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Thermosetting Polyphenylene Resin-- Its Synthesis and Use in Ablative Composites†

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SUMMARY

The synthesis of tractable polyphenylenes and their conversion to thermosetting resins by curing with p-xylylene glycol is described as suitable for the fabrication of reinforced laminates. Ablative performance tests are correlated with composition and the method of preparation of the polymer.

INTRODUCTION

Polyphenylenes can be defined broadly as polymers with repeating units of six-carbon aromatic rings in groupings corresponding to those of benzene, biphenyl, terphenyls, quaterphenyls, triphenylene, etc., and mixtures of these polymers. They have been recognized as theoretically one of the most stable of organic materials. However, their potential usefulness as hyperthermal, high-char-forming structural materials could not be realized until fusible polyphenylenes with adequate molecular weights were synthesized [1] and incorporated into thermosetting resins.

Polyphenylenes with average molecular weights possibly in the range of 5000 to 10,000 were prepared by Marvel [2-4] and Kovacic [5-18] and their co-workers. In the approach used by Marvel and by Lefebvre and

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Dawans [19], polyphenylenes were prepared by the polymerization of 1,3-cyclohexadiene followed by oxidation or by halogenation and subsequent dehydrohalogenation. Both methods reportedly gave poly-p-phenylenes which were infusible and intractable. Although such polymers have no functional groups which would make them curable, unreinforced resin pellets have been made by compaction of these infusible powders [13-18]. However, the required high pressures and the abrasiveness of the infusible particles prevent the fabrication of fiber-reinforced composite structures.

Other approaches to the synthesis of polyphenylenes were referred to in our previous report [1]. Polymeric products that were obtained by previous workers were either incompletely aromatic, infusible, or too low in molecular weight to have useful properties. Since that time, Ried and Freitag [20] and Stille and co-workers [21] have reported the synthesis of a colorless, readily soluble, very high melting, highly branched polyphenylene with excellent thermal stability. From the data in their reports, it would appear that their polymer had an average molecular weight of about 20,000 or more.

Our previous paper [1] described the synthesis of fusible soluble polyphenylenes with average molecular weights up to 3000 by oxidative cationic polymerization of o- and m-terphenyl, biphenyl, 1,3,5-triphenylbenzene, mixtures of these compounds, and mixtures of these compounds with benzene. Usually, the reaction method of choice was to allow a mixture of biphenyl and m-terphenyl to react with anhydrous aluminum chloride and anhydrous cupric chloride in a melt at 100-130°C. The current paper includes some improvements in the polymerization technique which made the process more readily adaptable to large-scale preparations. It also presents a method for curing polyphenylenes with p-xylylene glycol and for providing thermosetting resins suitable for the fabrication of fabric-reinforced laminates. Results of ablative performance tests were correlated with the composition and the method of preparation of the resin. Comparisons with other types of resins on the basis of ablative data are also presented.

SYNTHESIS OF FUSIBLE POLYPHENYLENES

Readily processable polyphenylenes, which were both soluble and fusible, were prepared by oxidative cationic polymerization of monomers chosen specifically to give highly branched polymers. The method was essentially that described in our previous paper [1] with some modifications, as herein noted. Preferably, the monomers were m-terphenyl and mixtures of

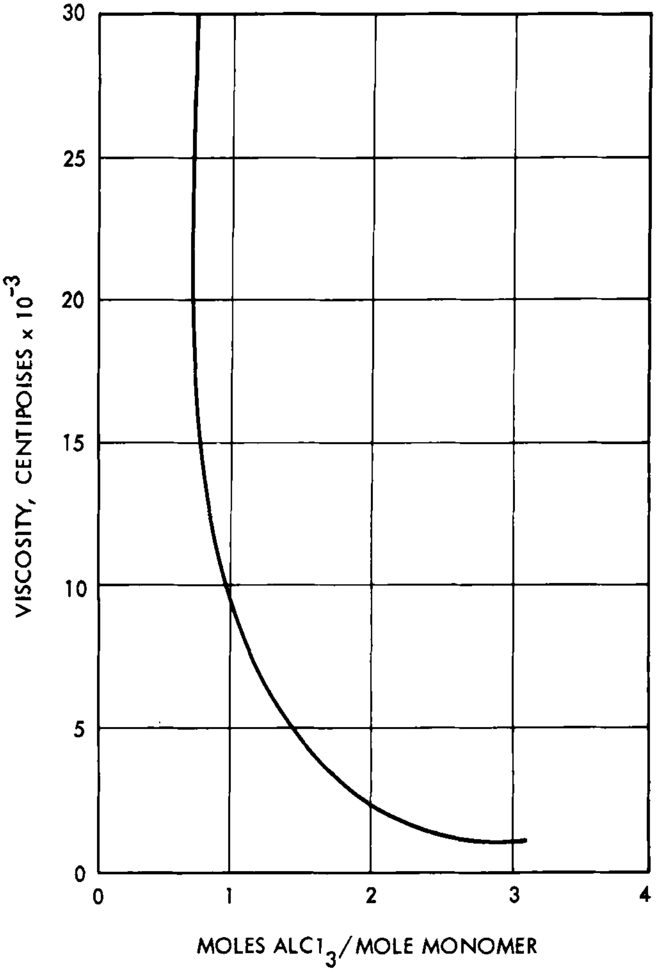


Fig. 1. Viscosity of m-terphenyl, biphenyl, aluminum chloride, and cupric chloride mixtures at the end of the reaction at 120°C.

m-terphenyl and biphenyl; the oxidant was cupric chloride, and the catalyst was aluminum chloride.

