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### The Synthesis and Characterization of Some Potential Ablative Polymers

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# The Synthesis and Characterization of Some Potential Ablative Polymers

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## SUMMARY

A series of polymers based on the reaction products of bis-(*o*-chloro-*p*-tolyl)ether, formaldehyde, and phenols have been synthesized. The char yields of these polymers, determined by thermogravimetric analysis, vary between 50 and 66%. The data indicate that char yield is influenced by the degree of cross-linking and that the char structure still possesses the phenyl ether unit. Incorporation of thermally stable fillers or substituents on the phenol can produce desired properties without weakening the polymer system. The high char yield and char stability of these polymer systems suggest potential merits in ablative applications.

## INTRODUCTION

Selected organic polymers have attracted increased attention in experimental programs concerned with practical heat shields for re-entry vehicles because of their char-forming and ablative characteristics. Among the common commercial polymers, phenolic resins have been found to give high yields of strong char.

The thermal stability of phenyl ether has been well established by its use in high-temperature heat transfer media. More recently, polymers possessing the phenyl ether unit have been reported to show improved thermal properties [1, 2].

Our experiences showed that incorporation of the phenyl ether unit into the structure of phenol-formaldehyde resin improved the thermal stability significantly [3, 4]. These results encouraged us to explore the use of this type of polymer in ablative applications.

The purposes of this work are to synthesize some phenyl ether-modified phenolic polymers from well-defined condensing species, to study the factors influencing the char-forming properties, and to try to establish the merit of this type of polymer as ablative plastics. The general scheme for synthesis is presented in Fig. 1.

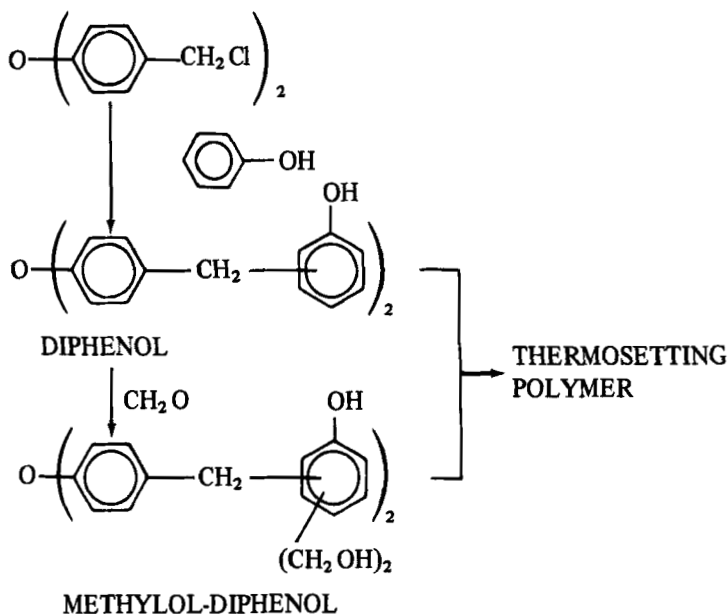
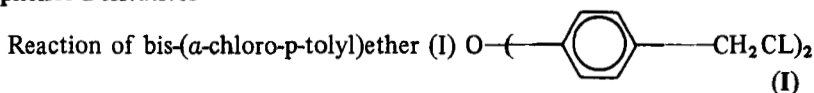


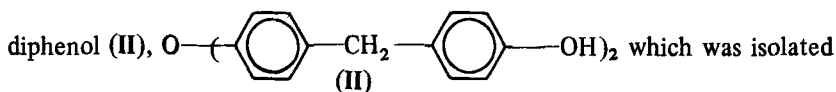
Fig. 1. General synthesis scheme.

