considerable number of sulfonic acid groups remained unreacted in the sample and that they slowly absorbed moisture from the air. Almost one-third of the sample volatilized when it was heated in vacuum to 465°C. Since benzenedisulfonic acid did not appear to produce as good a product as biphenyldisulfonic acid, the study was dropped.

Polyphenylene could be cured by heating it with 1,3-benzenedisulfonyl chloride in an open container. When a similar mixture was heated in a mold, however, the product was friable and incompletely cured.

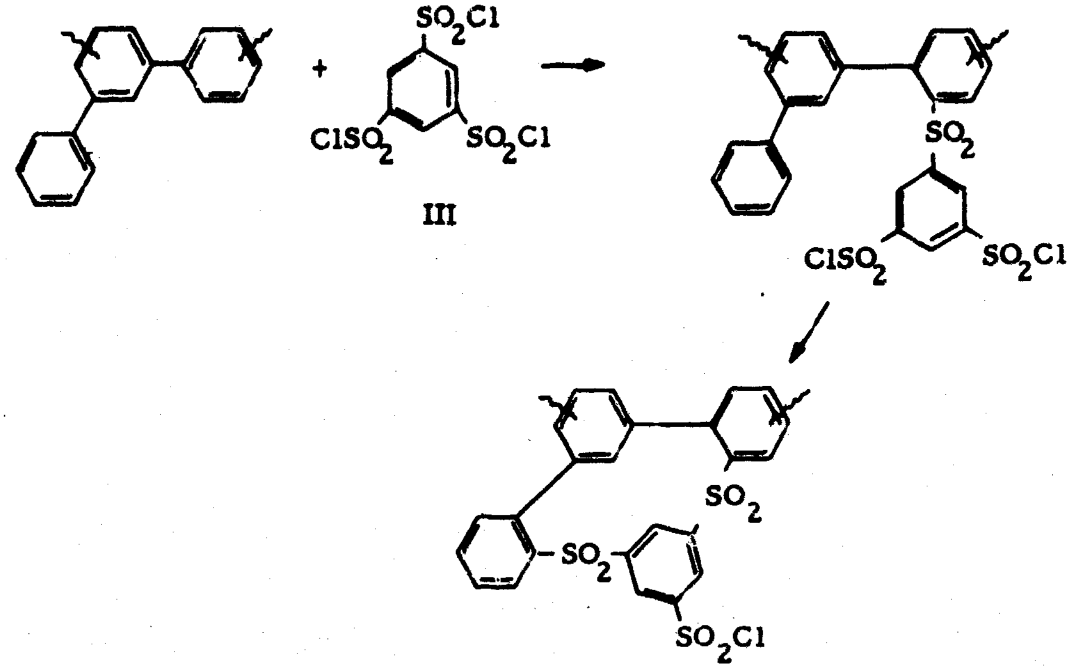
The results indicate that 4,4'-biphenyldisulfonic acid and 1,3,5-benzenetrisulfonyl chloride are superior to 1,3-benzenedisulfonic acid and 1,3-benzenedisulfonyl chloride as curing agents. Steric causes may be involved and can be discussed with reference to the following equations.



I



II



When 4,4'-biphenyldisulfonic acid (I) reacts with a polyphenylene molecule, the initial product will have a sulfonic acid group at a site which is remote from the original polyphenylene chain. The very remoteness of this group promotes its chances of reacting with a second polyphenylene molecule resulting in chain extension or cure. By contrast, when 1,3-benzenedisulfonic acid (II) or the corresponding disulfonyl chloride reacts with a polyphenylene molecule, the remaining reactive group is held relatively close to the original polyphenylene chain where it is in an excellent position for an intramolecular reaction with no increase in the molecular weight. The initial reaction product of polyphenylene and 1,3,5-benzenetrisulfonyl chloride (III) can also undergo the intramolecular reaction, but in this case a third reactive substituent remains, now directed away from the original chain, so that an intermolecular crosslinking reaction becomes favored. Other intramolecular or cyclizing reactions are possible in each case, but these are adequate to compare qualitatively the probability of intramolecular reactions.

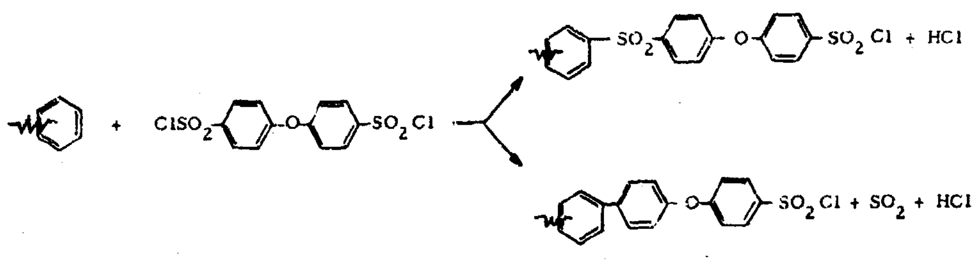
An attempt to cure polyphenylene with commercial 4,4'-biphenyldisulfonyl chloride was unsuccessful. The commercial product melted at 140-145°C, however, much lower than the literature values[8] (201°, 209-210°, and 211°C). An attempt was made to recrystallize this material from toluene, but the very small portion which was soluble in toluene and could be isolated in this manner melted at 95-165°C. The failure of this disulfonyl chloride to cure polyphenylene can therefore be ascribed to its very low degree of purity. High purity 4,4'-biphenyldisulfonyl chloride (m.p. 208°C) was synthesized from the acid and phosphorus pentachloride. It cured polyphenylene within 5-10 minutes when a mixture was heated in an open container. No attempt was made to cure the mixture in a mold.

Diphenyl ether-4,4'-disulfonyl chloride, which had been used previously with somewhat ambiguous results[2], was re-examined as a curing agent. The anticipated reaction is given by the following equation:

A 1:1 mixture by weight with polyphenylene was advanced by heating in an open container for 40 minutes at 180°C. The resulting mixture, which had a consistency suitable for molding, melted partially at 145°C and cured to a hard solid between 225° and 260°C in an open container. In a mold, however, a similar mixture remained fluid at 310°C and failed to cure. A 2:1 mixture of polyphenylene and curing agent remained uncured after 4 hours at 400°C in a mold. Claims have been made in the patent literature[7c,8] that reactions between sulfonyl chlorides and hydrocarbons are catalyzed by a wide variety of compounds, with cuprous chloride in particular being recommended. As a consequence, 2:1 mixtures by weight were combined with 0.2 part and with 0.04 part of cuprous chloride by weight and heated in a mold to 400°C. There was no apparent improvement.

No explanation can be offered for the failure to cure in a mold, especially in view of the exceedingly rapid reaction which was obtained with benzenetrisulfonyl chloride. Electron withdrawing substituents on the aromatic sulfonyl chloride may accelerate the curing reaction, and, if so, the benzenetrisulfonyl chloride would react more rapidly than diphenyl ether disulfonyl chloride. However, the difficulty in obtaining a cure seems to be uniquely associated with conducting the reaction in a mold under pressure.

Kinetic Studies. To understand better the mechanism of the polyphenylene-sulfonyl chloride reactions and to permit more rigorous control of these reactions, several experiments were carried out in solution using different reaction temperatures (210° and 246°C) and different catalysts, namely, aluminum chloride, cuprous chloride, and nickelous acetate. Di-tert.-butyl peroxide was also evaluated but at only 130°C. This limit was imposed because of the excessively high cleavage rate of the peroxide at higher temperatures. The peroxide proved to have virtually no catalytic effect. The reaction studied is illustrated below.



Reactions were carried out in boiling trichlorobenzene (at 210°C) or boiling tetrachlorobenzene (at 246°C). At both temperatures aluminum chloride induced the most rapid reaction and at both temperatures reactions which were catalyzed by cuprous chloride were not significantly faster than the uncatalyzed reactions. Cuprous chloride thus appeared to be rather ineffective. Its relative ineffectiveness in these experiments is in agreement with separate curing experiments carried out independently. Because this catalyst is expected to induce free radical reaction processes, however, it is quite possible that impurities are present in the polymer catalyst or disulfonyl chloride which act as radical chain terminators, thus inhibiting potential catalytic effects. Further work on cuprous chloride catalysis thus is warranted.

The most important observation made during these tests was that with aluminum chloride virtually three times as much acidic vapor was ultimately released at 246°C than at 210°C. This is attributed to the release of almost stoichiometric amounts of both sulfur dioxide and hydrogen chloride at the higher temperature and almost exclusively hydrogen chloride at the lower temperature. Apparently the reaction mechanism changes significantly within this relatively small temperature range (210-246°C), at least with the aluminum chloride catalyst. The presence of sulfur dioxide in the effluent gas stream was verified by precipitating it as barium sulfite. When the sulfite was precipitated at 80°C and collected by filtration its weight after drying corresponded to that indicated by the titration of effluent gases with sodium hydroxide solution.

Treated polymers were isolated from the reaction mixtures but their molding characteristics were not studied. Graphs illustrating the rates of these reactions are presented in Figures 11 and 12. The extent of reaction shown in these graphs was determined by titrating effluent gases with standard alkali and comparing the equivalents of evolved acid with the theoretical amount of hydrogen chloride expected. When sulfur dioxide is evolved the figures thus indicate greater than 100 percent reaction. The maximum extent of reaction is 300 percent because two equivalents (1 mole) of sulfur dioxide can be released for each mole or equivalent of hydrogen chloride.

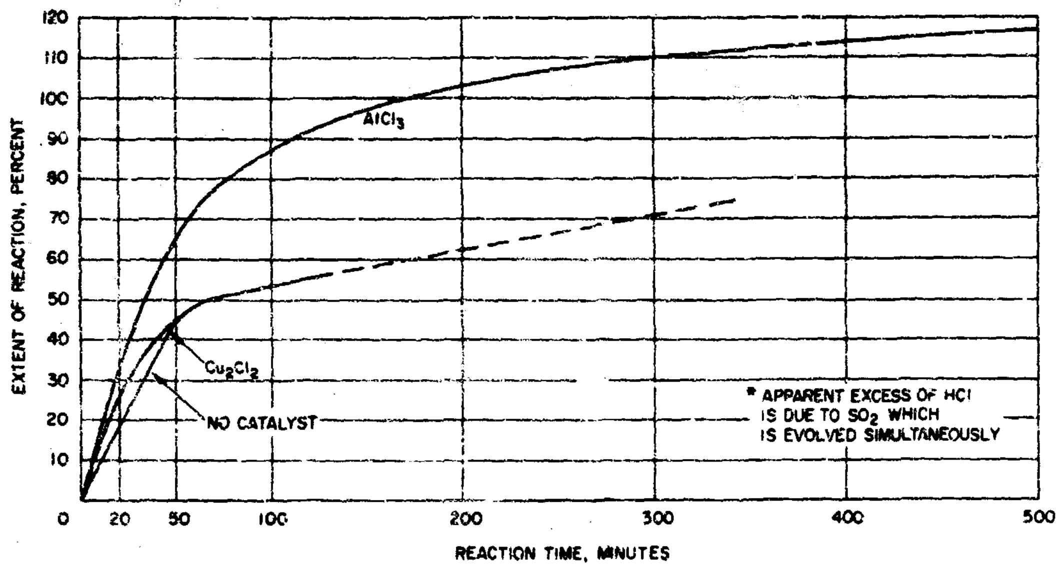


Figure 11. Rate of HCl evolution from catalyzed polyphenylene 4,4'-diphenyl ether disulfonyl chloride mixtures in trichlorobenzene at 210°C.

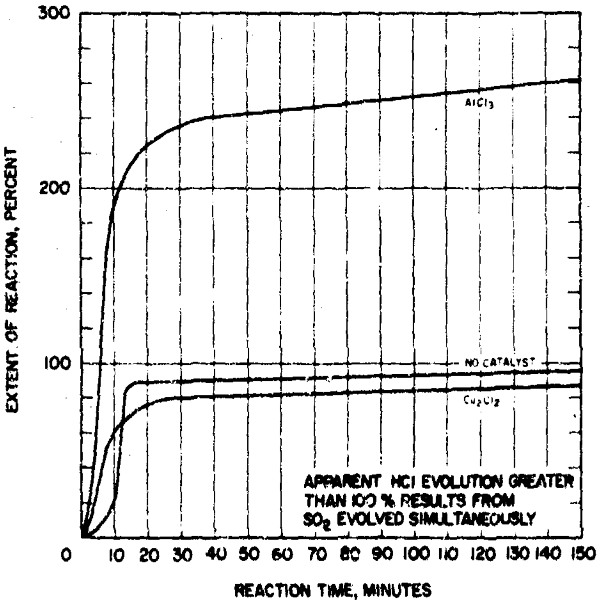
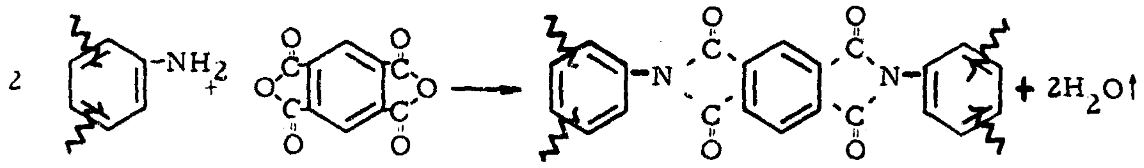


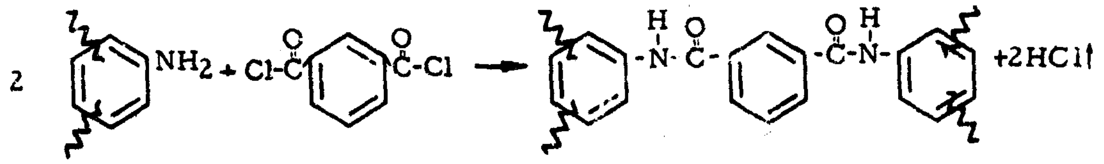
Figure 12. Rate of HCl evolution from catalyzed polyphenylene 4,4'-diphenyl ether disulfonyl chloride mixtures in tetrachlorobenzene at 246°C.

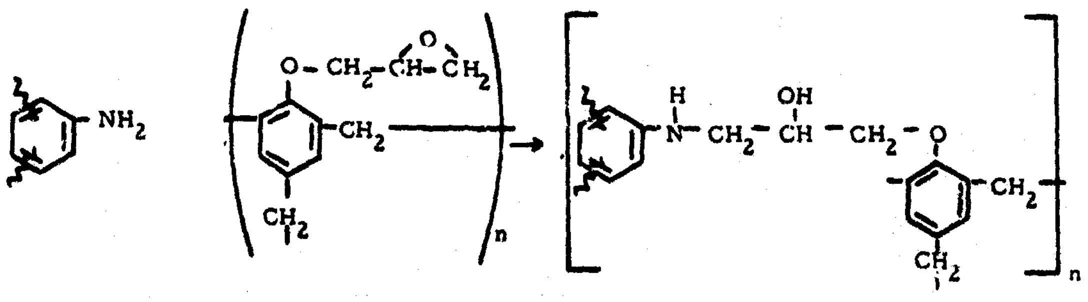
2. Cures via Aminated Polyphenylenes

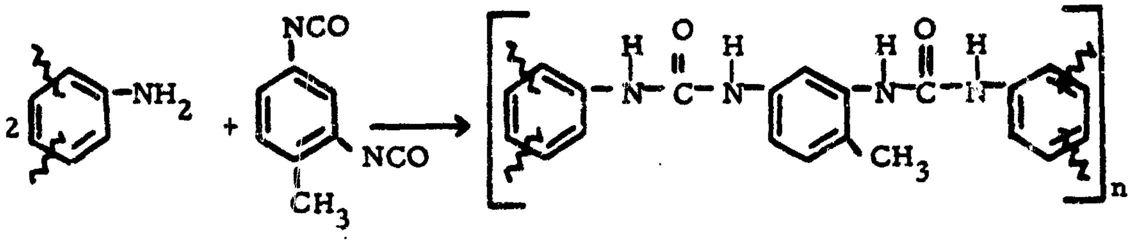
An investigation of methods of nitrating and subsequently aminating polyphenylene was undertaken because it was anticipated that such products could be cured by a variety of techniques. One of these techniques involved cures by pyromellitic dianhydride via the formation of pyromellitimide bridges. Such a cure process may be illustrated as follows:



Furthermore, cures could also be expected to occur with isophthaloyl or terephthaloyl chloride via the formation of amide bridges or with epoxyphenolics or diisocyanates. Each of these three processes is illustrated below:







Of the four cure processes described, the pyromellitic dianhydride process would be expected to yield the most stable resins by far. The only apparent disadvantage of such a process, although probably of minor importance, would be attributed to the evolution of traces of water during cure and postcure. A corresponding disadvantage would be encountered with phthaloyl chloride cures except that in this case hydrogen chloride would be evolved. Addition type cure processes, such as those which would occur with epoxyphenolics or diisocyanates, liberate no gaseous products during cure, however, the thermal stability of such resins would certainly be inferior to that of the resins previously described. Such addition type resins, however, could still have excellent ablative characteristics.