In bulk polymerizations, the problem of stirring was quite severe, and the molten polymer mass rapidly became too viscous to stir. A major decrease in viscosity was achieved by employing a molar excess of aluminum chloride relative to monomer. This effect probably can be attributed to the

Table 1. Typical Reaction Mixtures, Their Products, and Viscosities

Reactants[a]	Moles	Soluble portion, (10 vol % benzene-90 vol % naphtha)	Soluble portion,[b] % (chlorobenzene)	Insoluble portion,[b] % (chlorobenzene)	Melting point of chlorobenzene-soluble fraction, °C	Viscosity of reaction mixture at end of reaction,[c] cP
Biphenyl	0.13	64	18	18	154-230	Solid
m-Terphenyl	0.13					
$CuCl_2$	0.40					
$AlCl_3$	0.10					
Biphenyl	0.13	28	47	25	175-202	Estimated 2,000,000 to 3,000,000 Semisolid
m-Terphenyl	0.13					
$CuCl_2$	0.40					
$AlCl_3$	0.20					
Biphenyl	0.13	26	58	12	130-175	454,000
m-Terphenyl	0.13					
$CuCl_2$	0.40					
$AlCl_3$	0.40					
Biphenyl	0.13	24	30	44	150-184	151,000
m-Terphenyl	0.13					
$CuCl_2$	0.40					
$AlCl_3$	0.80					

Biphenyl	0.13	48	46	7	135-176	158,000
Santowax OMP[d]	0.13					
$CuCl_2$	0.40					
$AlCl_3$	0.40					
Biphenyl	0.40	18	52	31	132-177	447,000
$CuCl_2$	0.80					
$AlCl_3$	0.80					
Santowax OMP[d]	0.40	13	49	34	126-174	343,000
$CuCl_2$	0.80					
$AlCl_3$	0.80					

[a] Reaction time, 2 hr; temperature, 100°C.

[b] Soluble portion refers to portion extracted by continuous exhaustive process in a Soxhlet extraction apparatus. Chlorobenzene extractions followed the benzene-naphtha extractions.

Percent conversions are based on monomer. Yields based on $CuCl_2$ as the limiting reagent are higher values.

[c] Temperature was raised to 120°C for the viscosity measurements.

[d] Santowax OMP is a trade name of Monsanto Chemical Company. It consists of the ortho-, meta-, and para-isomers of terphenyl.

low fusion point of mixtures of the $AlCl_3$ • aromatic complex with excess aluminum chloride. Figure 1 illustrates the trend for a series of reactions in which only the aluminum chloride content was varied. Other data for these same reactions as well as for other typical preparations are presented in Table 1. It is apparent that the yield of useful, chlorobenzene-soluble polymer increased when the viscosity of the reaction mixture was reduced. Fluidity was a critical problem in preparing large quantities of polymer, and achieving greater fluidity was considered a significant improvement in the synthesis process.

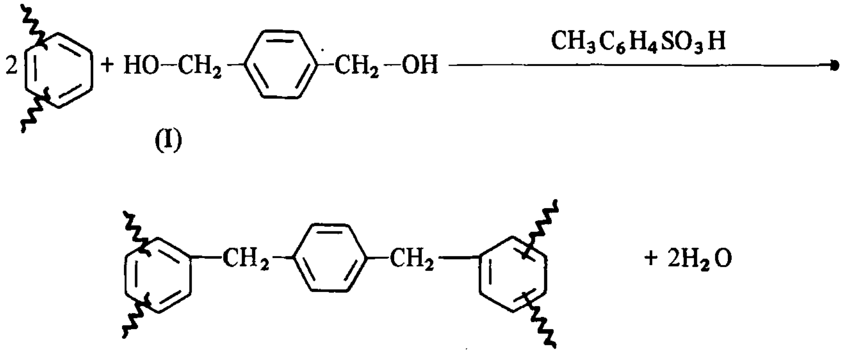
High reaction temperatures and long reaction periods tended to raise the yield of high molecular weight polymer. Generally, 3-4 hr at 100-200°C was sufficient to produce satisfactory yields (~30% based on the limiting reagent, cupric chloride) of chlorobenzene-extractable polymer in the 1000-1500 molecular weight range, whereas 6-10 hr at 130-150°C was preferred for the preparation of polymers in the 1800-2600 molecular weight range.

Temperature control in these preparations presented no serious problems, because the reactions were only mildly exothermic. Probably this was due in part to the evolution of gaseous hydrogen chloride, which cooled the reaction mixture. The most serious effect of poor temperature control was a diminished yield of useful polymer. Low temperatures (below 100°C) tended to produce larger quantities of polymer with very low molecular weights. Excessively high temperatures (about 170°C) caused large amounts of infusible polymer to form, and the fusible polymer fraction contained more chlorine than usual.

The initial reaction products were complex mixtures that had to be fractionated by suitable extraction procedures to isolate the useful polymer fraction [1]. With increased experience in the fabrication and testing of the cured resins, it became apparent that the most suitable fraction could be isolated by first removing the low molecular weight fractions by an exhaustive extraction with 10 vol % benzene-90 vol % naphtha mixture and then subjecting the residual polymer to extraction with chlorobenzene. The desired polymer fraction was the chlorobenzene-soluble portion.

CURING OF POLYPHENYLENES WITH p-XYLYLENE GLYCOL

Curing of the branched polyphenylenes was achieved by reaction of the polymer with a bis(hydroxymethyl)arene, such as p-xylylene glycol (I) or m-xylylene glycol, and an acid catalyst, such as p-toluenesulfonic acid. The overall reaction is illustrated below:

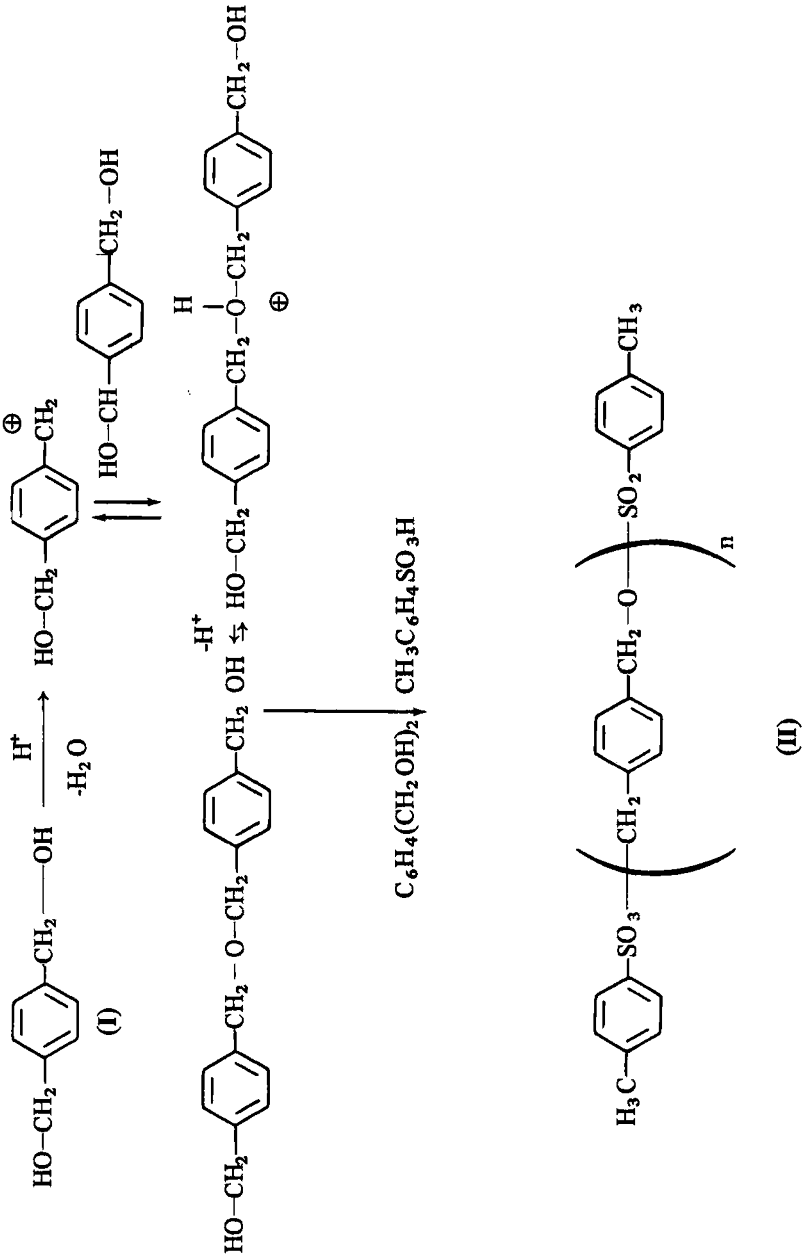


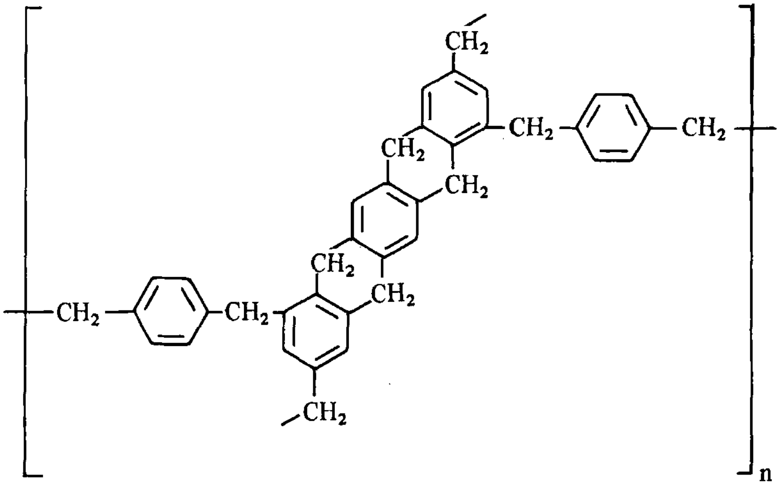
Initially, attempts were made to cure the polyphenylenes by molding intimate mixtures of polyphenylenes, p-xylylene glycol, and p-toluenesulfonic acid. However, these mixtures yielded poor products due to their heterogeneous nature at their melting points. To overcome this limitation, the xylylene glycol and the acid catalyst were converted into a reactive telomeric intermediate which was miscible with polyphenylene solutions and polyphenylene melts. p-Xylylene glycol and p-toluenesulfonic acid were heated in chloroform at reflux for 20-40 hr, and the water formed during the reaction was removed as the water-chloroform azeotrope. The proposed structure of the chloroform-soluble telomeric product (II) and the mechanism of its formation are indicated.

Based on the water evolved in the reaction, there were about three to four xylylene glycol units per chain. For the telomer (II) in which n = 4, the calculated molecular weight would be 806. This molecular weight has been verified experimentally.

The xylylene glycol telomer was quite sensitive to heat. When it was heated above 100°C for several minutes, it first formed a chloroform-insoluble white polymer and then rapidly converted to a very hard, black, insoluble, infusible resin. Both of the latter were useless as curing agents. The insoluble white polymer probably was a cross-linked or high molecular weight polyether similar to (II). A plausible structure for the black resin is (III). This structure contains ladder-like polymer moieties as well as nonladder methylene-bridged moieties.

Alternative solvents and catalysts were studied briefly. Higher boiling solvents, such as trichloroethylene and 1,1,2,2-tetrachloroethane, accelerated the reaction. Although the former solvent was satisfactory,


(I)
H^+
$-H_2O$
$-H^+$
$C_6H_4(CH_2OH)_2$
$CH_3C_6H_4SO_3H$
n
(II)