## DISCUSSION

### Diphenol Derivatives



with excess phenol produced a mixture of the three expected isomers of oxy-bis-*p*-phenylenemethylene)-diphenol. Treatment of this mixture with benzene precipitated a product rich in 4,4'-[oxy-bis-(*p*-phenylenemethylene)]-



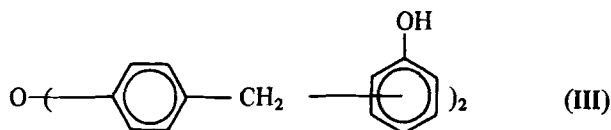
in 20% yield by recrystallization. The structure of (II) agrees with the NMR spectrum, which shows the presence of only para-substitution on the phenol. Analyses by gas-liquid chromatography (GLC) (Table 1) and gel-permeation chromatography (GPC) show that the benzene-soluble mixture

Table 1. Gas-Liquid Chromatogram of Diphenol (III)<sup>a</sup>

Diphenol	Area %
2,2'-isomer	11.0
2,4'-isomer	48.0
4,4'-isomer	40.0

<sup>a</sup>The mixture of diphenol isomers was converted to the ester with acetic anhydride. The mixed esters were chromatographed on a 40-cm 1/8-in. column, packed with 10% Apiezon L on 50/120 mesh Eagle-Picher Celatom. Column temperature was 315°C.

consists of all three isomers of oxy-bis-(*p*-phenylenemethylene)-diphenol (III)



and a small amount of "dimer." A possible general structure of the dimer could be that of (IV),

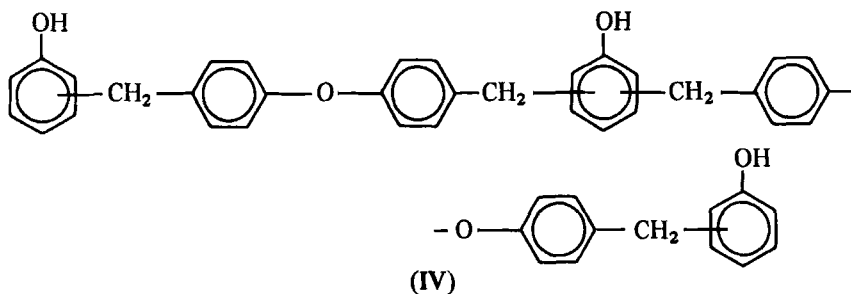
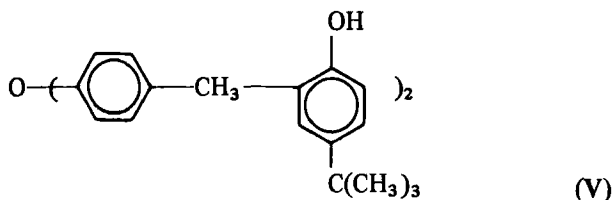


Table 2. Analyses of Monomers

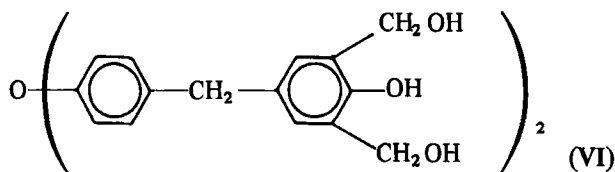
Monomer	Molecular formula	Molecular weight		% Carbon		% Hydrogen		% Hydroxyl	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
(II)	$C_{26}H_{22}O_3$	382	389	81.65	80.90	5.80	5.98	8.90	8.88
(III)	$C_{26}H_{22}O_3$	382	405	81.65	81.30	5.80	5.88	8.90	7.58
(V)	$C_{34}H_{38}O_3$	495	505	82.56	82.70	7.75	7.91	6.93	7.09
(VI)	$C_{30}H_{30}O_7$	502	501	71.71	71.40	6.02	5.97	20.30	19.81
(VII)	$C_{30}H_{30}O_7$	(502)	778	(71.71)	72.05	(6.02)	6.04	(20.30)	16.75
			885		71.40		6.20		16.60
			940		72.80		5.94		16.80

whose molecular weight of 670 corresponds well with the molecular weight of 660 shown in the GPC analysis. The presence of species of higher molecular weights is also indicated by the average molecular weight of the mixture (Table 2). When *t*-butylphenol was used instead of phenol, only a single product, 2,2' [oxy-bis-(*p*-phenylenemethylene)]-bis-(4-*t*-butylphenol) (V) was obtained.