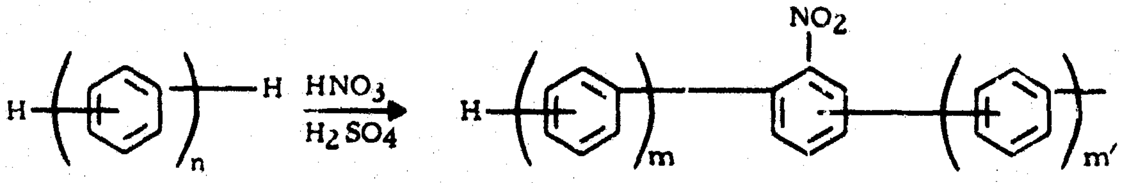
The goal of preparing useful aminated polyphenylenes was not achieved. It was no problem developing procedures for making nitrated polyphenylene suitable for reduction, but almost invariably the initially fusible polyphenylenes lost their fusibility and solubility characteristics during the nitration process. Furthermore, as a result of their loss of solubility it became impossible to purify either the nitrated polymer or the aminated polymer obtained by reduction thereof.

Since it was the specific objective of this program to develop cure processes for fusible polyphenylenes in the 2,000 to 3,000 mean molecular weight range, such polymers were used almost exclusively in these nitration studies. These polyphenylenes generally melt within a 250-350°C temperature range and consequently any increase in their melting points resulting from nitro group substitution tends to raise this range to over 400°C and yields virtually intractable materials. Even a nitration carried out on a polyphenylene in the 1200-1400 mean molecular weight range (m.p. 170°-200°C) produced intractable nitrated polymer. The only case in which a fusible nitrated polymer was obtained was in a reaction utilizing a polyphenylene of about 500 $\overline{M_n}$. In this case an oily product was isolated.

Two types of nitrating agents were used in these studies. One was red fuming nitric acid and the other was a mixture of concentrated sulfuric acid and concentrated nitric acid. In the various reactions the reaction periods ranged from 10 minutes to 3 hours and temperatures ranged from -50°C to 40°C. Because the higher temperatures and longer reaction periods proved to be excessive as indicated by the intractability of the products, shorter reaction times and lower temperatures subsequently were studied. In a reaction carried out at -25°C for 20 minutes only 17% of the rings were nitrated but even this product was largely intractable. Further lowering of reaction temperature to -45°C ultimately yielded a fusible nitrated polymer, but it was found to have only 2.3% of its rings nitrated and this was not considered adequate for further study. A table of these reactions is shown on the following page.

From an examination of these results it is apparent that with nitric acid sulfuric acid mixtures there is very little sulfonation and that it is negligible at temperatures below 40°C. It should be noted that the term intractable is applied to resins which fail to melt completely below 400°C. Whether complete melting would occur above this temperature was not established.

The first three reactions in Table II were carried out with varying order-of-addition but in most of the experiments which were carried out subsequently the polyphenylene powder was added to a pre-cooled mixture of the acids. No apparant advantage was achieved in using fuming nitric acid as compared to the mixed acids. An illustration of a typical nitration is presented as follows:



Experiment	Nitrating Agent	Reaction Period	Temperature Range °C	Approximate Percent Weight Increase	Melting Range °C	Percent Rings Nitrated Based On Weight Gain	Percent N	Percent N as NO_2	Percent Rings Nitrated Based On Percent NO_2	% S	% S as $-SO_3H$
C2426-6A	A	>2 hours	65°C	-			3.10	10.19	19	1.14	2.88
C2426-7B	A	2 hours	10-20°	13	>375		4.49	14.75	28	0.13	0.46
C2426-7C	B		5-45°	10	>400		5.92	19.45	40	0.34	0.86
C2426-10A*	B	3 hours	30 - 40	42	>400	68	8.84	29	66		
C2426-10B**	B	2 hours	≈10	-	90 - 130	-	10.11	33.2	80		
C2426-10D	B	15 minutes	10 - 36	26	234 - >400	41	4.44	14.6	28		
C2426-11A	B	30 minutes	20 - 40	24	229 - >400	39					
C2426-11C	B	10 minutes	5 - 15	15	295 - >400	25	3.46	11.4	20		
C2943-18-4	B	20 minutes	-45 ±5°C	-	255 - 303	-	0.42	1.4	2.3		
C2943-18-2	C	10 minutes	0 - 10	23	247 to >400	38					
C2943-18-1	C	30 minutes	0 - 10	33	240 to >400	55					
C2943-18-3	C	60 minutes	0 - 10	38	255 to >400	62					
C2943-19-5	B	20 minutes	-25 ±5°C		242 to 400		2.93	9.63	17		

*Polyphenylene used in this experiment had a $\overline{M.W.}$ of about 1200 - 1400.

**Polyphenylene used in this experiment had a $\overline{M.W.}$ <500.

A = 1 volume HNO_3 + 2 volumes H_2SO_4.

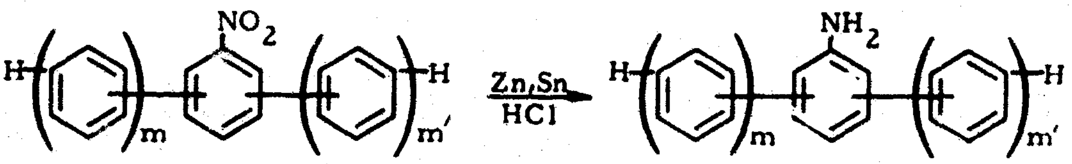
B = 1 volume HNO_3 + 1 volume H_2SO_4.

C = Red fuming HNO_3.

Table II. Nitrations of polyphenylene.

Generally it was difficult to isolate the nitrated polymers from the acid media by simple filtration because they became colloidally dispersed. It was found, however, that centrifugation was a highly satisfactory separation technique. After the initial separation polymers were washed several times with aqueous hydrochloric acid and again separated by centrifugation. Without hydrochloric acid in the wash water even centrifugation proved to be an unsatisfactory wash technique.

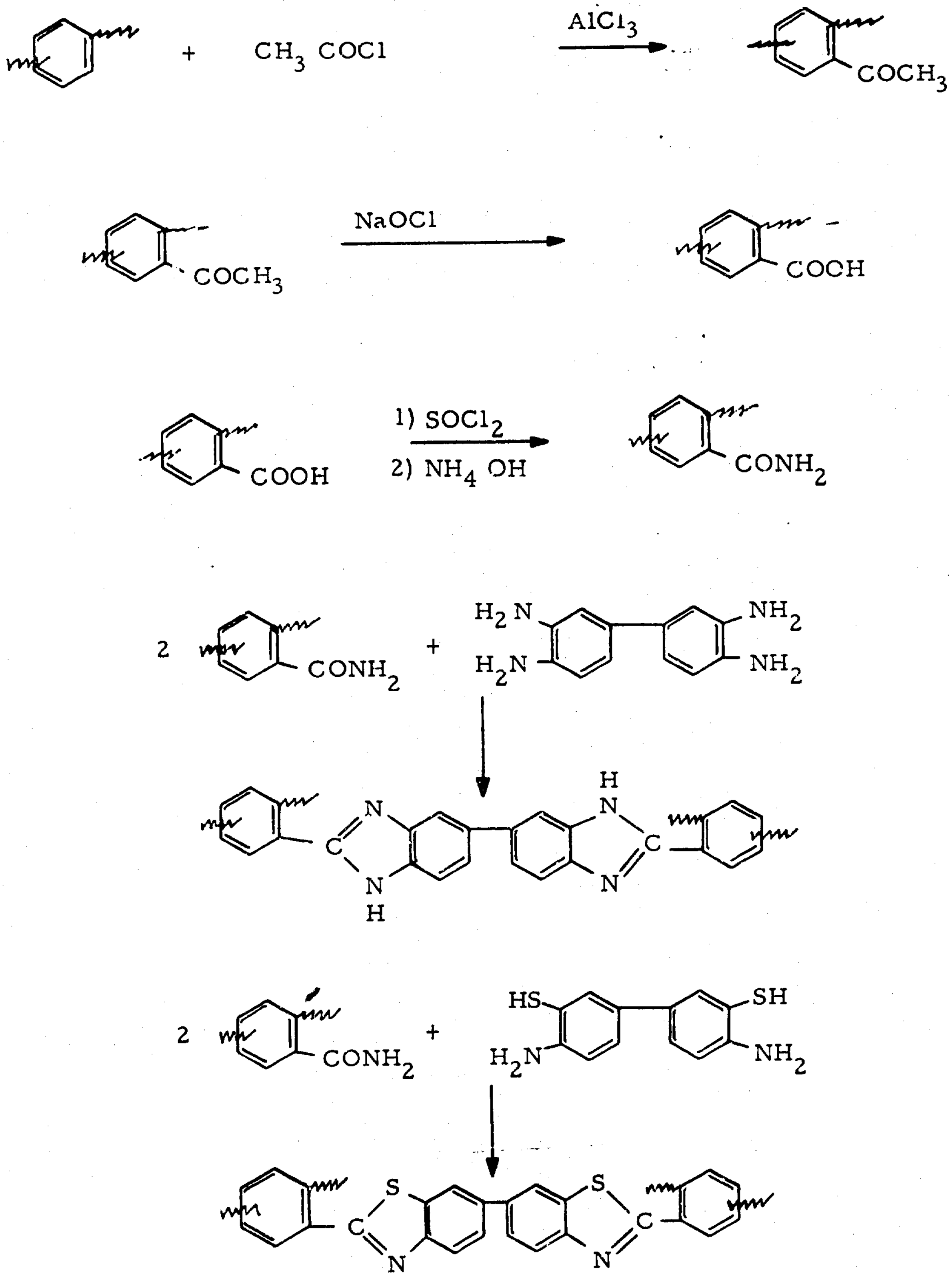
The colloidal character of the nitrated polymer suggested that reduction to aminated polymer might well be accomplished prior to separation of the resin from the acid. A sample of nitrated polymer was thus prepared and after dilution with water an effort was made to reduce it with a mixture of zinc and tin. Additional acid (hydrochloric) was also added to this reaction mixture. The proposed reduction is illustrated below:



After reduction and after isolation of the dried aminated polymer an effort was made to separate the fusible portion of the polyphenylene via continuous extraction with boiling chlorobenzene and trichlorobenzene. With the chlorobenzene 25% of the polymer was found to be extractable. No additional product was obtained with the higher temperature trichlorobenzene extraction. No further effort was made to prepare aminated polymer because no suitable nitrated polymer could be obtained.

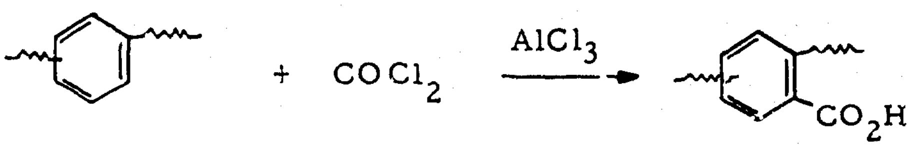
3. Benzimidazole and Benzothiazole Cures

Another process which was investigated for curing polyphenylenes involved the conversion of the polymer into a carboxylated intermediate which could be subsequently amidified or esterified. It was anticipated that either the amide or the phenyl ester could be cured with tetraaminobiphenyl or diaminobiphenyldithiol via the formation of benzimidazole or benzothiazole bridges respectively. These curing processes, as well as the synthesis leading to the amidified polyphenylene are illustrated below:


+
CH_3COCl
$AlCl_3$
$COCH_3$
NaOCl
$COCH_3$
COOH
COOH
1) $SOCl_2$
2) NH_4OH
$CONH_2$
2
$CONH_2$
+
H_2N
H_2N
NH_2
NH_2
N
C
N
H
H
N
C
N
2
$CONH_2$
+
HS
H_2N
SH
NH_2
S
C
N
S
C
N

Conversion of the carboxylated polyphenylene into the corresponding phenyl ester could be accomplished by treating the intermediate acid chlorides with phenol rather than with ammonium hydroxide. A disadvantage of using the phenyl esters as intermediates is that phenol would be liberated during the cure process instead of ammonia such as is liberated from the amides. Phenol, being a large molecule compared to ammonia, thus would contribute to a greater post-cure weight loss. Although the esters were not synthesized and evaluated, they could have a major advantage over the amides since they are likely to be fusible whereas none of the amides synthesized were fusible and consequently were not suitable for molding compounds.

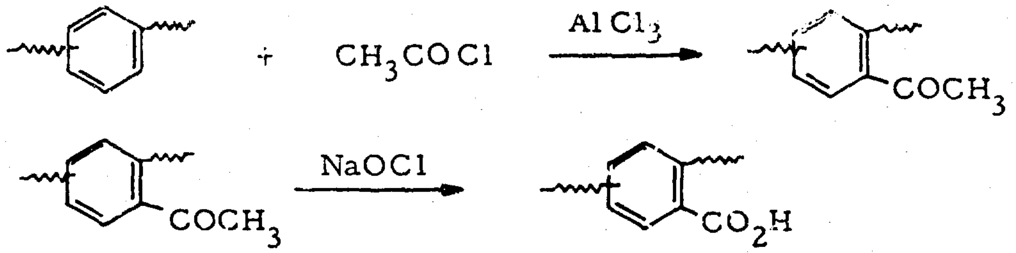
One method which was considered for the preparation of carboxylated polyphenylene was the Friedel-Crafts reaction of phosgene with the polymer as illustrated below.



At first the procedure used by Rueggeberg, Frantz and Ginsburg[9] for the synthesis of benzoic acid from benzene was followed. One sample of high molecular weight polyphenylene (≈ 2000 M_n), suspended in trichlorobenzene, was treated with two moles of liquid phosgene and one mole of aluminum chloride per phenylene ring. The mixture was kept in an ice bath for 17 hours and then at room temperature for 8 hours using a dry ice cooled condenser to keep the phosgene in the reaction mixture. The phosgene was then allowed to distill out of the mixture overnight and the remainder was poured onto ice and hydrochloric acid. The resultant polyphenylene was filtered off and suspended in boiling water to steam distill any adhering trichlorobenzene. The aqueous suspension was made about 2N in NaOH and was heated 30 minutes to dissolve carboxylated material. After filtering, the filtrate was acidified with hydrochloric acid, but no solid separated.

Another phosgene-aluminum chloride reaction was then carried out at a higher temperature. The same relative quantities of reactants were heated this time at 60 to 70°C for 7 to 8 hours, after which the phosgene was allowed to distill from the reaction mixture. This mixture was worked up as in the first run and yielded some white alkali-soluble, acid-insoluble polymer which appeared to be a carboxylated degradation product of the starting polyphenylene, since it melted over the range 126 to 149°C. There was also a generous amount of the original polyphenylene resin recovered. On the basis of these results it was concluded that the reaction with phosgene would not give the desired product under these experimental conditions, and that the use of more rigorous conditions would probably lead to a higher degree of polymer decomposition.