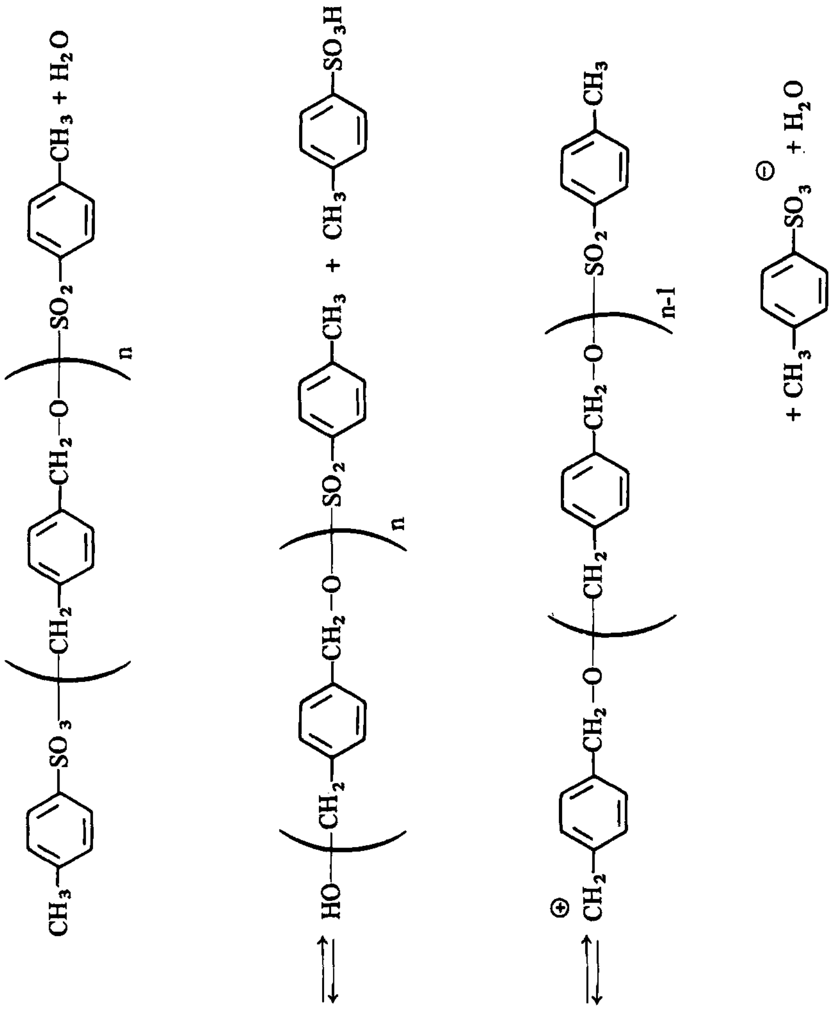


(III)

excessive polymerization could scarcely be avoided in the latter. The telomeric curing agent could also be prepared in a melt of the glycol and the acid catalyst, but the reaction was even more difficult to control. A sulfinic acid, such as benzenesulfinic acid, was approximately as effective as a sulfonic acid, whereas p-bromobenzenesulfonyl chloride and methyl p-toluenesulfonate were less effective and required more strenuous reaction conditions. Benzoic acid, oxalic acid, benzoyl chloride, perfluorooctanoyl chloride, and heptafluorobutyric anhydride, with or without additional water, were ineffective.

Chloroform solutions of the curing agent were blended with solutions of the polyphenylene in suitable halogenated solvents, such as chloroform, trichloroethylene, or chlorobenzene. The homogeneous solutions thus obtained were subsequently heated at 70-80°C for an extended period of time, preferably about 20 hr. Under these conditions, the curing agent and polyphenylene reacted to form an A-stage thermosetting copolymer. The reactions which occurred during this process as well as the reactions which occurred during final cure are shown on the following pages.

Adventitious moisture is present in sufficient quantity to initiate the process, which then generates water to continue the process.



(1)

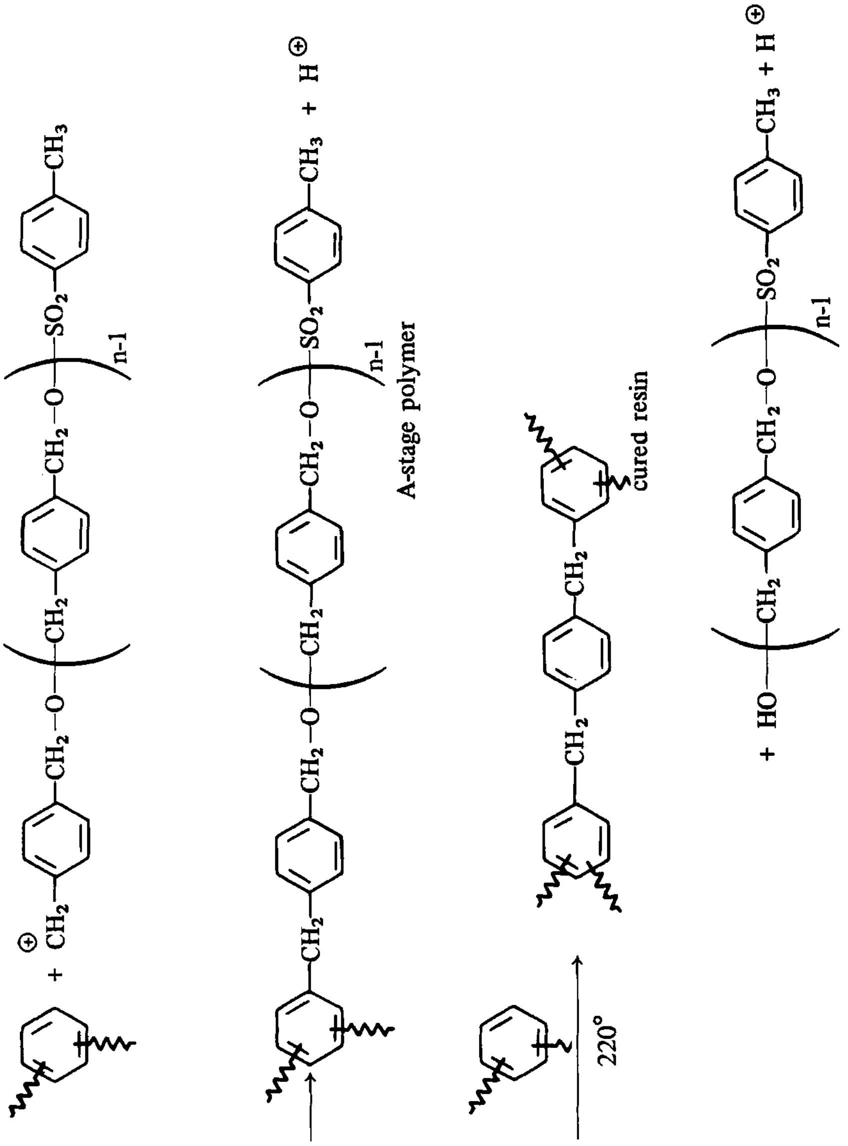
(2)

(3)

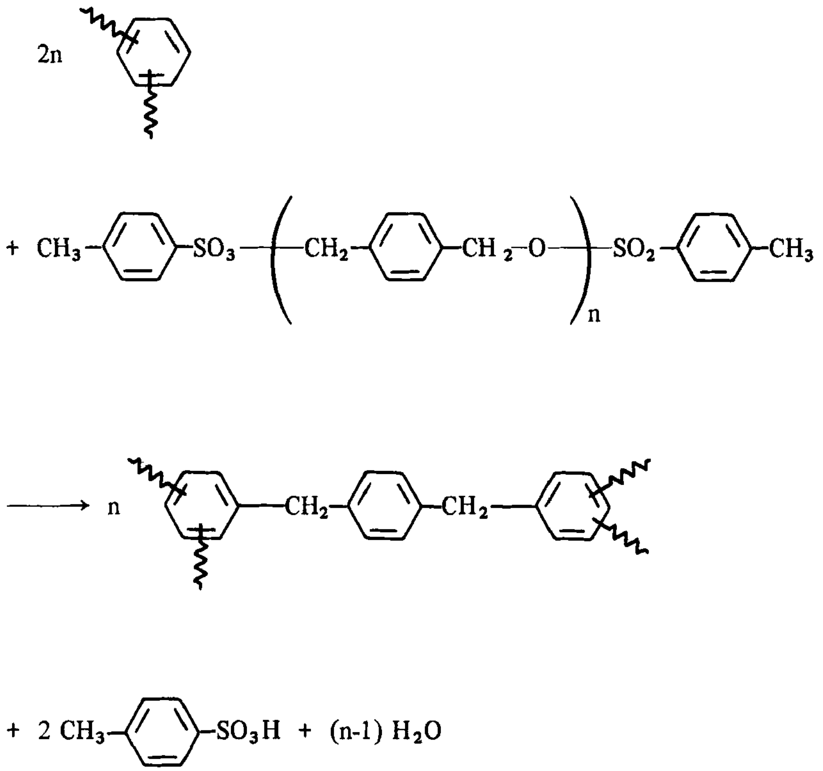
(4)

(5)

(6)


CH$_2$
CH$_2$–O
CH$_2$
SO$_2$
CH$_3$
n-1
+ H$^⊕$
A-stage polymer
220°
cured resin
+ HO
CH$_3$ + H$^⊕$

The over-all reaction is:



Although p-xylylene glycol polymerizes by itself, proof that it functions as an actual cross-linking agent has been obtained. Such proof was collected by conducting exhaustive extractions on samples of fully cured resin. These extractions showed that less than 10% of the resin was soluble. Extractions were carried out with boiling chlorobenzene. Fully cured resins were also free of sulfur.

Physical properties of fiberglass-reinforced laminates have also been determined. These data were, however, collected under a subsequent U.S. Air Force Materials Laboratory contract and have not yet been released for publication.

The synthesis of the telomer and the preparation of the A-stage thermosetting copolymer could also be accomplished in a single step by heating a mixture of fusible polyphenylene, p-xylylene glycol, p-toluenesulfonic acid, and chlorinated solvent at reflux with the continuous removal of water.

In the preceding paper, D. N. Vincent describes the apparent cure of intractable chlorinated para-polyphenylenes via hydrogen chloride evolution. These cures were achieved in the temperature range of 450-600°C which may be contrasted to the 200°C cures which are achieved by the xylylene glycol process described herein. The para-polyphenylenes used by Vincent also contained up to 8% chlorine, whereas the polyphenylenes used in our studies contained from 0.5 to 1.6% chlorine. These two processes thus are obviously quite different.

POLYPHENYLENE RESIN LAMINATES

Laminates were prepared from coated reinforcements, such as glass or carbon cloth, at 175-205°C under pressures of 1000-3000 psi. These laminates were then gradually heated to 288°C in a postcure cycle under nitrogen. Hyperthermal erosion tests were carried out on disks 1.0 cm thick and 2.5 cm in diameter by exposing them to electric arc-heated plasmas.

The optimum reaction period for preparing the A-stage copolymer was selected on the basis of a set of hyperthermal erosion tests. A heat flux of 550 Btu/ft^2/sec and a plasma of 20% oxygen in nitrogen were used. Exposure periods were 60 sec. Results of these tests are presented in Figs. 2 and 3.

Another study was made to relate the performance of laminates in the hyperthermal erosion tests to the polyphenylene:xylylene glycol weight ratio. The same test conditions were used as in the previous studies. A plot of the erosion depth as a function of this ratio is presented in Fig. 4. It should be noted, however, that in obtaining this set of data, the plasma arc test specimens were mounted with a 35° angle between the front face and the vertical rather than the 45° angle used in all other series of tests. This caused a change in the flame impingement angle and consequently caused a virtual doubling of erosion rates. Nevertheless, the results are highly significant since the curve still illustrates that the optimum weight ratio was slightly greater than 3.

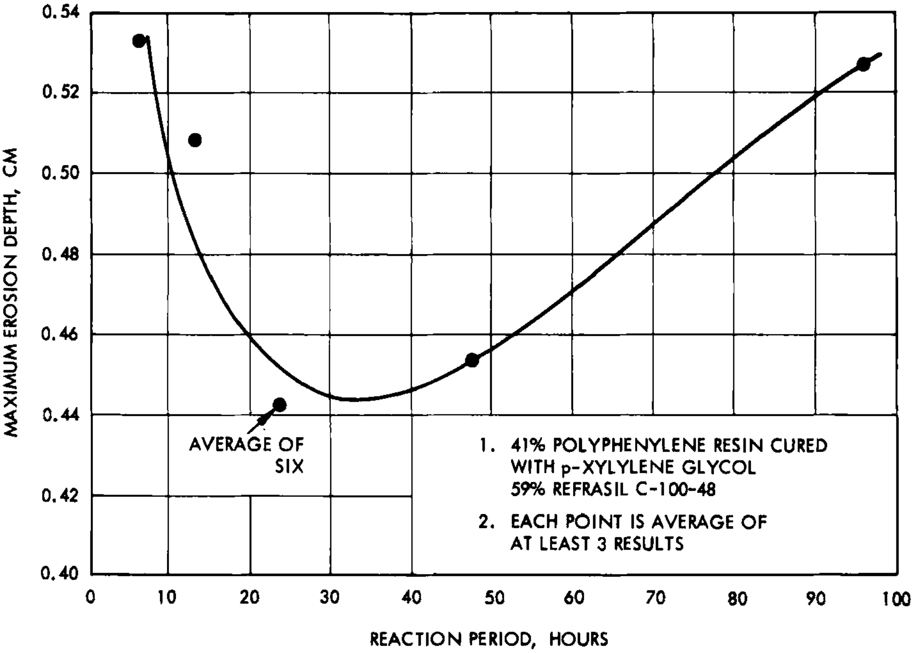


Fig. 2. Maximum hyperthermal erosion depth of p-xylylene glycol-cured polyphenylene composites as a function of the lacquer reaction period.