The second method examined for the preparation of carboxylated polyphenylene involved the two-step reaction shown in the following equations:



The first step was carried out by mixing the high molecular weight polyphenylene (M_n = 2000) with acetyl chloride and aluminum chloride in trichlorobenzene and heating at 60 to 70°C with stirring for several hours. The proportion of acetyl chloride per phenylene ring used in the reactions varied from 0.2 mole per ring to 0.4 mole per ring, depending upon the amount of acetylation desired. After hydrolysis with ice and hydrochloric acid, reaction mixtures were boiled to steam-distill the organic solvent and the acetylated polymers were collected by filtration. To remove any aluminum salts the solids were extracted twice with boiling concentrated hydrochloric acid and were washed thoroughly with water until the wash liquid was no longer acidic. When these products were dried in air, the yields appeared to be greater than theoretical, which is an 11.1 percent increase in weight for one acetyl group on 20 percent of the phenylene rings, and 22.1 percent increase in weight for one acetyl group on 40 percent of the phenylene rings. It developed that the trichlorobenzene could not be removed completely by steam distillation. When the product of the last acetylation reaction was heated at 100°C under vacuum, the increase in weight dropped from an apparent 62 percent to 17.4 percent, which is slightly below the theoretical increase of 22.1 percent.

An elemental analysis of this acetylated product showed the following composition:

Carbon	78.47 percent
Hydrogen	4.01 percent
Chlorine	9.06 percent
Ash	1.63 percent

The high chlorine content was rather surprising. It could arise from the presence of 1, 2, 4-trichlorobenzene retained by the product or from reaction of this solvent with the polyphenylene in the presence of aluminum chloride during the acetylation. To check on the first possibility, a small sample of the product was heated at 150°C at 1 to 2 torr for 22 hours; it lost 7.13 percent in weight. If this were all trichlorobenzene, the acetylated polyphenylene would have the following calculated composition:

Carbon	81.45 percent
Hydrogen	4.19 percent
Chlorine	5.25 percent
Ash	1.76 percent

This chlorine content is still quite high; however, about 2-3 percent of the chlorine can be attributed to the starting polymer which generally contains this amount.

The acetylated products were examined by infrared spectrometry. Resins were incorporated into potassium bromide pellets for this purpose. Spectra of the 20 percent acetylated polyphenylene and the 40 percent acetylated polyphenylene were very similar. Both showed carbonyl group absorption at 5.99 microns. Benzoyl groups, which are structurally similar, are reported to absorb at 5.88 to 5.95 microns.

The 20 percent acetylated polyphenylene melted partially from 317° to about 365°C, but then resolidified, and there was no further melting up to 400°C. The 40 percent acetylated polyphenylene did not melt up to 400°C, but turned balck and shrank when it was heated slowly on a melting point block; however, when placed directly on the melting point block at temperatures above 320°C, it partially liquified and resolidified very quickly while changing from brown to black.

Oxidation of the acetylated polyphenylene was attempted with four reagents — sodium hypobromite, sodium hypochlorite, sodium dichromate, and alkaline potassium permanganate. Oxidation with dichromate must be carried out carefully, since this reagent has been used to characterize para-polyphenylene by oxidation to terephthalic acid. Such an oxidation of phenylene rings in the polymer can be accomplished by alkaline permanganate also. The other two reagents, sodium hypobromite and sodium hypochlorite, are used specifically to oxidize methyl ketones to carboxylic acids.

The first oxidation with sodium dichromate was carried out on a 40 percent acetylated polyphenylene in refluxing glacial acetic acid for 25 hours. The reaction mixture was then poured into water and the insoluble brown oxidized polymer was filtered from the green solution. This solid was extracted with sodium hydroxide solution, and the extract was acidified, yielding about 18 percent of the theoretical amount amount of carboxylated produce. On repeating the reaction a 21 percent yield was obtained.

Another oxidation with sodium dichromate was carried out in refluxing acetic acid (90 percent) for a much shorter time, 4 hours. This This reaction mixture was worked up in the same way, but this time less than 1 percent of base-soluble, acid-insoluble carboxylated polymer was obtained. This reaction period is evidently much too short.

An oxidation of the 40 percent acetylated polyphenylene with potassium permanganate in aqueous sodium hydroxide was carried out by heating at 95 to 100°C for 40 hours. In this case about 2 percent of the theoretical yield of base-soluble, acid-insoluble material was obtained.

The oxidation with sodium hypobromite solution was carried out according to the procedure used by May and Mosettig[10] to oxidize an acetylated anthracene derivative. The 20 percent acetylated polyphenylene was stirred with a solution of bromine in aqueous sodium hydroxide solution plus pyridine for 16 hours at room temperature. After filtering off the insoluble material and acidifying, a negligible yield of product was obtained. The oxidation was then repeated in the presence of chloroform both at room temperature for several days and at reflux temperature (58°C) for 2-1/2 days. Neither time was any product obtained. However, this may be due to the presence of ethanol in the chloroform, which would react quickly with the sodium hypobromite reagent and destroy it.

Sodium hypobromite oxidation thus was attempted again using aqueous pyridine as the solvent but using a 40 percent acetylated polymer. In this case the reaction was carried out at 70-75°C for 22 hours and after isolating the alkali soluble - acid insoluble polymer fraction a 26 percent yield of carboxylated polyphenylene was obtained. This yield is essentially equivalent to that obtained in subsequent experiments with sodium hypochlorite.

Oxidation with sodium hypochlorite was also tried. The hypochlorite reagent was prepared by passing chlorine gas into sodium hydroxide solution until the desired amount had been absorbed. In the first run, the 20 percent acetylated polyphenylene was added to the hypochlorite solution without any organic solvent, and the mixture was stirred at 60 to 65°C for 24 hours. After working up the mixture in the usual way, an insignificant amount of product was obtained. A second run was carried out with pyridine added as solvent. After 25 hours at 70 to 80°C, the reaction mixture was worked up, yielding about 8 percent of the theoretical yield of base-soluble, acid-insoluble carboxylated polyphenylene. The third run was similar to the second, except that the 40 percent acetylated polyphenylene was used as substrate and the reaction time was extended to 40 hours at the same temperature (70 to 75°C). In this case a 21 percent yield of carboxylated product was obtained. Higher temperature oxidations carried out for even longer times thus appeared to warrant study.

An oxidation of the 40 percent acetylated polyphenylene by sodium hypochlorite was carried out at a higher temperature than was used previously. The reaction was carried out for 45 hours in refluxing pyridine (96°C), and a yield of 62 percent of carboxylated polyphenylene was obtained. This oxidation was then repeated on a scale six times as great, but the yield obtained this time was only 34 percent. The inconsistency of the reaction was further shown when an oxidation of a sample of 20 percent acetylated polyphenylene, by the method used to give the best yield with the 40 percent acetylated polyphenylene, gave only a 14 percent yield of product, and a second run with the 20 percent acetylated polyphenylene gave a negligible yield.

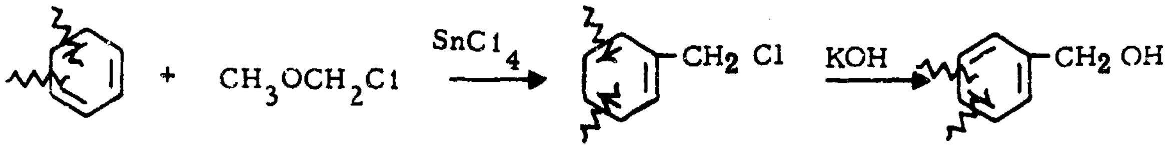
The next step in the amide synthesis was carried out on carboxylated polyphenylene which had been derived from 40 percent acetylated polyphenylene. The carboxylated polymer was heated at reflux with an excess of thionyl chloride for 2 hours. After the reaction mixture was poured into cold concentrated ammonium hydroxide, the solid product (amide) was collected by filtration and washed with water until all the excess base was removed. It was then dried thoroughly.

To determine the feasibility of curing the amide with diaminobenzidine a mixture of these two materials was heated at 250°C under nitrogen. Ammonia was readily evolved demonstrating that interaction had occurred. The resulting product, however, was a powdery solid which did not melt below 400°C and which thus did not appear to be useful as a molding compound. A more extensive evaluation of this latter reaction would of course be highly desirable.

4. Methylene Crosslinks. Hydroxymethylation of Polyphenylene

A series of experiments was conducted aimed at modification of polyphenylene molecules in such a way that the resin would cure with only one methylene group per crosslink rather than two which are formed when the standard xylylene glycol-based curing agent is used. All experiments involved an initial chloromethylation step followed by hydrolysis with alkali to convert the initial product to a hydroxymethylated derivative. All experiments were carried out as after-treatments on various molecular weight fractions of polyphenylene, and no direct syntheses of chloromethylated polyphenylenes were undertaken. Two basic methods of chloromethylation were tried.

The first method used was that of Cambron[11] employing formaldehyde and hydrochloric acid. This method was ineffective, giving only marginal substitution even with highly soluble, low molecular weight polyphenylene resin. The second method employed chloromethyl methyl ether with stannic chloride catalyst similar to a procedure by Fuson, et al,[12] but using trichloroethylene as solvent in anhydrous systems. The chloromethyl methyl ether-stannic chloride procedure did yield chloromethylated polyphenylenes with quite significant degrees of substitution based on observed increase in weight and on the presence of OH absorption in the infrared spectra of hydrolyzed derivatives. The reaction is illustrated as follows:



The reaction products were not homogeneous in composition. It is not known whether the products varied in solubility because of molecular weight distribution or because of variation in degree of substitution. Based on the only clear evidence at hand, infrared spectra, it is believed that the acetone-soluble fraction of the product was both lower in molecular weight and more highly substituted than the acetone-insoluble fraction.

B. EXPERIMENTAL

1. Sulfone Crosslinks and Phenylene Crosslinks

a. Starting Materials

The sources and grades of the commercial products tested as crosslinking agents were as follows:

4,4'-biphenyldisulfonic acid — Eastman practical grade (90 percent)

1, 3, 5-benzenetrisulfonyl chloride – Eastman "white label." Also, Hughes synthesized.

1, 3-benzenedisulfonic acid – Eastman technical grade (m-benzenedisulfonic acid)

1, 3-benzenedisulfonyl chloride – K & K Laboratories

4, 4'-biphenyldisulfonyl chloride – Gallard-Schiesinger Chemical Mfg. Corp. Also, Hughes synthesized.

Synthesis of Diphenyl Ether 4, 4'-disulfonyl Chloride (D1516-15)

Chlorosulfonic acid (587g, 5.04 moles) was added dropwise with constant stirring to a cold solution of phenyl ether (118g, 0.706 mole) in anhydrous chloroform (590 ml). The reaction temperature was maintained at 0±5°C. A steady evolution of hydrogen chloride was noted. When the addition was completed the reaction mixture was allowed to warm to ambient temperature and stirring continued for one hour. The reaction mixture was then cautiously poured over cracked ice (4Kg) to destroy excess chlorosulfonic acid, and the organic phase was separated and combined with the chloroform recovered from several washes of the aqueous acid. After removal of the chloroform at ambient pressure the white product was dried in vacuum. It weighed 217g and was 84% of the theoretical yield. After redissolving in chloroform the solution was filtered and the product was reprecipitated with naptha. One half of the product was recovered initially, but upon concentrating the filtrate a second batch of crystals was isolated. The product melted at 115-125°C and weighed 138g, (54 percent of theory).

Synthesis of 1, 3, 5-Benzenetrisulfonyl Chloride (D1516-25)

A slurry of m-benzenedisulfonic acid disodium salt (175 g, 0.63 mole), mercury (8.1 g) and oleum (175 ml, 15%) was stirred at about 270°C for 12 hours. The reaction mixture was then dissolved in water (2500 ml) and neutralized hot with calcium carbonate. Precipitated calcium sulfate was then removed by filtration. After washing the precipitate with hot water the combined filtrates were then treated with saturated aqueous sodium carbonate solution until a phenolphthalein end point was achieved. The solution was then evaporated to dryness in vacuum at 125°C. After the initial drying the solid product was pulverized and dried further at 140°C for 4 hours. The benzenetrisulfonic acid sodium salt weighed 199 grams and represented an 83 percent yield.

The benzenetrisulfonic acid salt (199 g, 0.52 mole) was then mixed with phosphorus pentachloride (238 g, 0.95 mole) and heated at reflux (115°C), with constant stirring, for 17 hours. A small amount (20 ml) of the volatile $POCl_3$ was removed and additional PCl_5 (100 g, 0.48 mole) was added. An aliquot of the reaction mixture was removed at this point and indicated that the yield was about 25 percent. Additional PCl_5 (100 g, 0.48 mole) was then added and the reaction was run for an extra 24 hours. The reaction mixture was then poured over crushed ice, filtered, and washed with ice water. Ethylene chloride was then used to extract the trisulfonylchloride and the solution was dried over anhydrous magnesium sulfate. After evaporation to dryness the crude product (36g, 19 percent) was vacuum dried at 125°C. Recrystalization from benzene yielded product melting ca. 189°C.

Synthesis of 4,4'-Biphenyldisulfonyl Chloride (D1516-28)

A mixture of 4,4'-biphenyldisulfonic acid (20 g, 0.064 mole) and phosphorus pentachloride (27g, 0.13 mole) was heated at reflux for about 16 hours. Additional phosphorus pentachloride (25g, 0.12 mole) was then added and reflux was continued for 2 hours. The reaction mixture was then poured over crushed ice and the product was collected by filtration, then dissolved in ethylene chloride, and the solution was dried with magnesium sulfate. After filtration the ethylene chloride was removed from the filtrate by distillation. The crude sulfonyl chloride was recrystallized from xylene. It then weighed 10.7g and melted at 198-205° C. A second recrystallization yielded 7.5g of product melting at 208° C.

Polyphenylenes

Polyphenylene D1081-1-1 was derived from a 1:1 molar mixture of biphenyl and terphenyl. It was isolated by continuous extraction with hot solvents, being insoluble in chlorobenzene and soluble in 1, 2, 4-trichlorobenzene. It had a melting range of 225 to 270°C, and a composition of 90.00 percent carbon, 4.80 percent hydrogen, 1.60 percent chlorine, and 3.47 percent ash.

Polyphenylene C-3125-20-3 consisted of the combined products of several polymerizations. It was soluble in boiling 1, 2, 4-trichlorobenzene and insoluble in boiling chlorobenzene and melted at 260 to 300° C. Before it was used it was ground to pass through an 80 mesh screen.

Other similar polyphenylenes are identified below occasionally only by melting range and/or average molecular weight.

b. Attempted Curing of Sulfonated Polyphenylene

Sulfonation of Polyphenylene with Sulfuric Acid

C3004-57-1. Polyphenylene (D1081-1-1, 1.0027g.) was stirred with concentrated sulfuric acid (20 ml.) for 24 hours at 250°±10°C. The mixture was then allowed to cool and was added to concentrated hydrochloric acid (200 ml.). After 2 days, the polymer had come out of suspension and was isolated by centrifugation. It was washed once with water and twice with dilute hydrochloric acid, sufficient acid being used to keep the polymer out of solution. After evaporation of most of the aqueous acid the black product was dried in a desiccator; weight, 1.0322g. Most of the product was soluble in water, but a small quantity of insoluble material indicated the product was not entirely homogeneous. It failed to melt on heating to 400°C.

Sulfonation of Polyphenylene with Chlorosulfonic Acid

D1081-2-5. Polyphenylene (D1081-1-1, 1.0010g) was suspended in 1, 1, 2, 2-tetrachloroethane (10 ml) and chlorosulfonic acid (99 percent, 0.453g) was added over a period of 1-1/2 hr. with stirring. After 19-1/2 hr. of stirring at room temperature the product was filtered off, washed with chloroform, and dried in vacuum for 16 hr. at 36-60°C; weight, 1.239g. The product failed to melt on being heated to 400°C. A small quantity of volatile material was released at 105-120°C, and above 375°C it turned from greenish-black to chocolate brown. The analysis is given in Table 1.

D1081-1-2. Polyphenylene (1081-1-1, 1.000g) was treated as above but with more chlorosulfonic acid (0.742g). The product weighed 1.439g. It was not completely homogeneous, but except for a few unreacted particles it failed to melt at temperatures up to 400°C. At 105-110°C it gave off a volatile product and turned brown near 400°C.

D1081-2-2. Polyphenylene (D1081-1-1, 1.0003g) was treated as above but with less chlorosulfonic acid (0.245g). The product weighed 1.094g. It melted in part at 255°C, but failed either to melt completely or to solidify completely on being heated to 400°C. It turned from greenish black to chocolate brown during heating.

Pyrolysis of Sulfonated Polyphenylene

C3004-56-1-A and B. A portion of the finely ground sulfonated polyphenylene D1081-2-5 (0.0661g) was heated under vacuum for 1-3/4 hr. in a silicone oil bath at 110°-130°C. The weight of the residue (C3004-56-1-B) was 0.0566g. Its analysis is given in Table I.