PLASMA ARC TEST RESULTS

Tables 2, 3, and 4 present additional results of plasma arc tests. Data in Table 2 were obtained at Hughes Aircraft Company using a reconstituted air plasma and a heat flux of 550 Btu/ft^2/sec. Values below 1.00 demonstrate performance superior to the standard phenolic resin. Data in Tables 3 and 4 were obtained at Avco Corporation and have been taken from a report by Mitchel [22]. Samples tested at Avco were prepared at Hughes under separate USAF contracts.

It is noteworthy that in comparable heat flux plasma arc tests carried out on leached glass (Refrasil C100-48)-reinforced composites the polyphenylene was equivalent to phenolic, although in higher heat flux environments, where low alkali carbon cloth reinforcements were used, polyphenylene was highly superior to the phenolic (see Table 3).

Table 4 presents data on carbon cloth-reinforced composites. This table

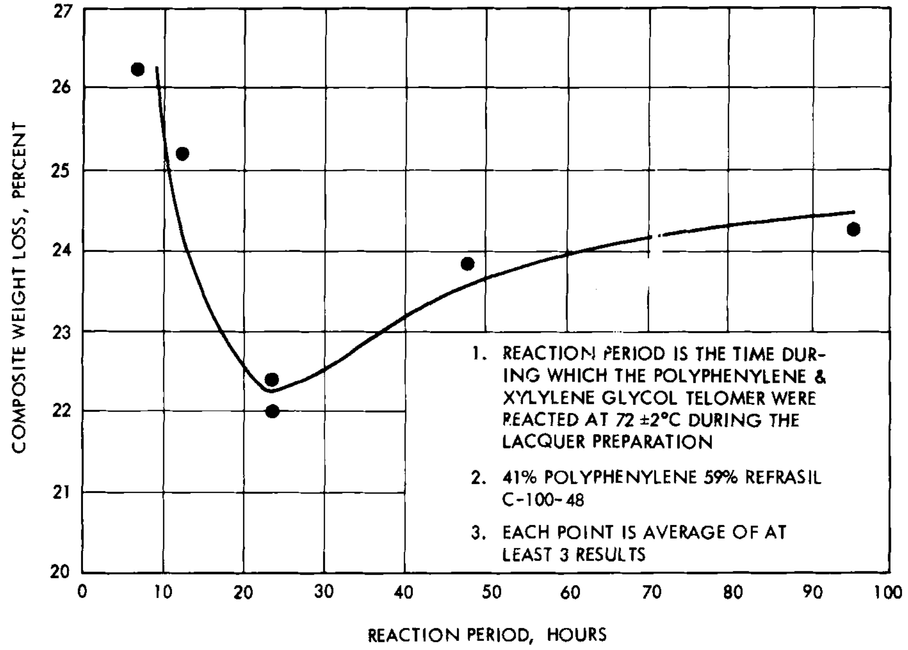


Fig. 3. Hyperthermal weight loss of xylylene glycol-cured polyphenylene composites as a function of the lacquer reaction period.

is divided into five sections representing the different test environments and the different resin contents. Sections A, B, and C compare sets of data on reinforced but unfilled resins.

At a heat flux of 540 Btu/ft^2/sec (Table 4, section A), the polyphenylene carbon cloth composite is compared with a phenolic resin, again demonstrating the superiority of the polyphenylene.

At 1020 and 1500 Btu/ft^2/sec (sections B and C, respectively), polyphenylene also performs extremely well. In these tests the Abchar 412B† was superior to both Abchar 412† and 413†. Sections D and E present data on various resins, including various polyphenylene resins, DEN 438 epoxy-novolac, CTL-91 LD phenol formaldehyde, and phenylphenol phenol formaldehyde, which have been filled with intractable polyphenylene (Abchar 700).†

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†See definitions in footnote, Table 4.

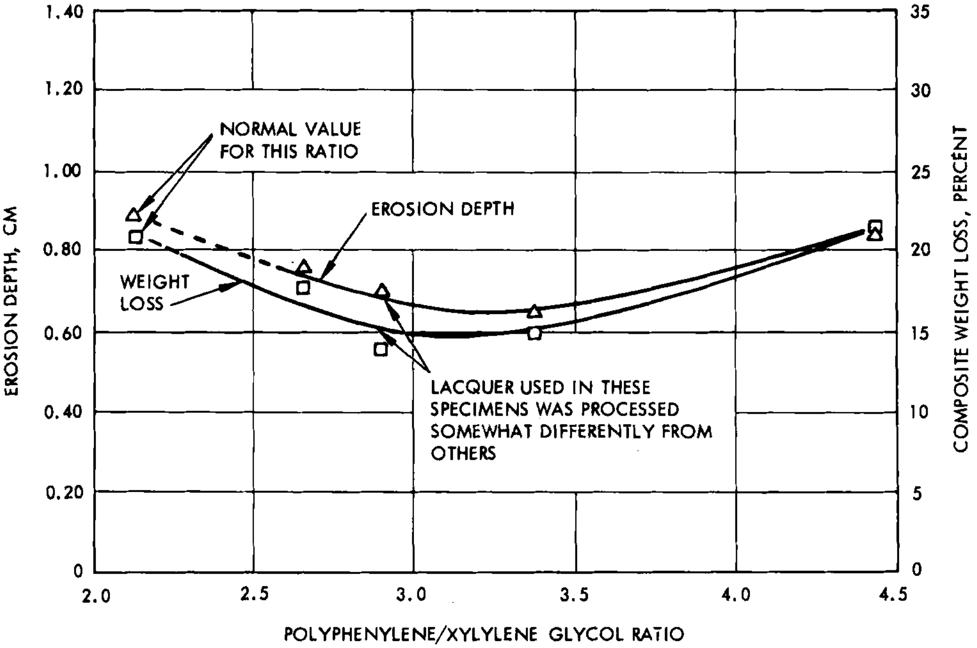

Fig. 4. Hyperthermal erosion depths of polyphenylene-xylylene glycol composites as a function of the polyphenylene:xylylene glycol ratio.

Table 2. Plasma Arc Test Results
(550 Btu/ft^2/sec for 1 min using 20% O_2-80% N_2)

Resin	Sample weight loss relative to standard	Relative ratings: Thickness change relative to standard	Relative ratings: Volume change relative to standard
91 LD phenolic standard[a]	1.00	1.00	1.00
Polyphenylene-Abchar 412[b]	0.84	0.66	0.61

[a] Cincinnati Testing Laboratories–phenolic resin.
[b] 40% resin on CCA-1 carbon cloth.

Table 3. Ablation Test Results on Various Resin Composites

Resin chemical type	Reinforcing agent	Resin designation	Resin content (pbw)	Environment[a]	Heat of ablation (Btu/lb)		Cold wall heat of insulation (Btu/lb)		Steady-state loss rate		Ablative performance index
					Cold-wall	Thermochem	50°F	200°F	Lb/ft²-sec	In./sec	
Phenolic	Refrasil	CTL 91 LD	37	A	12,400	6,200	4,300	8,800	0.043	0.0051	2.35
Polyphenylene	Refrasil	Abchar 413	37	A	11,700	4,400	4,000	12,000	0.046	0.0056	2.12
Polybenzimidazole	Refrasil	Imidite 2803	34	A	10,100	4,600	5,000	9,200	0.052	0.0074	2.07
Phenolic	Low-alkali carbon cloth	CTL 91 LD	37	C	22,500	310	8,300	14,000	0.064	0.0087	3.49
Polyphenylene	Low-alkali carbon cloth	Abchar 413	36	C	30,600	3,800	9,200	17,000	0.047	0.0070	4.85
Phenolic	Low-alkali carbon cloth	CTL 91 LD	37	B	26,800	1,100	4,400	8,200	0.038	0.0051	2.94
Polyphenylene	Low-alkali carbon cloth	Abchar 413	36	B	46,000	1,000	2,800	5,300	0.023	0.0035	4.63

[a] A: 540 Btu/ft^2/sec; B: 1020 Btu/ft^2/sec; C: 1500 Btu/ft^2/sec.

AVCO test specimens were 3/4 in. in diam X ½ in. thick, whereas the Hughes test specimens were 1 in. in diam X ½ in. thick.

EXPERIMENTAL

Raw materials, reagents, and solvents were procured in as high a state of purity as possible and then generally used as purchased without further purification. Only the xylylene glycol required recrystallization before use.

Plasma arc test results, obtained at Hughes Aircraft Company, are presented in Figs. 2, 3, and 4 and in Table 2. Other plasma arc test results, obtained at the Avco Corporation, are presented in Tables 3 and 4. The data in Table 4 were extracted from a report by Mitchel [22]. In Tables 3 and 4 the Avco Corporation data have been averaged (where duplicate tests were run), rounded off, and divided into eight categories in order to present the data in a more concise and significant manner.

POLYPHENYLENE

Method 1

A 4-liter beaker was fitted with an oil bath and high torque stirrer. The bath was heated to 115°C and then biphenyl (200 g, 1.30 mole) and m-terphenyl (281 g, 1.30 mole) were added. When the contents of the beaker were completely molten and mixed, anhydrous aluminum chloride (267 g, 2.0 mole) was added all at once. With the mixture kept at 115 ± 5°C and with good agitation, anhydrous cupric chloride (538 g, 4.0 mole) was added in small portions. Considerable evolution of hydrogen chloride took place during this addition, so that care had to be exercised to avoid excessive foaming. After the addition of the cupric chloride, the reaction mixture was stirred at 115 ± 5 ° C for 2 hr. Then the mixture was removed, while keeping the flask hot, and added to 4 liters of hot, concentrated hydrochloric acid. The product was thoroughly dispersed in the acid, filtered, dispersed again in 4 liters of 6N hydrochloric acid, filtered, and washed with water until the washings were neutral to litmus. The product was dried in vacuum at 120°C and then subjected to an extraction in a Soxhlet extraction

Table 4. Ablative Test Results on Carbon Cloth-Reinforced[a] Composites

	Material characterization parameters				
Resin system designation[b]	Cold-wall heat of ablation (Btu/lb)	Cold-wall heat of insulation (Btu/lb)		Steady-state loss rate X 10^3	
		50°F	200°F	in./sec	lb/ft^2-sec
A: 36% resin-540 Btu/ft^2/sec					
91 LD	16,700	2,800	5,700	4.5	32
Abchar 412	25,800	2,700	5,400	2.8	21
B: 36% resin-1020 Btu/ft^2/sec					
Imidite 2803	19,500	3,700	6,100	9.8	67
Abchar 413	31,800	3,400	6,200	4.6	32
Abchar 500	31,000	3,500	6,700	4.6	33
Abchar 412B	37,700	3,300	5,500	3.9	28
C: 36% resin-1500 Btu/ft^2/sec					
Imidite 2803	27,300	7,900	13,000	8.0	57
Abchar 412	25,000	9,700	17,400	8.1	58
Abchar 412B	29,600	8,300	15,000	7.3	52
91 LD	16,500	10,000	13,800	12.3	88
Abchar 413	26,600	8,200	14,400	8.0	55

Table 4. (continued)

	Material characterization parameters				
Resin system designation[b]	Cold-wall heat of ablation (Btu/lb)	Cold-wall heat of insulation (Btu/lb)		Steady-state loss rate × 10^3	
		50°F	200°F	in./sec	lb/ft^2-sec
D: 30% resin-1020 Btu/ft^2/sec					
DEN 438 + Abchar 700	31,000	3,900	7,800	5.4	33
Abchar 412B + Abchar 700	50,000	3,200	7,100	2.9	20
Abchar 413 + Abchar 700	36,000	3,400	6,500	4.1	27
HAC PPP + Abchar 700	40,000	3,300	6,500	3.8	24
91 LD + Abchar 700	59,700	3,600	7,500	2.5	17
E: 30% resin-1500 Btu/ft^2/sec					
Den 438 + Abchar 700	19,400	12,800	15,400	12.9	80
Abchar 413 + Abchar 600	21,900	9,600	14,800	10.0	66

Abchar 413 + Abchar 700	31,000	10,800	17,000	7.2	49
HAC PPP + Abchar 700	31,700	11,100	16,000	7.2	49
91 LD + Abchar 700	29,400	8,800	15,400	6.9	49
Abchar 412B + Abchar 700	30,400	8,500	15,700	7.2	50

[a] CCA-1 carbon cloth (HITCO Corporation).

[b] Resin system designations:

Abchar 412, 412B, and 413 = thermosetting polyphenylene (Hughes Aircraft Company). Abchar 412 refers to a copolymer with two parts by weight polyphenylene per part of xylylene glycol; Abchar 413 has three parts by weight polyphenylene to xylylene glycol; and 412B is the same as 412 except that the polyphenylene portion had a mean molecular weight of 900 ± 100, in contrast to the 412 which utilized polyphenylene in the 1200 ± 200 mean molecular weight range.