A second portion of D1081-2-5 (0.0664g) was heated under vacuum for 30 min. in a metal bath at 375-380°C. The residue (C3004-56-1-A) weighed 0.0559g. Its analysis is also given in Table I.

c. Cures with 4, 4'-Biphenyldisulfonic Acid

Behavior of Commercial 4, 4'-Biphenyldisulfonic Acid During Heating. A small quantity of the practical grade 4, 4'-biphenyldisulfonic acid was heated on a melting point block. At 48°C it partially melted and by 90°C it was resolidified. At 110°C it partially melted again, and above 150° volatiles were evolved. When all the volatiles were lost, it resolidified. At 250°C it melted completely and white fumes were given off. On continued heating the melt darkened and became viscous between 300°C and 340°C. By 400°C the material was essentially a solid.

When a melt of 4,4'-biphenyldisulfonic acid was heated in larger quantities, it fumed, became viscous, and eventually turned solid in the same manner. The viscous material was soluble in water, while the final solid was hard, insoluble, and infusible.

Curing of Polyphenylene with Commercial 4,4'-Biphenyldisulfonic Acid.

Typical reactions are described

C3004-61-y-1. 4,4'-Biphenyldisulfonic acid (2.02 g) was placed in a glass container suspended in a silicone oil bath at 176°C. When it melted to a gray liquid, polyphenylene (D1081-1-1, ground to pass through a 100 mesh screen, 2.00 g) was added. After a few minutes the soft putty-like mass gave off white fumes and turned to a dry gray-green powder.

A portion of a similar gray-green powder was heated on a melting point block. At 245°C it softened and flowed under slight pressure. On continued heating it solidified to a cohesive black solid which failed to melt up to 410°C.

The powder was compressed under 18,000 psi in a cold mold and then heated until flow began. When the sample withstood 4500 psi, it was heated under this pressure for 1-1/3 hr. with the platen temperature at 550°F. The molded part flaked easily and expanded and softened when it was heated over a flame, indicating incomplete cure.

C3004-60-x-2. 4,4'-Biphenyldisulfonic acid (2.00g) and polyphenylene (D1081-1-1, 1.00g) were reacted as above at 185-186°C to form a gray-green powder. The powder was thoroughly mixed. and the container was transferred to a metal bath. No change occurred until the temperature of the bath reached 252°C, at which point the mass softened. By the time the temperature reached 263°C the stirred mass formed a soft, black ball, most of which was removed for molding. The traces which remained became very hard within 10 min. after the mixture softened and was held at temperatures below 268°C.

C3004-64-x-2-3. 4, 4'-Biphenyldisulfonic acid (6.01g) and polyphenylene (D1081-1-1, 3.01g) were prepolymerized to a gray-green powder as described above. The prepolymer was transferred to a metal bath and heated with stirring. At 255° it softened, and after 10 min. at 255-265°C it formed a tacky black ball. It was removed, cooled, and ground into a powder.

The black powder was placed in a mold and heated under contact pressure with the platen temperature at 550°F. After 8 min. flow began. After 28 min. at contact pressure, a pressure of 28,000 psi was applied and heating was continued for 2-1/2 hr. The molded part which was obtained was cured but fairly brittle.

A portion of the cured pellet (0.383g) was placed in an evacuated tube and heated in a metal bath at 340°C. A white solid and a light brown liquid condensed in the cooler portion of the tube. After 3/4 hr. at 340°C, the temperature was raised to 450°C over a period of 1/2 hr. and then kept at 430-460°C for another 3/4 hr. The residue was cooled, weighed and analyzed for sulfur; weight, 0.276 g; S, 8.52%.

C-3125-20-A. 4, 4'-Biphenyldisulfonic acid (25.01g.) was melted in a container heated with an oil bath at 140° C, and polyphenylene (C-3125-20-3, 25.01g.) was added. After being stirred and heated for 15 minutes at 140 to 150°C, the product was a dry, dark brown powder. It was cooled and ground to pass through an 80 mesh screen. When a portion was heated on a melting point block, it softened at 260°C and melted at 290°C.

C-3125-20-B. This material was obtained by heating C-3125-20-A over a temperature range of 180 to 228°C for 30 minutes. On a melting point block it softened at 265°C and, without melting completely, it was cured at temperatures up to 315°C.

Data for molding pellets from C-3125-20-A and C-3125-20-B are given in Table III, along with compressive strengths and analytical data for the best products. The postcure was carried out under argon for 18 hours at 275°F, 120 hours at 275 to 600°F, and 1 hour at 600°F. Portions of the postcured pellets were powdered and heated under vacuum. A small quantity of a light tan solid condensed on the cooler upper walls of the container. Data for this treatment and analytical data for the products are also shown in Table III.

TGA and DTA data were obtained for a cured polymer powder derived by crushing pellet C-3125-20-B-2-2. The first set of data was obtained in a static air environment and is included for comparison with the data obtained in nitrogen. Heating rates of 20°C/min were employed, and the ΔT scale for the DTA results was 0.5°C/in. The temperatures noted by the analyst have been corrected for non-linearity of the thermocouples. These thermal plots are illustrated in Figures 1 through 4.

Recrystallization of Commercial 4,4'-Biphenyldisulfonic Acid

Commercial 4,4'-biphenyldisulfonic acid (Eastman practical grade, 100 g) was dissolved in 65 ml of water, treated with 5g of activated charcoal (Nuchar), and filtered through a bed of Celite. An additional 35 ml of water was used to wash the filter bed. Concentrated hydrochloric acid (600 ml) was added to the filtrate, which was bright blue but turned to a yellowish green when the acid was added. The solution was seeded with a few crystals of acid and stirred to accelerate crystallization (slow crystallization yielded bluish crystals). The white needles were filtered off and dried in a desiccator over anhydrous calcium sulfate and sodium hydroxide pellets. The dry acid weighed 25.4g. Acid that was purified in this manner showed traces of melting at 131°C and 246°C, but melted rapidly and completely at 260-265°C. It was deliquescent, and consequently the melting point depended on the amount of water which was absorbed from the air.

Curing of Polyphenylene with Recrystallized 4,4'-Biphenyldisulfonic Acid. Investigation of Conditions of Resin Advancement.

C-2943-54. Polyphenylene (12g) with a melting range of 215-250°C and recrystallized 4,4'-biphenyldisulfonic acid (12g) were mixed and ground together with a mortar and pestle. Portions of the mixture were heated in an open container in a metal bath, with the time and temperature for each portion being as recorded in the table

Sample	C-3125-20-A-1	C-3125-20-A-2	C-3125-20-B-1	C-3125-20-B-2-1	C-3125-20-B-2-2
Vacuum drying time, hours	2	1	Not dried	1	1
Drying temperature, °F	160	230		230	230
Initial weight, g.	7.00	7.00	7.50	6.00	6.00
Loaded into cold or hot mold	Cold	Cold	Cold	Cold	Hot
Contact time, minutes	15	15	15	15	15
Temperature, °F	530	530	530	530	530
Pressure, psi	3000	3000	3000	3000	3000
Cure time, minutes	120	120	120	120	120
Molded weight, g.	4.4 (some mechanical loss)	5.72	5.48	5.00	4.23
Weight after post-cure, g.	3.20	5.49	4.64	3.50	3.73
Percent weight loss in postcure	27	4.0	15.3	30.0	11.8
Appearance	Cracked	Not completely cured; expanded in postcure	Large cracks	Good pellet	Good pellet
Compressive strength, psi				2760	1850
Elemental analysis:					
Percent C				84.34	83.53
Percent H				4.06	3.97
Percent S				3.04	2.99
Percent Cl				1.36	1.36
Percent ash				1.92	2.54
Vacuum heating:					
Temperature, °C				330-406	340-475
Time, minutes				60	40
Percent weight loss				12.08	11.89
Elemental analysis of non-volatile residue					
Percent C					85.99
Percent H					3.94
Percent S					2.70
Percent Cl					1.10
Percent ash					2.10
Analysis of volatile condensate					
Percent S					0.43

Table III. Data for polyphenylene cured with 4,4'-biphenyldisulfonic acid.

below. Each portion was then dried under vacuum at 110°C for 1-1/2 hours, then heated to 400°C in a mold and held at that temperature for 30 minutes. After an initial compression at room temperature, the sample was heated under contact pressure until the product was able to withstand greater pressure without excessive material loss from the mold. Pellets B, C, D, E and H were made in this manner (see the table below).

Another 4g portion of the mixture was mixed with 0.5 ml of water, then heated at 180°C for 14 minutes. During this time the mixture became fluid and then turned to a dry powder. The powder was further advanced, dried under vacuum, and cured to pellet F as shown below in the table.

	Advancement			Molding		
Pellet	Temperature, °C	Time, minutes	Melting Range of Advanced Resin, °C	Softening Temperature, °C	Temperature at Which Pressure Held, °C	Nature of Product
B	218	30	Melted partially above 245, solidified at 290	185	281	Cured but brittle
C	250	9	Melted partially above 280	380	Held pressure throughout molding	Cured but brittle
D	265	3	Half melted above 220; solidified at 300	250	–	Cured, no strength
E	220	15	Half melted above 240; solidified at 300	287	360	Cured; good pellet, not brittle
F	180 220	14 15	Most melted at 230-250; solidified at 275	280	350	Cured; best pellet
G	220	15	Most melted above 225; solidified at 290	281	355	Cured, but very brittle
H	180 275	11 3	Melted partially above 228; solidified at 260	–	353	Cured, but brittle

Pellet G was molded from a powder prepared by adding 2.0g of polyphenylene to 2.0g of recrystallized acid dissolved at room temperature in a minimum quantity of water and drying the resulting mixture overnight in a desiccator. The powder was advanced as shown in the table and dried for 1-1/2 hours at 110°C in a vacuum before molding.

Reinforced Pellets With Untreated Carbon Cloth

Portions of the molding powders C-3125-20-A and C-3125-20-B were combined and used to mold a laminate with carbon cloth (Hitco

CCA-1, dried 2 hours at 240°F). The molding conditions were essentially the same as those employed for C-3125-20-B-2-1 (Table II). The resin failed to wet the carbon cloth, and consequently the pellet disintegrated along the planes of the cloth.

Treatment of Carbon Cloth With 4, 4'-Biphenyldisulfonic Acid

C-3125-43-2. A solution of commercial 4, 4'-biphenyldisulfonic acid (10g) in water (30 ml) was sprayed onto a piece of carbon cloth (Hitco CCA-1, 5 x 10-1/2 inches) which was then dried in an oven for 3-1/2 hours at 120°C The cloth was then quite stiff and easy to cut into sections without fraying. The sections were then placed in molten 4, 4'-biphenyldisulfonic acid at 250 to 280°C for 1/2 hour. After being cooled, the cloth was washed thoroughly with water and dried 2 hours at 150 to 160°C. It was slightly stiffer than the original cloth and had lost much of the original tendency to fray at the edges.

C-2943-48. A solution containing 25g of 4, 4'-biphenyldisulfonic acid in 25 ml of water was sprayed onto both sides of an 8-1/2 x 11-inch piece of carbon cloth. The coated cloth was first dried in an oven at 125°C for 2 hours and then heated for 2-1/2 hours at 190°C and for 30 minutes at 258°C. This treatment seemed to be as satisfactory for molding reinforced parts as the method used and required less acid.

Treatment of Carbon Cloth With Low-Melting Polyphenylene

C-3125-45-1. Carbon cloth (Hitco CCA-1) was sprayed very lightly with "Krylon" acrylic spray (to prevent fraying) and cut into sections. The sections were treated with molten polyphenylene for 3-1/2 hours at 220 to 230°C. A chlorobenzene-soluble fraction of polyphenylene with a melting range of 140 to 235°C was used. After being cooled, the cloth was washed repeatedly with chloroform to remove excess polyphenylene and was dried for 3 hours in vacuum at 110°C.

Fabrication of Reinforced Discs Using Treated Carbon Cloth

C-2893-25. A 3/4 inch diameter composite pellet was fabricated from the acid-treated cloth (C-3125-43-2, 3.72g) and a molding powder similar in composition to C-3125-20-B (D-1411-19d, 3.72g). The molding powder was not dried prior to use. The material was loaded into a hot mold and was cured at 530°F for 2 hours at 3000 psi. Excessive flow occurred during molding, so that the cured pellet weighed only 4.82g, indicating a resin content of only 22.8 percent. The resin had penetrated and wetted the cloth to yield a uniform part, although its strength was such that it could be pulled into two pieces with the fingers because of the low resin content.

C-2943-26. Commercial 4,4'-biphenyldisulfonic acid (15.0g) was melted at 163-166°C and polyphenylene (m.p. 260-300°C, 15.0g) was added with stirring. After 11 minutes of heating, the mixture became a dry powder. A melting point determination revealed that a small percentage melted at 250°C but that no additional melting occurred at temperatures up to 355°C. The mixture was advanced by heating at 205-230°C for 15 minutes, at which point the soft, black product weighed 26.5g. It was ground to a powder and stored in a desiccator.

Three 3/4 inch diameter reinforced pellets were molded from this powder and two types of treated carbon cloth. Pellet No. 1 was made with cloth treated with 4,4'-biphenyldisulfonic acid (C-3125-43-2) and pellets Nos. 2 and 3 were made with cloth treated with low melting polyphenylene (C-3125-45-1). A quantity of powder equal in weight to the weight of the cloth was sprinkled between the plies of cloth and loaded into a cold mold. The mold was placed in a press with platens preheated to 300°C and heated for 4 hours under pressures up to 3000 psi. The postcure was carried out under argon in a heat-programmed oven with the following schedule: 18 hours at 135°C (275°F), 114 hours at 135 to 450°C (842°F) at 5°F/hr. cooled to 93°C (200°F) prior to removel from oven. Data and results appear on the following page.

Number	Number of Plies	Charge Weight, g	Molded Weight, g	Loss of Weight, g	Molded Percent Resin	After Postcure			
						Weight	Weight Loss	Percent Resin	Appearance
1	9	1.76	1.42	0.34	38.0	1.34	0.08	34.3	Strong part; cloth was wetted but remained fuzzy at edges; very small cracks in resin surface.
2	23	3.74	3.15	0.59	40.6	2.91	0.24	35.7	Part expanded in postcure.
3	20	4.58	3.45	1.13	33.6	3.10	0.35	26.1	Strong part; cloth was wetted, but fuzzy edges are exposed; very small cracks in resin surface.

C-2943-38-1. Two trichlorobenzene-soluble, chlorobenzene-insoluble batches of polyphenylene (31g with m. p. 255-320°C and 9g with m.p. 220-270°C) were combined with melted commercial 4, 4'-biphenyldisulfonic acid (40g) and heated with stirring at 166°C until the mixture became a powder (about 26 minutes). A portion of this powder was heated on a melting point block and found to melt only partially above 280°C. The powder was advanced by heating at 230°C for 15 minutes.

When an attempt was made to mold a reinforced specimen from this powder and carbon cloth that had been treated with 4, 4'-biphenyldisulfonic acid (C-2943-37), the resin failed to wet the cloth and the plies separated. The flow during molding was considered inadequate.

C-2943-40. Polyphenylene (m.p. 215-255°C, 40g) was added to melted commercial 4, 4'-biphenyldisulfonic acid (40g) with stirring at 175°C. Because of difficulty experienced in mixing the two components adequately, the mixture was cooled and ground to a powder in a mortar. The mixture was then reheated at 175°C until it turned powdery (about 10 minutes). When a portion was heated slowly on a melting point block, it melted at 213-230°C and hardened at 245°C; when it was heated rapidly, it melted only partially above 225°C and solidified at 280°C. The yield of powder was 71g.

Reinforced discs 2 inches in diameter were molded from the above powder and an equal weight of carbon cloth that had been treated with 4, 4'-biphenyldisulfonic acid (C-2943-37, 42, and 48). The powder was first vacuum dried at 110°C for 1 hour, then loaded into a cold mold and into a 277°C (530°F) press, and molded at 3000 psi for 2 hours. Excessive flow occurred, and consequently the resin contents were low. A heat-programmed postcure to 400°C caused large additional weight losses. Specimen No. 2 was partially delaminated when it was removed from the mold. Data are recorded below.