Abchar 500	Thermoplastic polyphenylene (Hughes Aircraft Company) in the 1600-2500 molecular weight range.
Abchar 600	para-Polyphenylene (Hughes Aircraft Company).
Abchar 700	Intractable branched polyphenylene, $\overline{MW} > 2500$.
CTL-91 LD	Standard phenolic resin (Cincinnatti Testing Laboratories).
DEN 438	Epoxy-novolac (Dow Chemical Company).
Imidite	Polybenzimidazole (Narmco, AF-R-151).
PPP	p-Phenylphenol phenol formaldehyde. This resin was first developed in research sponsored by the Plastics and Composites Branch of the U.S. Air Force Materials Laboratory and conducted in 1962-1964 at Hughes Aircraft Co.

Table 5

Fraction	% Yield based on monomers	Remarks
Soluble in 10 vol % benzene-90 vol % naphtha	50-60	Low melting solid (60-120°C)
Soluble in chlorobenzene	20-30	mp 130-175°C Useful fraction $\overline{\mathrm{MW}}$ 800-1200
Insoluble in chlorobenzene[a]	20-30	Some softening above 250°C

[a] Higher molecular weight fusible fractions can also be isolated and have been described earlier [1].

apparatus. The very low molecular weight fraction was first removed by exhaustive extraction for 48 hr using 10 vol % benzene-90 vol % naphtha.* The insoluble residue was vacuum dried and subjected to an extraction for 48 hr using chlorobenzene. The chlorobenzene-soluble fraction thus far had been found to be the most useful product and could be recovered by removing the solvent with a rotary evaporator. The fusible product was dark brown. A summary of the results of many preparations is shown in Table 5.

Method 2

By increasing the molar ratio of aluminum chloride to monomers to 2:1, a decrease in viscosity was effected as well as a slightly greater yield of chlorobenzene-soluble polyphenylene. A 2-liter beaker was fitted with an oil bath and high torque stirrer. The beaker was heated to 115°C and then

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*It should be noted that previously 20 vol % benzene-80 vol % naphtha was used as a solvent. However, it was found that by using a 10 vol % benzene-90 vol % naphtha, slightly lower molecular weight polymers were isolated which could be molded at lower temperatures (177°C or 350°F) and pressure (500 psi), whereas the previous conditions were 204°C (400°F) and 3000 psi.

Table 6

Fraction	% Yield based on monomers	Remarks
Soluble in 10 vol % benzene-90 vol % naphtha	40-50	Low melting solid
Soluble in chlorobenzene	30-40	mp range 130-175°C Useful fraction $\overline{MW}$ 800
Insoluble in chlorobenzene	10-30	

biphenyl (77 g, 0.50 mole) and m-terphenyl (113 g, 0.50 mole) were added. When the monomers were completely molten and mixed, anhydrous aluminum chloride (267 g, 2.0 mole) was added all at once. With the mixture kept at 115 ± 5°C and with good agitation, anhydrous cupric chloride (538 g, 4.0 mole) was added in small portions. Slow addition was necessary, since considerable foaming occurred due to the evolution of hydrogen chloride. After the addition of the cupric chloride, the reaction mixture was stirred at 115 ± 5°C for 2 hr. At this point the reaction mixture was quite viscous but sufficiently fluid when hot to be mixed with an ordinary laboratory stirrer. It was then dispersed in 4 liters of hot, concentrated hydrochloric acid, and the suspension was filtered with a fritted glass filter. The polymer was dispersed again in 4 liters of hot, 1:1 hydrochloric acid and filtered and washed with water until the washings were neutral to litmus. The product was dried in vacuum at ca. 120°C and subjected to an extraction in a Soxhlet extraction apparatus. The very low molecular weight fraction was first removed by extraction for 48 hr with 10 vol % benzene-90 vol % naphtha. The insoluble fraction was vacuum-dried and extracted with chlorobenzene for 48 hr. The chlorobenzene-extractable fraction, which has thus far been found to be the most useful product, was recovered by removing the solvent with a rotary evaporator. The product was brown and fusible. A summary of the results of many preparations is shown in Table 6.

TELOMERIC CURING AGENT

The p-xylylene glycol (available as 1,4-benzenedimethanol from Aldrich Chemical Company and as p-xylene-α, α'-diol from Eastman) was first recrystallized from benzene-ethanol since the purity of the commercial product was variable, and the impurities were detrimental. p-Xylylene glycol (35.0 g, 0.253 mole), p-toluenesulfonic acid monohydrate (10.5 g, 0.055 mole), and chloroform (350 ml) were mixed and heated at reflux for 20-24 hr. The resulting solution was filtered. The product should be kept free from moisture or damp air because of the tendency to hydrolyze. After standing for several days at room temperature, a small amount of crystals generally formed. These readily redissolved upon warming.

An equally satisfactory curing agent was made by substituting m-xylylene glycol for the para-isomer.

THERMOSETTING COMPOSITE

In a typical preparation, polyphenylene (20 g, soluble in chlorobenzene and insoluble in 10 vol % benzene-90 vol % naphtha) was dispersed in cold trichloroethylene (50 ml). The mixture was stirred under reflux to effect solution. Then either a chloroform or a trichloroethylene solution of the p-xylylene glycol telomer containing the equivalent of 10 g of p-xylylene glycol was added and the mixture was heated at reflux for 20-24 hr. This lacquer was used to prepare laminates, or the solvent could be removed under reduced pressure and ambient temperatures to yield a molding powder.

In a typical molding, the resin was advanced somewhat by vacuum drying at 71°C for at least 15 min.† It was then molded at 204°C (400°F) and 3000 psi for 120 min and cooled slowly to 93°C (200°F) before ejection from the mold. A typical postcure cycle involved heating for 18 hr at 135°C (275°F) and for 108 hr during which the temperature gradually rose from 135 to 288°C (275 to 550°F). It was then kept at 288°C for 6 hr and finally allowed to cool slowly.

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†When the polyphenylene molecular weight was in the 800-1000 $\overline{\text{MW}}$ range, much longer B-staging periods were desirable. In some cases, those periods have been over 24 hr. Lacquers made from polymer in this $\overline{\text{MW}}$ range can be molded at 177°C (350°F) and 500 psi.

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