Number	Number of Plies	Charge Weight, g	Molded Weight, g	Loss of Weight, g	Percent Resin	Postcured Weight, g	Postcure Loss of Weight, g	Percent Resin
1	34	54.78	39.52	15.26	30.7	33.30	6.22	17.7
2	34	61.82	39.39	22.43	21.5	33.34	6.05	7.29

The actual resin content may have been slightly higher than shown, especially for No. 2, because of an undetermined weight of acid adhering to the cloth and included in the weight of the cloth. Nevertheless, it was clear that the resin should have been advanced further.

Water Soluble Resins from Polyphenylene and Excess 4, 4'-Biphenyldisulfonic Acid

D1081-5-1. 4, 4'-Biphenyldisulfonic acid (4.0g) was heated to 169°C and powdered polyphenylene (D1081-1-1, 1.005g) was added. The mixture was a soft paste at first, but soon became a greenish-black powder. More acid (6.0g) was added, and the soft mixture soon became a powder again. It was then heated in a metal bath at 260-280°C for 1 hr. The mixture was a bubbling, fuming liquid which slowly increased in viscosity as the bubbling decreased.

After being allowed to cool, the mixture was stirred with water (200 ml) for several hours. The water solution was centrifuged, and the undissolved material was collected and dried; weight, 0.462g. It softened partially at 205°C, increased in viscosity at 330-340°C, and was solid at 345°C. The material was readily dispersed in aqueous acetone, but was only partially soluble.

Hydrochloric acid was added to the remaining black, aqueous solution until a large quantity of gray precipitate was formed. Water was added until most of this solid redissolved, and the mixture was stirred thoroughly to insure equilibrium conditions. A second black product was isolated by centrifugation, collected, and dried; weight, 0.9236g. This product was completely soluble in water. It softened completely at 220°C and flowed easily at this temperature. At 330-340°C the viscosity increased considerably, and the sample no longer flowed under pressure at 360°C. No further melting occurred up to 400°C.

C-3125-39-1. 4,4'-Biphenyldisulfonic acid (40g) was melted and heated to 138°C, and polyphenylene (C-3125-20-3, 10g.) was mixed in. The mixture, which was quite fluid at first, was heated gradually to 230°C. Gases were evolved above 180°C and the material increased in viscosity as the temperature was raised from 180 to 230°C over a period of 15 minutes. The material was cooled and ground to a powder (C-3125-39-1) which was dark gray in color. A solubility test showed that the dark-colored components of the mixture were quite insoluble in water.

C-3125-40-1. A portion (2g) of C-3125-39-1 was heated in a bath at 245°C. It became quite viscous and formed a stiff ball within 12 minutes.

C-3125-40-2. Another portion (1g) of C-3125-39-1 was heated with 4,4'-biphenyldisulfonic acid (1g) at 270 to 278°C. Both the viscosity of the mixture and the solubility in water increased on heating. A maximum solubility was noted after 26 minutes.

C-3125-41-1. Still another portion (1g) of C-3125-39-1 was mixed and heated with 4,4'-biphenyldisulfonic acid (0.5g) at 270 to 285°C. Maximum solubility in water was noted after about 3 minutes, but the product was less soluble than C-3125-40-2.

C-3125-44-1. The major portion (30g) of C-3125-39-1 was mixed and heated with an equal quantity of 4,4'-biphenyldisulfonic acid as in C-3125-40-2. After 38 minutes of heating at 250 to 295°C it was adjudged from periodic tests with small portions to have achieved maximum solubility. The mixture was then cooled, and as much as possible was dissolved in 280 ml. of water. The undissolved material was separated by centrifugation and dried in a vacuum desiccator; weight, 10.5g. This insoluble product weighed about 4.5g more than the polyphenylene from which it was derived, and consequently there was no assurance that any of the reacted polyphenylene remained in solution. However, 400 ml. of concentrated hydrochloric acid was added to the remaining solution to precipitate an additional 17.9g of black material.

C-2943-28. A mixture of polyphenylene (m.p. 260-300°C, 10g) and commercial 4, 4'-biphenyldisulfonic acid (100g) was heated for 1 hour in an open container in a metal bath at 250-260°C. During this period the solubility in water was checked periodically, but the anticipated degree of solubility was not achieved. A small portion was therefore heated at 270-280°C to determine the optimum heating period for maximum solubility. The entire mixture was consequently heated for 1-1/2 hours at this temperature.

The mixture was cooled and taken up in 400 ml of water. An insoluble product (C-2943-28-1) was separated by centrifugation, washed three times with water, and dried; it weighed 8.8g. The black supernatant solution was combined with sufficient concentrated hydrochloric acid to precipitate a fraction (C-2943-28-2) which, after isolation by centrifugation and drying, weighed 9.5g. Product C-2943-28-1 was insoluble in hot water or hot aqueous acetone and failed to melt at temperatures up to 400°C. Product C-2943-28-2 was fairly soluble in hot water, was completely soluble in aqueous acetone, melted at 230°C and resolidified at 340°C.

A lacquer was made by dissolving the product C-2943-28-2 in 7.5 ml water and 22.5 ml acetone. This lacquer was used to dip-coat carbon cloth which had been treated with 4, 4'-biphenyldisulfonic acid (C-2943-37). The coated cloth was air-dried for 30 minutes and vacuum-dried at 110°C for 1 hour. The coated plies were loaded into a cold mold and heated in a press at 530°F for 2 hours. Contact pressure was used for 15 minutes, after which a pressure of 3000 psi was applied. Adequate flow was observed, but the cloth was not wetted and the plies separated easily.

d. Cures with 1, 3, 5-Benzenetrisulfonyl Chloride

D1081-8-1. 1, 3, 5-Benzenetrisulfonyl chloride (1.00g.) was heated in a test tube placed in an oil bath at 200°C. It melted to a clear liquid which gave no indication of polymerization, but a small quantity of white solid condensed in the cooler upper portion of the tube. To the liquid was added polyphenylene (D1081-1-1, 1.00g.) which had been ground to pass through an 80 mesh screen. The lump which formed initially was crushed, and the material was thoroughly mixed. Within 2 to 5 minutes it softened to a black, fluid mass, and within 10 minutes it formed a cohesive, gummy ball. This product was cooled, ground to a powder, and heated on a melting point block. It softened only slightly at 1[illegible]0°C, became a hard (but still granular) solid by 240°C, and failed to melt on further heating.

D1081-9-2. Polyphenylene (D1081-1-1, 2.00g) was added to molten 1, 3, 5-benzenetrisulfonyl chloride (1.00g), and the mixture was heated as above in a bath at 194°C. After 1-1/2 to 2 minutes the powder turned black and appeared moist but did not melt. After 3 minutes of heating, the somewhat lumpy product was removed and ground with a mortar and pestle. When a small portion was reheated to 195°C, it softened and then cured without melting.

The bulk of the powder was cured in a mold at temperatures up to 400°C and pressures up to 50,000 psi. From the increase in pressure it was apparent that the major reaction took place between 200 and 300°C. At 330 to 340°C gases and powder were expelled from the mold in bursts. There was no flash during the cure. The pellet which was obtained was black, quite hard and brittle.

Several pieces (0.4012g) of the pellet were heated under vacuum for 1 hour at temperatures rising from 285 to 405°C. A light yellow solid condensed in the cooler upper portions of the container, the first condensate being deposited at 330-340°C. The residue weighed

0.3430g, corresponding to a 14.51 percent loss in weight. Thermogravimetric analysis of the residue in nitrogen with a temperature rise of 20°C per minute yielded the following data on weight loss: 400°C, 0.5 percent; 500°, 2.4 percent, 600°, 7.5 percent; 700°, 12.7 percent; 800°, 14.8 percent; 850°, 16.4 percent.

D-1081-11-2. 1,3,5-Benzenetrisulfonyl chloride (1.2052g) was heated in a test tube by means of an oil bath at a temperature of 195°C. Some of the material volatilized from the melt and condensed as a white solid in the upper portions of the container. The remaining melt was dissolved in chloroform, the polyphenylene (D1081-1-1, 2.4107g) was added, and after several minutes of refluxing, the solvent was removed under reduced pressure with constant stirring. The residue, which was greenish-brown, was ground in a mortar and thoroughly mixed. This powder was heated in a mold at temperatures up to 406°C and pressures up to 45,000 psi. Most of the reaction appeared to take place between 180° and 220°C, and gases and powder were expelled at 340-360°C. The pellet thus obtained was not consistent in appearance throughout, the upper central portion being considerably more porous and friable than the lower and outer portions.

The bottom portion of the pellet was heated from 306° to 453°C over a period of 3 hours in vacuum. This treatment caused the pellet to shatter and to lose 11.21 percent in weight.

C-3125-27-1. A chlorobenzene-soluble fraction of polyphenylene (m.p. 138-152°C, 2.00g) and 1,3,5-benzenetrisulfonyl chloride (1.00g) were dissolved together in chloroform, and the solvent was evaporated under reduced pressure with constant stirring. The residue was ground to a powder, thoroughly mixed, and dried in a vacuum oven at 100-110°C for 1 hour. When an attempt was made to cure this mixture in a mold, excessive flow occurred at temperatures above 160°C, and the entire sample was lost from the mold.

D-1411-20a. 1,3,5-Benzenetrisulfonyl chloride (3.00g) was heated to 200°C, and polyphenylene (C-3125-20-3, 6.00g) was added to the melt. After 3 minutes of vigorous stirring at this temperature the sample was cooled and ground with a mortar and pestle.

A pellet was prepared by loading the powder into a hot mold at 300°F and curing it at 570°F and 3000 psi over a period of 2 hours. A small amount of flash was observed, and the pellet (3.49g) weighed 88.8 percent as much as the charge (3.93g). The pellet was removed only after the mold cooled overnight to room temperature. Small cracks were present in the pellet, which nevertheless was hard, had sharp edges, and retained considerable strength.

D-1516-24-1. A lacquer of polyphenylene (1000 $\overline{\text{M.W.}}$, 20g), benzenetrisulfonyl chloride (10g) and chloroform (150 ml) was prepared and heated at reflux with stirring for about 16 hours. Carbon cloth laminates were molded at 400°F and 3000 psi. Post cure in argon was 18 hr. at 275°F, then 96 hr. 275 → 752°F.

D-1516-24-2. A lacquer of polyphenylene (1000 $\overline{\text{M.W.}}$, 24g), benzenetrisulfonyl chloride (8g) and chloroform (150 ml) was prepared and heated at reflux with stirring for 16 hours. Carbon cloth laminates were molded at 400°F and 3000 psi. Post cure in argon was 18 hr. at 255°F, 96 hours 275 → 752°F.

D-1516-24-2. A lacquer of polyphenylene (1000 $\overline{\text{M.W.}}$, 24g), benzenetrisulfonyl chloride (6g) and chloroform (150 ml) was prepared and heated at reflux with stirring for 16 hours. Carbon cloth laminates were molded at 400°F and 3000 psi. Post cure in argon was 18 hours at 255°F, then 96 hours 275 → 752°F.

e. Cures with Mixtures of 4, 4'-Biphenyldisulfonic Acid and 1, 3, 5-Benzenetrisulfonyl Chloride

C-3125-21-1. 4,4'-Biphenyldisulfonic acid (1.002g) was melted and heated to 170°C and 1,3,5-benzenetrisulfonyl chloride (0.505g) was added with stirring. The mixture was not homogeneous, however, and a solid floated on the melt. Polyphenylene (D1081-1-1, 2.006g) which had been passed through a 100 mesh screen was stirred into the mixture, and heating was continued for 5 minutes. The product, which was a powder with a moist appearance and which contained some white crystals, was finely ground and thoroughly mixed. When a portion of the mixture was heated on a melting point block, it melted at 235-255°C.

After being compressed in a cold mold, the material was heated to 285°C over a period of 3-1/4 hours. Excessive flow occurred at temperatures over 220°C, and the part was therefore molded under virtually no additional pressure. As a consequence, the pellet was fairly porous and brittle, and it was cured and infusible.

The pellet was put through the following postcure cycle: 18 hours at 275°F, 12[illegible] hours at 275-600°F, and 1 hour at 600°F. The loss in weight was about 4 percent.

C-3125-22-2. 1,3,5-Benzenetrisulfonyl chloride (0.806g) and 4,4'-biphenyldisulfonic acid (0.308g) were heated together at 195°C, slightly above the melting point (189-192°C) of the trisulfonyl chloride. The mixture of curing agents became solid at this temperature.

C-3125-22-3. 4,4'-Biphenyldisulfonic acid (0.300g) and melted and heated to 192-195°C, and polyphenylene (D-1081-1-1, 2.003g), ground to pass through a 100 mesh screen, was mixed with it. After 3 minutes of heating, the apparently dry, brown mixture was removed and ground to a fine powder. 1,3,5-Benzenetrisulfonyl chloride (0.800g) was melted and heated to 192-195°C in another container, and the mixture was added. A lump formed immediately. After 3 minutes of heating, during which the material was mixed as well as possible, the product was removed and ground with a mortar and pestle. When a portion was heated slowly on a melting point block, it did not melt but turned black around 250°C. When it was dropped on the hot block at 250°C or above, however, it melted partially, emitted white vapors, and turned black and hard.

The material was compressed in a cold mold, then cured at temperatures up to 392°C and at pressures up to 10,000 psi. An internal increase in pressure at 200-300°C indicated that reactions took place in this temperature range, but only a very small amount of flash was observed. Gases and solids were expelled with a popping sound at 309-321°C. The molded part was rather porous and very friable.

C-3125-25-1. Using the procedure described for C-3125-22-3, the following were reacted at 190-192°C: 4,4'-biphenyldisulfonic acid (0.508), polyphenylene (D1081-1-1, 2.001g), and 1,3,5-benzenetrisulfonyl chloride (0.751g). Curing in a mold was accomplished by heating to 330°C over a period of 3-1/4 hours at pressures up to 9000 psi. Very slight flow occurred, and gases and powder were expelled in bursts at 302-309°C. The molded part was very friable. It ignited over a burner, but formed a hard char with essentially the same size and shape as the original.

C-3125-28-1. 4,4'-Biphenyldisulfonic acid (1.002g) was melted and heated to 185-190°C, and 1,3,5-benzenetrisulfonyl chloride (0.502g) was added. This mixture consisted of a froth or foam of solid material floating on a liquid. Polyphenylene (D1081-1-1, 2.005g) which had been passed through a 100 mesh screen was added, and after about 10 minutes of heating and stirring the mixture was a dark grayish-green powder. It was transferred to a vacuum oven, where it was heated for 1-1/2 hours at 100-110°C, then stored in a desiccator.

After compression of the powder in a cold mold under 25,000 psi, it was cured at temperatures up to 429°C and pressures up to 8000 psi over a period of 1-3/4 hours. Some viscous material flashed from the mold between 200° and 280°C. Gases and dry particles were expelled above 302°C. The pellet so formed was hard and dense at the bottom, but somewhat friable at the top. It did not change shape or soften when ignited over a burner.

C-3125-33-1. A powder was prepared as described for C-3125-28-1 but was heated more slowly in a mold. Flow was first noticed at a temperature of 195°C, and some liquid flash was still present at a temperature of 418°C about 4-3/4 hours later. Heating was nevertheless halted and the cooled pellet was removed. It was somewhat friable at the edges. In spite of what appeared to be an incomplete cure, the pellet maintained its shape during postcure in a vacuum. A 1.68 percent loss in weight occurred during 5-3/4 hours of heating from 156° to 331°C. An additional 8.87 percent loss in weight took place during 2-1/2 hours in which the temperature was raised from about 330° to 412°C. A yellowish-white residue collected in the cooler portions of the container.

C-2943-32-A. Commercial 4,4'-biphenyldisulfonic acid (7.0g) was melted and heated to 185-190°C. To this mixture was added 1,3,5-benzenetrisulfonyl chloride (3.5g) and trichlorobenzene-soluble, chlorobenzene-insoluble polyphenylene (m.p. 250-320°C, 14g) which had been ground to pass through a 100-mesh screen. The mixture was stirred at this temperature for 10 minutes, at which time it had become a dry powder. It was ground in a mortar and dried for 2 hours at 100-110°C at 1-2 torr. The yield was 21.6g.

Three unreinforced pellets were molded from this powder. The powder for No. 1 was loaded into a cold mold, whereas those for No. 2 and No. 3 were loaded into a mold at 149°C (300°F). All pellets were heated in a press at 300°C (572°F) for 4 hours at 3000 psi. The heat-programmed postcure consisted of 18 hours at 135°C (275°F), 114 hours at 135 to 450°C (842°F) at 5°F/hr, cooling to 93°C (200°F) prior to removal from the oven. Molding data are given below.

Number	Charge Weight, g	Molded Weight, g	Loss of Weight, g	Postcured Weight, g	Postcure Loss of Weight, g
1	8.00	7.52	0.48	5.98	1.54
2	8.00	7.13	0.87	5.68	1.45
3	7.00	6.62	0.38	5.37	1.25

Pellet No. 2 broke as it was removed from the mold, and No. 3 had cracks which were apparent on the surface. Pellet No. 1 appeared to be quite good on the surface, but when the interior was exposed, a network of fissures was revealed.

f. Cures with Other Sulfonic Acids and Sulfonyl Chlorides

Curing of Polyphenylene with 1, 3-Benzenedisulfonic Acid

C-3125-6-M-1-2. 1, 3-Benzenedisulfonic acid (2.0g) was melted in a glass tube suspended in an oil bath at 174-176°C, and polyphenylene (D1081-1-1, 2.0g) which was powdered to pass through a 100 mesh screen was added. The mixture fumed, but it remained a brown paste after 12 min. of heating. A small portion was heated on a melting point block, and at 220° it solidified but was soft and compressible.

C-3125-5-M-2. 1, 3-Benzenedisulfonic acid (1.0g) and polyphenylene (D1081-1-1, 2.0g) were heated as described above in an oil bath at 191-196°C for 15 min. The mixture remained brown, wet, and granular in appearance. It was transferred to a metal bath at 229-235°C, and after 5 min. it turned to a black, dry powder. A portion was removed after 12 min. at 229-245° and was found to be infusible at temperatures up to 365°C.

C-3004-65-m-1. Polyphenylene (D1081-1-1, 2.002g) which had been passed through a 100 mesh screen was combined with a melt of 1, 3-benzenedisulfonic acid (1.998g) at a temperature of 174°C. The mixture was stirred and heated for 47 minutes while the temperature was raised to 198°C. During this time the soft mixture turned from brown to black.

The mixture was compressed in a cold mold and then heated up to 349°C over a period of 3 hours under pressures up to 12,000 psi. Flow was apparent between 100° and 260°C. Much of the curing seemed to take place around 300°C as indicated by an increase in pressure. The pellet secured in this manner was quite hard at first, but it seemed to lose some of its strength on storage in air.

Several weeks after its preparation a portion of the pellet was heated in vacuum for 2-1/4 hours at temperatures up to 465°C. A white solid deposited in the cooler portions of the container at temperatures up to 335°C; this turned yellow at higher temperatures, but little additional material was deposited. The sample lost 31.44 percent of its weight as volatiles.

Curing of Polyphenylene with 1,3-Benzenedisulfonyl Chloride

C-3125-16. It was first determined that 1,3-benzenedisulfonyl chloride could be heated to 310°C without evidence of polymerization. To another melted portion of the disulfonyl chloride (1.006g) at 117°C was added polyphenylene (D1081-1-1, 1.001g). The fuming mixture was stirred and heated to 192°C over a period of 35 minutes. A gradual increase in viscosity was observed above 150°C, and eventually the material became a hard ball.

C-3125-17-1. Polyphenylene (D1081-1-1, 1.002g) was mixed with molten 1,3-benzenedisulfonyl chloride (1.002g) at 140°C, and the mixture was kept at this temperature in an open container for 18 hours. It was converted to a fairly hard ball, which, however, retained some resiliency and was not brittle.

C-3125-18-1. Polyphenylene (D1081-1-1, 2.001g) was reacted with 1,3-benzenedisulfonyl chloride (2.002g) at temperatures of 142 to 158°C over a period of 25 minutes. This treatment converted the mixture to a soft ball.

The product was heated to 400°C in a mold at pressures up to 12,000 psi. About 2-1/2 hours elapsed as the temperature rose from 150° to 400°C. Gases and solid particles escaped from the mold in bursts at about 320°C, and thin strands of soft material were extruded. The molded product was friable and incompletely cured.

Curing of Polyphenylene with 4,4'-Biphenyldisulfonyl Chloride

C-3125-31-1. Commercial 4,4'-Biphenyldisulfonyl chloride (0.501g) was melted and heated to 165°C, at which temperature some gases were evolved. Polyphenylene (D1081-1-1, 0.503g) was stirred into the melt to form a soft, black paste. Continued heating to 385°C caused more gases to be produced, and the mixture became drier in appearance, but it remained soft and uncured.

C-2943-80. 4,4'-Biphenyldisulfonyl chloride (D1516-28, 0.50g) was mixed with polyphenylene (D1081 1-1, 0.50g) and heated in a metal bath at 220°C. The mixture melted, started to harden within 5 minutes, and turned to a hard product in 20 minutes. On heating this product to 240°C, a small portion melted, but the entire mixture resolidified at 300°C and underwent no further apparent changes on heating to 400°C.

Curing of Polyphenylene with Diphenyl Ether 4,4'-Disulfonyl Chloride

C-2943-49. Small quantities of an intimate mixture of polyphenylene (D-1081-1-1, m.p. 225-270°C) and diphenyl ether 4,4'-disulfonyl chloride were heated with stirring in an open container placed in an oil bath. The time, bath temperature, and results were as follows:

15 minutes, 150°C:	Partially fluid mixture darkened, but there was no apparent increase in viscosity.
15 minutes, 160°C:	Mixture darkened after 10 minutes, started to thicken at 15 minutes.
15 minutes, 170°C:	Mixture darkened after 5 minutes, started to become more viscous at 10 minutes and appeared to have consistency suitable for molding at 15 minutes. Melted on melting point block at 70-170°C and hardened at 210-245°C.
30 minutes, 170°C:	Mixture changed on heating as noted above. Melted at 90-200°C, hardened at 225-250°C.
40 minutes, 180°C:	A rather stiff, viscous mixture was produced. Melted partially above 145°C, solidified at 225-260°C.

C-2943-50-A. An intimate mixture of polyphenylene (D-1081-1-1, m.p. 225-270°C, 1.5g) and diphenyl ether 4,4'-disulfonyl chloride (1.5g) was heated at 180°C for 40 minutes in an open container, then heated in a mold. At 197°C it became too fluid to hold pressure. The temperature was held at 250°C for 45 minutes and at 310°C for 30 minutes, but the sample failed to cure and hold pressure.

C-2943-50-B. A mixture of polyphenylene (D-1081-1-1, 3.0g) and diphenyl ether 4,4'-disulfonyl chloride (1.5g) was advanced in an open container at 180 °C for 40 minutes and then heated rapidly in a mold. At 257 °C the sample became too fluid to hold pressure, and after 4 hours at 400 °C it was still uncured.

C-2943-51-A. Polyphenylene (D-1081-1-1, 2g), diphenyl ether 4,4'-disulfonyl chloride (1g), and cuprous chloride (assay 89.8 percent, 0.2g) were ground together in a mortar and heated in an open container at 180°C for 30 minutes. When a small portion of the mixture was heated on a melting point block, it melted partially at 190°C and solidified at 300°C. When it was heated in a mold, the sample failed to hold pressure above 239°C and was still quite soft after 30 minutes at 400°C.

C-2943-52-A. Polyphenylene (D-1081-1-1, 3.0g), diphenyl ether 4,4'-disulfonyl chloride (1.5g), and cuprous chloride (0.06g) were mixed intimately and heated at 180 °C for 30 minutes. The resulting mixture melted partially above 200 °C and solidified at 300 °C when heated on a melting point block. In a mold it failed to hold pressure above 256 °C and remained soft and uncured after 4 hours at 400 °C.

Chloromethylation of Polyphenylene. Method of Cambron.[11]

Four experiments were run on various molecular weight fractions of polyphenylene using paraformaldehyde, hydrochloric acid, and phosphoric acid catalyst. Two experiments were run in glacial acetic acid, which had no solvent action with even low molecular weight polyphenylene, and two in tetrachloroethane, which exhibited some solvent action. The following experiment was carried out on polyphenylene resin having an average molecular weight of 2000-3000.

C-2222-28. Polyphenylene resin (2000-3000 $\overline{MW}$ range, 28.8g) and 1,1,2,2-tetrachloroethane (80 ml) were slurried in a reaction flask and syrupy phosphoric acid (27 ml), concentrated hydrochloric acid (56 ml), and paraformaldehyde (18g) were added. The stirred mixture was refluxed for 24 hours at 98-100°C. The product was then washed with water to neutrality and dried in a vacuum desiccator. The dry powder was then washed with aqueous sodium sulfite, then left overnight in an aqueous-alcoholic potassium hydroxide solution, finally washed again to neutrality, dried and weighed. The weight of recovered solid was 26.5g, indicating strongly that no chloromethyl substitution had occurred. No evidence of substitution was observed based on solubility or melting point changes, and there was no indication of OH absorption in the infrared spectrum, from a mineral oil mull, of the recovered solid.

Chloromethylation of Polyphenylene. Method of Fuson.[10]

Three experiments were run on polyphenylene resins using chloromethyl methyl ether with stannic chloride catalyst in trichloroethylene. The latter was chosen as the reaction medium because of its good solvent action on polyphenylenes and because of lower probability of ethylenic compounds entering into a Friedel-Crafts reaction. The following reaction is representative of the procedure employed in these experiments.

C-2222-31. Polyphenylene resin (≃800 $\overline{MW}$ range, 15g), trichloroethylene (35 ml), chloromethyl methyl ether (15g), and anhydrous stannic chloride (10 ml) were placed in a flask. The flask was then placed in a 25°C water bath and the reaction mixture was stirred overnight. Following this, the flask was heated at 50°C for four hours with stirring. The reaction mixture was poured into acetone and centrifuged. Undissolved residue was washed several times with acetone to remove residual stannic chloride, and the solvent was removed under vacuum. At this point the product still contained some acetone-soluble polyphenylene. The acetone solution was washed several times with concentrated hydrochloric acid, then washed to neutrality with water. Remaining volatiles were removed from the dark viscous product under vacuum, yielding 4.6g of a brittle solid, soluble in common solvents and melting at 110-120°C.

The acetone-insoluble portion of the product was left to stand overnight in an aqueous-alcoholic potassium hydroxide solution, then centrifuged and washed to neutrality with water. The potassium hydroxide solution was acidified with nitric acid, then tested with silver nitrate solution, giving a strong test for chloride ion. This rigorously dried product weighed 13.5g neglecting losses, showed no acetone solubility and little solubility in chlorinated solvents. No indication of OH absorption was observed in the infrared spectrum, taken in a mineral oil mull. Melting point data were inconclusive. However, materials balance indicated that this portion of the product had undergone substitution. Presumably the product crosslinked during oven drying, or the extent of substitution was too slight to affect readily measurable properties.

Nitrations of Polyphenylene with Nitric Acid-Sulfuric Acid Mixtures (C2426)

6A. A sample of polyphenylene (5g, $\phi Cl(-)$, $\phi Cl_3(+)$) was slurried in concentrated sulfuric acid (10 ml) at ambient temperature and a mixture of concentrated nitric acid (5 ml) and concentrated sulfuric acid (5 ml) was then added very cautiously because of the frothing which occurred. Temperatures rapidly rose to 65°C following each part of the addition. After the addition was completed, stirring was continued for several hours, and the reaction mixture was then diluted with a large volume of water. Filtration was not possible even through a Millipore filter, and consequently the polymer was isolated by centrifugation. It was washed repeatedly with water and centrifuged after each washing. This was followed by drying for about 30 min. at 150°C then for several hours at 50°C. Only 4.8g of product was recovered due to accidental spillage.

7B. A sample of polyphenylene (5g, $\emptyset\mathrm{Cl}(-)$, $\emptyset\mathrm{Cl}_3(+)$) was slurried in concentrated sulfuric acid (20 ml) and cooled to 0 ± 10 °C. While maintaining this temperature a mixture of concentrated nitric acid (5 ml) and sulfuric acid (10 ml) was gradually added. The addition took 40 min., and when it was completed, stirring was continued for 1-1/4 hours while gradually warming the reaction mixture to 18 °C. After dilution with water and after centrifugation and repeated washings with hydrachloric acid, the nitrated polymer was pressed dry on filter paper and subsequently vacuum dried at 50-60 °C. The black product weighed 5.67g and failed to melt even at 375 °C. .

7C. A sample of polyphenylene (5g, $\emptyset\mathrm{Cl}(-)$, $\emptyset\mathrm{Cl}_3(+)$) was slurried in concentrated sulfuric acid (20 ml) and the mixture was cooled to about 10 °C. Concentrated nitric acid (20 ml) was then carefully added over a 40 min. period while maintaining the temperature at 0 ± 5 °C. Heat was then applied and the temperature gradually rose from 5 °C to 45 °C over a 30 min. period, after which it was allowed to cool to 36 °C over the next 45 min. Upon completion of the reaction the mixture was diluted with a large volume of water and the product was collected by centrifugation. It was then repeatedly washed with hydrochloric acid and repeatedly centrifuged. After partial drying on filter papers, the black polymer was thoroughly dried in vacuum at 50-60 °C. It weighed 6.62g.

10A. Polyphenylene (4.68g, 140 mesh, melting range 170-200 °C, $\overline{\mathrm{M.\,W.}} \simeq 1200\text{-}1400$) was gradually added to a mixture of concentrated sulfuric acid (20 ml) and concentrated nitric acid (20 ml) at about 30 °C. The heat of reaction caused a small temperature rise to about 40 °C. After stirring for 3 hours the mixture was diluted with water, then filtered. The nitrated polymer then was repeatedly washed with water and refiltered. After drying under vacuum at about 60 ° - 70 °C the resin weighed 6.66 grams indicating about 68 percent of the rings were nitrated. It failed to melt at 400 °C.

10B. Polyphenylene (5.00g, melting range 95-150 C, $\overline{\text{M. W.}}$ < 500) was slurried in a mixture of concentrated sulfuric acid (20 ml) and concentrated nitric acid (20 ml) at about 10°C. The mixture was stirred for 2 hours, then diluted with water, and the tarry product was repeatedly washed by decantation. After vacuum drying, the product weighed 4.16g and melted at 90-130°C. This weight is not indicative of the actual final weight because volatile products were lost during the vacuum drying process.

10D. Polyphenylene (5g, melting range 250-320°C) was gradually added to a mixture of concentrated nitric acid (20 ml) and concentrated sulfuric acid (20 ml) at 15 ± 5°C. When the addition was completed the temperature rose to 36 °C but was lowered again to 13 °C. After 15 minutes the reaction mixture was diluted with water and the polymer was collected by filtration. It was repeatedly washed, then vacuum dried. The product weighed 6.3g and melted at 234->400°C.

11A. Reactants used in this experiment were the same as in 10D above. The reaction period was 1/2 hour with the temperature being maintained at 30 ± 10 °C. After clean-up as previously described the polymer weighed 6.2 grams. Based upon weight of the product 38 percent of the rings were nitrated. Partial melting occurred over 229 °C but complete melting was not observed at 400 °C.

11C. Reactants used in this experiment were the same as those used in 10D above. The polymer addition was made at 5 °C and the temperature rose to 15 °C. After 10 minutes at 10-15 °C the reaction was stopped by pouring the reaction mixture into a large volume of water. Polymer was collected by filtration, thoroughly water washed, and vacuum dried. It weighed 5.74g and melted partially above 295°C but failed to melt completely at 400 °C. Based upon the weight of product about 25 percent of the rings were nitrated.

C-2943-18-4. Polyphenylene (5.0g., melting range 250-320 °C) was slurried in a mixture of concentrated nitric acid (20 ml) and concentrated sulfuric acid (20 ml) at a temperature of -40° to -50°C. The reaction mixture was stirred for 20 minutes while maintaining the temperature as indicated. The mixture was then poured into a large volume of water and the precipitated polymer collected by filtration. It was then washed twice with distilled water, twice with 10 percent aqueous NaOH and several times again with water. After drying at 100 °C under vacuum the resin weighed 4.83g. and melted at 255-303°C.

Nitration of Polyphenylene with Red Fuming Nitric Acid (C-2943)

18-2. Polyphenylene (5.0g, melting range 250-320°C) was slurried in red fuming nitric acid (30 ml) and reacted at 0-10°C for 10 minutes. The reaction mixture was then diluted with water and centrifuged. After repeated washings and centrifugations the polymer was dried at 100 °C under vacuum. It weighed 6.15g and melted partially between 247 ° and 400 °C. Complete melting did not occur. Based upon the weight gain an estimated 39 percent of the rings had been nitrated.

18-3. A second nitration was carried out using the same reactants and conditions as used in 18-2 above except that the reaction was run for 1 hour. In this case the nitrated polymer weighed 6.9g and melted partially between 255 ° and 400 °C. Total melting did not occur. Based upon the weight gain an estimated 58 percent of the rings were nitrated.

18-1. A third nitration was carried out using the same reactants and clean up procedures as in 18-2 and 18-3 above except that in this case a 30 minute reaction period at 0-10 °C was used. The dried nitrated polymer weighed 6.66 grams and partially melted between 240° and 410°C. Total melting was not observed. Based upon weight gain approximately 54 percent of the rings had been nitrated.

Preparation of Aminated Polyphenylene. C2426-8B.

Polyphenylene (5g, ϕCl(-), ϕCl_3(+)) was added to a solution of nitric acid (20 ml) and sulfuric acid (20 ml) maintained at 5 ± 5°C. After the polymer was thoroughly dispersed, the slurry was heated to 50°C over a 3/4 hr. period and allowed to cool to 43°C over the next hour. It was then stirred overnight at ambient temperature and was subsequently diluted with water (300 ml). The nitrated polymer was collected by centrifugation and suspended in a solution of water (200 ml) and hydrochloric acid (25 ml, 12N). Mossy zinc (5g) and powdered tin (5g) were then added over a 2-3 hr. period, and the mixture was collected and meticulously washed with concentrated ammonium hydroxide to remove inorganic residues. After vacuum drying at 60°C the polymer weighed 11.2g, which indicated it still contained inorganic residues.

The crude polymer was then extracted continuously for 3 days with boiling chlorobenzene and 1.28g. of extractable polymer was isolated (23% yield assuming 5.5g of nitrated polymer had been formed). A subsequent extraction with boiling trichlorobenzene failed to yield additional product.

Reaction of Polyphenylene with Phosgene (C-1951-47)

A 100 ml flask was fitted with a Teflon-blade stirrer, a dry ice condenser, and a thermometer. In the flask were placed 3.8g of polyphenylene (0.050 mole calc. as monomer) (insoluble in boiling chlorobenzene but soluble in boiling trichlorobenzene, finer than 80 mesh), 6.7g (0.05 mole) of granular aluminum chloride, 19 ml of 1,2,4-trichlorobenzene, and 9.9g (0.100 mole) of liquid phosgene. The mixture was heated at 60 to 70°C with stirring for 7 to 8 hours, after which the unreacted phosgene was allowed to distill during the next 7 hours at 60 to 70°C. The mixture was poured into a dilute hydrochloric acid solution, which was then filtered by gravity. The solid was suspended in boiling water for some time to steam-distill the organic solvent. Sodium hydroxide was added, and the alkaline mixture was held at 80 °C for 30 minutes and filtered. The light yellow filtrate was acidified with hydrochloric acid, which caused the separation of 1.8g. of white solid melting at 126-149 °C (uncorr., block). The brown solid recovered weighed 6.8g. These weights were measured after drying in air.

Acetylation of Polyphenylene (C-1951-31, 49)

20 percent Acetylation. A 100 ml. flask was fitted with a Teflon-blade stirrer, a condenser, and a thermometer. In the flask were placed 3.8g (0.05 mole or monomer) of polyphenylene (same as above, C-1951-47), 0.72 ml (0.79g, 0.010 mole) of acetyl chloride, and 19 ml of 1,2,4-trichlorobenzene. Aluminum chloride (1.7g, 0.013 mole) was added with stirring and the mixture was heated at 60 °C for 8 hours and then was stirred at room temperature for 16 hours. The mixture was poured onto hydrochloric acid and ice, and the organic solvent was then steam-distilled. The solid was filtered off, boiled with water to remove acid, and filtered again. The yield after air-drying was 4.50g (18 percent increase in weight). When the solid was placed on a melting point block, it started to melt at 317 °C. The amount of liquid increased up to 365 °C, but then the liquid resolidified. There was no further melting up to 400 °C.

40 percent Acetylation. This was carried out in the same apparatus, on double the scale. In the flask were placed 7.6g (0.10 mole of monomer) of polyphenylene, 2.88 ml (3.14g, 0.040 mole) of acetyl chloride, 38 ml of 1,2,4-trichlorobenzene, and 6.8g (0.052 mole) of aluminum chloride. The mixture was heated at 60-70 °C with stirring for 17 hours and then was worked up as above. To make sure the product was free of aluminum salts, it was heated to boiling twice with concentrated hydrochloric acid and twice with

water. After drying in vacuum the yield was 12.3g (62 percent increase in weight). The product was then held at 100°C under vacuum (about 1 torr) for 24 hours to remove adhering solvent; the yield was then 8.92g (17 percent increase in weight).

Dichromate Oxidation of Acetylated Polyphenylene (C-1951-40)

A mixture of 0.928g of 40 percent acetylated polyphenylene (0.004 mole of acetyl if pure) in 20 ml of glacial acetic acid was treated with 4.77g (0.016 mole) of powdered sodium dichromate dihydrate (technical grade) and then refluxed (115°C) for 25 hours. The reaction mixture was then poured into 200 ml of water and filtered (the filtrate was green from reduced dichromate). The brown precipitate was washed with water and then treated with sodium hydroxide solution. After removing the insoluble material, the solution was acidified with hydrochloric acid. The brown solid which formed was filtered off, washed, and dried in air. The yield of 0.168g was 18 percent of the starting material.

Permanganate Oxidation of Acetylated Polyphenylene (C-1951-43)

A mixture of 0.928g of 40 percent acetylated polyphenylene (0.004 mole of acetyl if pure), 2.09g (0.0132 mole) of potassium permanganate, 30 ml of water, and 0.052g (0.0013 mole) of sodium hydroxide was heated at 95-100°C with stirring for 40 hours. It was then filtered by gravity and the residue was washed with water. The filtrate and wash liquid were acidified with hydrochloric acid. Only about 0.020g of solid separated.

Hypobromite Oxidation of Acetylated Polyphenylene (C-1951-35)

A mixture of 0.844g of 20 percent acetylated polyphenylene (0.002 mole of acetyl if pure), 7 ml of pyridine, 7 ml of 25 percent (w/v) aqueous sodium hydroxide solution, and 0.55 ml (1.71g, 0.0107 mole) of bromine was stirred at room temperature for 16 hours. After addition of 1.2g of sodium bisulfite the mixture was filtered and the filtrate acidified. The brown precipitate which formed was filtered off and dried in air; yield, 0.070g.

Hypochlorite Oxidation of Acetylated Polyphenylene (C-1951-41)

A solution made by dissolving 3.52g (0.088 mole) of sodium hydroxide in 24 ml of water, cooling to room temperature, and bubbling in 2.72g (0.0384 mole) of chlorine gas was added to a mixture of 0.928g of 40 percent acetylated polyphenylene (0.004 mole of acetyl if pure) and 24 ml of pyridine. The mixture was stirred at 70-75°C for 40 hours and then filtered. The filtrate was acidified and the precipitate was collected, redissolved in aqueous sodium hydroxide solution (not all the precipitate redissolved), and reprecipitated. The product was filtered off and dried in air. The yield of 0.200g was 22 percent of the starting material.

Hypobromite Oxidation of Acetylated Polyphenylene (C-1951-52)

To a mixture of 0.928g of 40 percent acetylated polyphenylene (0.004 mole of acetyl if pure) in 24 ml of pyridine was added a solution made by dissolving 3.52g (0.088 mole) of sodium hydroxide in 24 ml of water and adding 6.14g (0.0384 mole) of bromine. The mixture was stirred at 70-75°C for 22 hours and then filtered. After treatment with sodium bisulfite, the filtrate was acidified and the precipitate collected. The precipitate was redissolved in aqueous sodium hydroxide solution (not all the precipitate dissolved) and reprecipitated by acidification. The product was filtered off, washed with water, and dried in air. The yield of 0.240g was 26 percent of the starting material.

Hypochlorite Oxidation of Acetylated Polyphenylene (C-2943-30-A)

A solution made by dissolving 3.52g (0.088 mole) of sodium hydroxide in 24 ml of water, cooling to room temperature, and bubbling in 2.72g (0.0384 mole) of chlorine gas, was added to a mixture of 0.928g of 40 percent acetylated polyphenylene (0.004 mole of acetyl if pure) and 24 ml of pyridine. The mixture was stirred and refluxed

(96 °C) for 45 hours and then filtered. After acidification, the precipitate was collected, redissolved in aqueous sodium hydroxide solution, and reprecipitated. The product was filtered off and dried in air. The yield of 0.580g was 62 percent of the starting material.

Polyphenylenecarboxamide (C-2943-45-A)

A mixture of 0.522g of carboxylated polyphenylene (derived from 40 percent acetylated polyphenylene, and containing 0.00223 mole of carboxyl group if pure) in 2.5 ml (4.1g, 0.034 mole) of thionyl chloride was refluxed 2 hours and then poured into 10 ml of cold concentrated ammonium hydroxide solution. The precipitate was filtered off and washed with water until the wash liquid was neutral. The yield of dried product was 0.341g, which is 65 percent of the starting material.

Synthesis of Acetylated Polyphenylene (D1516-20A)

Polyphenylene (50g, 0.67 mole) with a mean molecular weight of 2000 ± 500, acetyl chloride (19 ml, 20.3g, 0.26 mole) and anhydrous aluminum chloride (45g, 0.34 mole) were stirred in trichlorobenzene (250 ml) for 17 hours at 60-70 °C. Hydrogen chloride evolution continued for 2 hours. The crude produce was washed several times with concentrated hydrochloric acid then naphtha. After vacuum drying at 150°C, the product weighed 53.9g. Based upon the 3.9g weight increase observed the polymer contained 14 percent acetyl groups by weight.

Synthesis of Polyphenylenecarboxylic Acid (D1516-20B)

Chlorine gas (73g. 1.04 moles) was bubbled into aqueous sodium hydroxide (95g, 2.4 mole/650 ml H_2O) at room temperature. The sodium hypochlorite thus prepared was then added to a sample (25g) of 14 percent acetylated polyphenylene suspended in pyridine. After stirring and heating at 96 °C for 45 hours the reaction mixture was acidified with aqueous hydrochloric acid and filtered. The polymer was washed with dilute alkali, then again with dilute acid. After drying under vacuum the polymer weighed 28.2g (27.2g theory).

Synthesis of Polyphenylenecarboxylic Acid Amide (D1516-20C)

Carboxylated polyphenylene (25g, ≈ 0.113 mole CO_2H) was mixed with thionyl chloride (196g, 1.62 mole) and heated at reflux for 4 hours. The reaction mixture was poured over cold concentrated aqueous ammonia (500 ml) and the precipitated amide was collected by filtration and washed until neutral. After vacuum drying the amide weighed 23.0g.

III. MATERIALS EVALUATION

All plasma arc test specimens which were evaluated in this program were reinforced with Carbon cloth (Hitco CCA-1) or Refrasil (C-100-48). Most specimens contained the former. In fabricating these samples efforts were made to produce laminates with an ultimate resin content of 40 percent after postcure and most specimens ended up in the range of 40 ±5 percent although in several instances resin contents were as high as 62 percent. The variations were of course attributed to the experimental nature of these resins and the lack of information of their flow properties, optimum molding temperatures and pressures. In some cases the resin content was high because of the additional "resin" consisting of biphenyldisulfonic acid on the treated carbon fabrics. Special care must be taken, therefore, in comparing plasma arc test results of unknowns with standards. When resin content varies from the standards excessively comparisons are not warranted. The plasma arc test results are useful nevertheless if corresponding unknowns are compared. Many of the preferred curing techniques were also selected in part on the quality of the composite structures as determined visually. The importance of resin content variation is exemplified very well by comparing data from samples C2943-68-3 and -68-4. In these instances the resin is the same but the former has 45 percent resin whereas the latter has only 35 percent.

Plasma arc tests were carried out using a heat flux of 550 BTU/ft^2/sec. and a plasma of reconstituted air (20 percent O_2 + 80 percent N_2). Test duration was 60 seconds except in the case of the two 3/4 inch diameter specimens. These specimens were only 1/4 inch thick rather than the usual 1/2 inch and thus tests were shortened to 30 seconds.

The best plasma test results were obtained with composites made from polyphenylene lacquers. Those made from dry resin lay-ups were invariably inferior but the procedure had to be used when lacquers were not feasible. Results of plasma arc tests are presented in detail in Table IV as well as in a condensed form in Table V. Data in the latter table is average data, from duplicate samples.

Specimen No.	Composition						Fabrication Parameters					Composition After Postcure		Weig	
	Resin		Curing Agent		Reinforcement										
	Number	Weight	Benzene-trisulfonyl Chloride	Biphenyl-disulfonic Acid	Carbon Cloth	Refrasil C100-48	No. of Plies	Charge Wt. grams	Molded Wt. grams	Weight After Postcure	% Weight Loss in Postcure	% Resin	Reinforcement	Before	Aft
3/4" Diameter Specimens - Carbon Cloth															
D1516-19	D1516-19	50	25	--	untreated		20	2.63	2.55	2.48	2.8	42.3	57.7	2.6	1.
91LD	91LD		--	--	untreated		42	6.25	6.05	5.80	4.1	42.5	57.9*	2.4	1.
2" Diameter Specimens - Carbon Cloth															
C2943-40A-1	C2943-40A	40	--	40	C2943-37			61.8	39.4					28.3	21.
-40A-2	-40A	40	--	40	-37									26.9	19.
-59-1	-59	48	--	48	-61B		30	67.36	48.22	42.19	12.5	58.5	41.5	28.5	20.
-59-2	-59	48	--	48	-61B		30	67.18	43.66	38.59	11.6	54.7	45.3	29.2	21.
91LD-1	91LD		--	--	untreated		32	35.95	35.45	34.00	4.1	45.4	54.6*	33.6	24.
91LD-2	91LD		--	--	untreated		32	34.96	34.52	33.60	2.7	44.8	55.2*	33.5	23.
1" Diameter Specimens - Carbon Cloth															
-65-B$_4$	-65B	56	28	--	-69A		34	18.14	16.20	13.21	18.5	61.4	38.6*	5.5	3.
-65-B$_3$	-65B	56	28	--	-69A		34	18.15	16.22	13.56	16.4	62.4	37.6*	6.4	3.
-65-B'$_2$	-65B	56	28	--	-66A		34	14.84	12.18	10.12	16.9	49.6	50.4*	6.6	3.
-65-B'$_1$	-65B	56	28	--	-66A		34	18.29	15.33	13.22	13.8	61.4	39.6*	6.1	3.
-65-B'$_6$	-65B	56	28	--	-66A		34	13.92	12.52	10.34	17.4	50.7	49.3*	6.2	3.
-68-1	-68	54	--	36	-71A-1		34	14.92	13.16	10.78	18.1	52.7	47.3*	6.2	3.
-68-2	-68	54	--	36	-71A-2		34	15.22	12.74	10.34	18.8	50.7	49.3*	6.3	3.
-71B-1	-71B	27	10	--	-66A		76	31.90	30.73	24.95	18.8	54.3	45.7*	6.3	3.
-71B-2	-71B	27	10	--	-66A		76	31.90	30.73	24.95	18.8	54.3	45.7*	6.4	3.
-76A-1	-76A	32	8	16	-71A-2		70	35.80	33.47	26.53	20.7	60.4	39.6*	5.6	2.
-76A-2	-76A	32	8	16	-71A-2		70	35.80	33.47	26.53	20.7	60.4	39.6*	5.6	2.
-66-B$_1$	-66B	50	25	--	untreated		34	8.83	8.75	8.07	7.8	3.93	60.7	7.3	4.
-66-B$_2$	-66B	50	25	--	untreated		38	9.28	9.16	8.40	8.3	38.7	61.3	7.4	5.
-66-B$_3$	-66B	50	25	--	untreated		38	9.54	9.42	8.62	8.5	38.6	61.4	7.3	4.
91LD-3-1	91LD		--	--	untreated		40	9.82	9.63	9.49	1.5	39.9	60.1	7.3	4.
91LD-5-2	91LD		--	--	untreated		74	19.29	18.75	18.50	1.3	39.5	60.5	7.3	4.4
1" Diameter Specimens - Refrasil Cloth															
C2943-65B"-1	C2943-65B	56	28	--		X	20	12.48	11.79	11.02	6.5	38.3	61.7*	7.5	6.0
-65B"-2	-65B	56	28	--		X	20	12.51	11.85	10.96	7.5	38.0	62.0	7.5	6.2
-68-3	-68	54	--	36		X	20	12.28	9.68	9.28	4.1	46.7	53.3*	8.4	4.8
-68-4	-68	54	--	36		X	46	28.64	27.22	24.15	11.3	35.2	64.8*	7.7	6.8
D1516-24-1$_1$	D1516-24-1	20	10	--		X	24	12.44	12.14	11.37	6.3	34.8	65.2	8.4	7.
-24-1$_2$	-24-1	20	10	--		X	24	12.40	11.70	11.24	3.9	34.3	65.7	8.5	7.6
-24-2$_1$	-24-2	24	8	--		X	24	12.52	12.18	11.52	5.4	36.1	63.9	8.5	8.
-24-2$_2$	-24-2	24	8	--		X	24	12.62	12.08	11.50	4.8	35.5	64.5	8.4	7.
-24-3$_1$	-24-3	24	6	--		X	24	12.48	12.18	11.50	5.6	35.8	64.2	8.4	7.
-24-3$_2$	-24-3	24	6	--		X	24	12.48	11.94	11.48	3.9	35.7	64.3	8.4	7.6
91LD-2-1	91LD		--	--		X	48	28.00	27.21	26.29	3.4	39.9	60.1	8.5	7.1
91LD-2-2	91LD		--	--		X	48	28.00	27.35	26.46	3.3	40.3	59.7	8.3	6.

*Based on estimated weight of reinforcement. Reinforcements which were treated to improvement wetting lost weight during cure and consequently the % reinforcem

†Only 30 sec. duration

Table IV. Specimen fabrication parameter plasma arc test results.

n Parameters			Composition After Postcure		Plasma Arc Test Data (60 sec.)													
lded Wt. ams	Weight After Postcure	% Weight Loss in Postcure			Weight (grams)				Thickness (inches)				Volume (inches³)				Temp. °C	
			% Resin	Reinforcement	Before	After	Loss	% Loss	Before	After	Change	% Change	Before	After	Change	% Change	Front	Back
3/4" Diameter Specimens - Carbon Cloth																		
.55	2.48	2.8	42.3	57.7	2.6	1.3	1.3	50	0.239	0.137	0.102	42.7	0.1058	0.0698	0.0360	34.0	2300	376†
.05	5.80	4.1	42.5	57.9*	2.4	1.2	1.2	50	0.239	0.172	0.067	28.0	0.1058	0.0820	0.0239	22.5	2280	369†
2" Diameter Specimens - Carbon Cloth																		
.4					28.3	21.3	7.0	25	0.478	0.339	0.139	29.1	1.501	1.362	0.175	11.7	2360	277
					26.9	19.1	7.8	29	0.472	0.326	0.146	30.9	1.482	1.261	0.221	14.9	2280	245
.22	42.19	12.5	58.5	41.5	28.5	20.8	7.7	27	0.479	0.312	0.167	34.9	1.504	1.275	0.229	15.2	2300	300
.66	38.59	11.6	54.7	45.3	29.2	21.6	7.6	26	0.480	0.336	0.144	30.0	1.507	1.250	0.257	17.1	2280	361
5.45	34.00	4.1	45.4	54.6*	33.6	24.3	9.3	28	0.475	0.367	0.108	22.7	1.492	1.388	0.104	7.0	2320	277
4.52	33.60	2.7	44.8	55.2*	33.5	23.7	9.8	29	0.476	0.386	0.090	18.9	1.495	1.415	0.080	5.4	2380	249
1" Diameter Specimens - Carbon Cloth																		
6.20	13.21	18.5	61.4	38.6*	5.5	3.0	2.5	45	0.406	0.190	0.216	53.2	0.319	0.142	0.177	55.2	2295	533
16.22	13.56	16.4	62.4	37.6*	6.4	3.7	2.7	42	0.407	0.249	0.158	38.8	0.320	0.173	0.147	45.9	2220	871+
.18	10.12	16.9	49.6	50.4*	6.6	3.2	3.4	52	0.409	0.252	0.157	38.3	0.321	0.171	0.150	46.7	2300	486
5.33	13.22	13.8	61.4	38.6*	6.1	3.3	2.8	46	0.405	0.211	0.194	47.9	0.318	0.163	0.155	48.7	2360	871+
2.52	10.34	17.4	50.7	49.3*	6.2	3.5	2.7	43	0.408	0.211	0.197	48.2	0.321	0.170	0.151	47.0	2320	784
3.16	10.78	18.1	52.7	47.3*	6.2	3.9	2.3	37	0.407	0.250	0.157	38.5	0.320	0.189	0.131	40.9	2295	467
2.74	10.34	18.8	50.7	49.3*	6.3	3.9	2.4	38	0.406	0.273	0.133	32.7	0.319	0.193	0.126	39.4	2200	281
0.73	24.95	18.8	54.3	45.7*	6.3	3.6	2.7	43	0.403	0.214	0.189	46.8	0.318	0.171	0.147	46.2	2300	495
0.73	24.95	18.8	54.3	45.7*	6.4	3.9	2.5	39	0.407	0.248	0.159	39.0	0.320	0.186	0.134	41.8	2130	411
3.47	26.53	20.7	60.4	39.6*	5.6	2.9	2.7	48	0.407	0.188	0.219	53.8	0.320	0.141	0.179	55.9	2340	622
3.47	26.53	20.7	60.4	39.6*	5.6	2.9	2.7	48	0.408	0.209	0.199	48.7	0.321	0.145	0.176	54.8	2380	519
8.75	8.07	7.8	3.93	60.7	7.3	4.7	2.6	36	0.403	0.259	0.144	35.7	0.318	0.219	0.099	31.1	2335	804
9.16	8.40	8.3	38.7	61.3	7.4	5.1	2.3	32	0.406	0.278	0.126	31.5	0.318	0.228	0.091	28.5	2350	339
9.42	8.62	8.5	38.6	61.4	7.3	4.9	2.4	33	0.406	0.271	0.135	33.2	0.319	0.230	0.089	27.8	2290	511
9.63	9.49	1.5	39.9	60.1	7.3	4.3	3.0	42	0.405	0.304	0.101	24.9	0.318	0.206	0.112	35.2	2390	195
8.75	18.50	1.3	39.5	60.5	7.3	4.4	2.9	40	0.405	0.269	0.136	33.5	0.318	0.221	0.097	30.5	2360	198
1" Diameter Specimens - Refrasil Cloth																		
2.79	11.92	6.5	38.3	61.7*	7.5	6.0	1.5	20	0.404	0.203	0.201	49.7	0.317	0.232	0.085	26.8	2140	open T. C.
1.85	10.96	7.5	38.0	62.0	7.5	6.2	1.3	17	0.397	0.242	0.155	39.0	0.312	0.239	0.073	23.3	2060	177
9.68	9.28	4.1	46.7	53.3*	8.4	4.8	3.6	43	0.407	0.223	0.184	45.2	0.320	0.171	0.149	46.5	2005	521
7.22	24.15	11.3	35.2	64.8*	7.7	6.8	0.8	11	0.408	0.289	0.119	29.1	0.321	0.267	0.054	16.8	2070	177
2.14	11.37	6.3	34.8	65.2	8.4	7.6	0.8	10	0.405	0.273	0.132	34.[illegible]	0.318	0.276	0.012	13.2	2050	222
1.70	11.24	3.9	34.3	65.7	8.5	7.6	0.9	10	0.407	0.257	0.150	36.8	0.320	0.276	0.044	13.7	2090	196
2.18	11.52	5.4	36.1	63.9	3.5	8.1	0.4	5	0.405	0.301	0.104	25.6	0.318	0.291	0.027	8.4	2040	181
2.08	11.50	4.8	35.5	64.5	8.4	7.5	0.9	10	0.407	0.249	0.158	38.8	0.320	0.269	0.051	15.9	2100	179
2.18	11.50	5.6	35.8	64.2	8.4	7.8	0.6	7	0.405	0.278	0.127	31.3	0.318	0.273	0.045	14.1	2065	372
1.94	11.48	3.9	35.7	64.3	8.4	7.6	0.8	9	0.404	0.295	0.109	26.9	0.317	0.265	0.052	16.4	2050	141
7.21	26.29	3.4	39.9	60.1	8.5	7.1	1.4	16	0.407	0.305	0.102	25.0	0.320	0.281	0.039	12.1	2100	132
7.35	26.46	3.3	40.3	59.7	8.3	6.7	1.6	20	0.406	0.260	0.146	35.9	0.319	0.257	0.062	19.4	2065	197

ng lost weight during cure and consequently the % reinforcement is only approximate.

IV. Specimen fabrication parameters and plasma arc test results.

1

2

Specimen	% Resin	% Weight Loss	% Thickness Change	% Volume Change
3/4" - Carbon Cloth				
D1516-19	42	50	43	34
91LD	42	50	28	23
2" - Carbon Cloth				
2943-40A		27	30	13
-59	56	27	32	16
91LD	45	28	21	6
1" - Carbon Cloth				
2943-65B	62	43	43	50
-65B'	50	47	44	47
-68	52	37	36	40
-71B	54	41	43	44
-76A	60	48	51	55
-66B	39	34	33	29
91LD	40	41	29	32
1" - Refrasil Cloth				
2943-65B"	38	18	45	25
-68-3	47	43	45	46
-68-4	35	11	29	17
-24-1	34	10	35	13
-24-2	36	8	33	12
-24-3	36	8	29	15
91LD	40	18	30	16

Table V. Condensed data on plasma arc tests of polyphenylene composites.

IV. ROCKET NOZZLE FABRICATION

One experimental rocket nozzle was prepared during the course of this program. The resin used in its preparation was a chloroform soluble resin derived from a fusible polyphenylene with a mean molecular weight of 1000 and a melting point of 170-200°C. The curing agent used therein was benzenetrisulfonyl chloride.

The postcured nozzle contained 40 percent resin solids and 60 percent carbon cloth (CCA-1, H. I. Thompson Co.) A data sheet on the fabrication process is shown on the following page. Nozzle specifications are described in an earlier report.[13]

ROCKET NOZZLE FABRICATION PARAMETERS
Contract No. AF 33(615)-3479

Reference N. Bilow - L. Miller

Data Sheet No. ______

Code No. ______

Sample Type Nozzle Insert

MATERIALS

	Designation	Source	% by Wt
Resin	Polyphenylene - C2943-66-B	HAC	40
Reinforcement	Carbon Cloth CCA-1	HITCO	60
Filler			

PROCEDURE

Raw Material Preparation Oven dry carbon cloth at 240°F. Lacquer used as received, impregnate cloth with spatula method

Coating Preparation **Wt Reinforcement** 109.4 gm ; **% Reinforcement Desired** 55 ; **Final Wt Desired** 202 gm

Batch No.	Composition of Coated Material	Pre-curing Conditions			
		30 Min Air Dry	20 Min at 160 °F	Min at °F	
1	Wt, gm		201.9		
	Resin Content-%		45.9		
2	Wt, gm				
	Resin Content-%				

Sample	1	2	3	4
No. of Plies	200			
Initial Wt, gm	140.0			
Wt Reinforcement, gm	75.78			
Contact Time, Min.	None			
Temperature, °F	400			
Pressure, psi	3000			
Cure Time, Min.	180			
Molded Wt, gm	137.2			
Resin Content, as molded wt-%	44.8			
Postcure wt, gm	126.4			
Final Resin Content wt-%	40			
Density, gm/cc	1.37			
Vol-% Voids in Resin	23.8			
Barcol Hardness				
Molded Thickness, in.				
Machined wt, gm	67.0			

Postcure 18 Hrs at 275°F, 96 hrs 275 to 752°F, cool to 200°F to remove. Argon atmosphere.

Remarks ______

Researcher J. Madden **Book No.** C2983 **Page No.** 62

V. REFERENCES

1. N. Bilow and L. J. Miller, "Synthesis of New Ablative Plastics for Rocket Nozzles. Part II. Polyaromatic Erosion-Resistant Plastics," ASD-TDR-63-56, January 1964.

2. N. Bilow and L. J. Miller, "Ablative Phenolic and Polyphenylene Resins," AFML-TR-65-8, March 1965.

3. D. W. Thomson and G. F. L. Ehlers, "Preparation and Properties of Aromatic Polysulfonates," ASD-TDR-63-53, March 1963.

4. Courtot and Lin, *Bull. Soc. Chim. France* (4), *49*, 1047 (1931).

5. N. Bilow and L. J. Miller, "Synthesis of New Ablative Plastics for Rocket Nozzles," ASD-TDR-63-56, January 1963.

6. J. Rahm and F. Juracka, *Chem. Listy*, *50*, 837 (1956); *Chem. Abs.*, *50*, 15475f (1956).

7. (a) E. B. McCall and R. J. Roberts, Brit. pat. 919,088, Feb. 20, 1963; (b) E. B. McCall and R. J. Roberts, Can. pat. 666,641, July 9, 1963; (c) P. J. S. Bain and E. B. McCall, Brit. pat. 959,605, June 3, 1964; (d) E. B. McCall and W. Cummings, Brit. pat. 964,543, July 22, 1964; (e) E. B. McCall and W. Cummings, Brit. pat. 970,911, Sept. 23, 1964; (f) E. B. McCall and S. A. Hughes, Brit. pat. 976,201, Nov. 25, 1964; (g) W. Cummings, Brit. pat. 976,611, Dec. 2, 1964; (h) E. B. McCall and R. J. Roberts, U. S. pat. 3,197,520, July 27, 1965; (i) E. B. McCall and W. Cummings, Brit. pat. 1,014,554, Dec. 31, 1965; (j) E. B. McCall and R. J. Roberts, U. S. pat. 3,231,629, Jan. 25, 1966.

8. (a) H. Meerwein et al., *Chem. Ber.*, *90*, 841 (1957); *Chem. Abs.*, *52*, 9003c (1958); (b) C. S. Marvel and P. D. Caesar,

J. Am. Chem. Soc., 73, 1097 (1951); (c) P.C. Dutla and D. Mandal, J. Indian Chem. Soc., 32, 339 (1955); Chem. Abs., 50, 9743i (1956).

9. W.H.C. Rueggeberg, R.K. Frantz and A. Ginsberg, Ind. Eng. Chem., 38, 624-626 (1946).

10. E.L. May and E. Mosettig, J. Am. Chem. Soc., 69, 3036-3037 (1947).

11. Cambron, Can. J. Research, 17B, 10 (1939).

12. Organic Reactions, Vol. I, p. 68, John Wiley and Sons, 1942.

13. N. Bilow, R.I. Akawie, and A.J. Tuckerman, Synthesis of New Plastics and Plastic Composites for Rocket Nozzles, ASD-TDR-62-326 April 1962.

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13. ABSTRACT

The object of this program was to obtain crosslinked polyphenylene resins through the identification of chemical curing agents and the development of curing processes. Improved resinous matrices of this type were expected to have improved ablative performance characteristics, mechanical properties, and processability.

Nitration, carboxylation, and sulfonation of polyphenylene polymers were accomplished in an effort to introduce reactive sites on the polymer for subsequent copolymerization or polymerization. Only the latter process yeilded a useful product. Suitable cures were obtained with a trifunctional sulfonyl chloride and a disulfonic acid.

A polyphenylene thermosetting resin was prepared by dissolving the aromatic sulfonyl chloride in chloroform lacquers of polyphenylene. The resin was then applied to carbon and high silica fabric, dried to a tacky state, plies cut and stacked in a mold, and then transformed into a hard composite by the application of heat and pressure. Ablative characteristics of the composite were determined, and benzene trisulfonylchloride cured polyphenylene was superior to the state-of-the-art phenol formaldehyde resins.

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Rocket Nozzles						
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