### Methylol-Diphenol Derivatives

Reaction of diphenol (II) with excess formaldehyde under alkaline condition yielded 5,5'-[oxy-bis-(*p*-phenylenemethylene)]-bis-(2-hydroxy-*m*-xylene-*a,a'*-diol)(VI).



The structure is supported by elemental analysis, molecular weight determination, GPC, and NMR spectrum. Under similar conditions, diphenol (III) produced a very complex mixture, methylol-diphenol (VII).

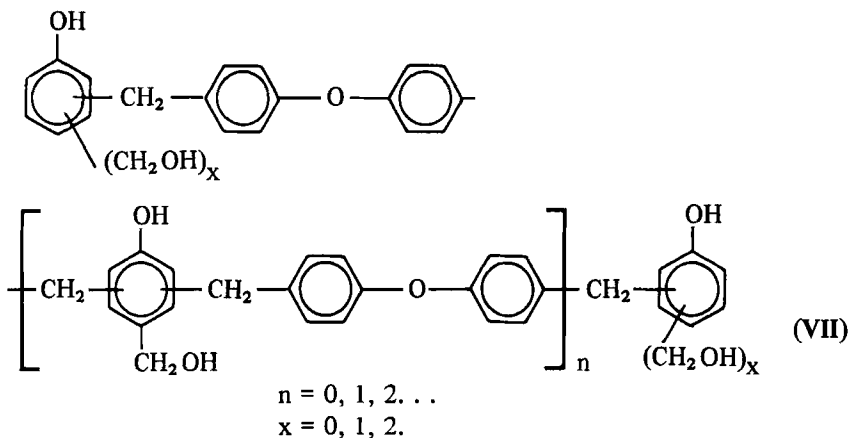


Table 3. Compositions, Analyses, and Char Yields of Polymers

Series	Composition <sup>a</sup>				Char yields (%)	% C	% H
	Diphenol		Methylol-diphenol				
	(II)	(III)	(V)	(VI)			
A	1.0		1.0		65.0	79.40	5.84
	1.5		1.0		65.4	79.90	5.59
	2.0		1.0		60.3	80.90	5.62
B		1.0					
				1.0		79.20	5.79
		1.3		1.0		80.80	5.70
		1.5		1.0		80.90	5.65
C		2.0		1.0		81.40	6.49
	0.5		1.0				
	1.0		1.0			81.90	5.68
				1.0	54.0		
				1.0	50.6	81.80	6.42

<sup>a</sup>The molar ratio is the ratio of equivalents of reactive positions per mole of diphenol to equivalents of CH<sub>2</sub>OH group per diphenol unit.

Analysis by GPC indicates the existence of species with molecular weights of 505, 925, and 1200. The elemental analysis shows 2.4-2.7 hydroxymethyl groups per diphenol unit (Table 2).

### Thermosetting Polymers

Three series of polymers were prepared in the form of cylindrical billets. Their compositions and analyses are shown in Table 3. The polymers were prepared by conventional methods used in the molding of thermosetting resins, i.e., under nitrogen pressure and at high temperature. It was found necessary to remove entrapped air as much as possible before the final curing operation. Continuous bleeding of nitrogen at the molding pressure helped to remove the water formed from the resin matrix. Gradual heating and cooling helped to prevent rupture due to thermal stress.

### Char Yields of Polymers

The char yields obtained from thermogravimetric analysis (TGA) are shown in Table 3. Polymers from series A, prepared from pure condensing species (II) and (VI), give higher char yields than those in series B in all corresponding molar ratios. The char yields also depend on the relative amount of the cross-linking reactant, the methylol diphenol. A molar ratio of 1.3 diphenol to 1.0 methylol-diphenol is evidently close to the optimum formulation for maximum char yield.

As expected, series C, using some diphenol (V) which carries the *t*-butyl group, gives much lower char yields. The effect of the *t*-butyl group in the resin structure on the char yields is shown in Table 4. The results suggest that the *t*-butyl group is eliminated during char formation, probably as gaseous hydrocarbons.

All the char residues exhibit good dimensional and mechanical stability in spite of the considerable amount of gaseous products generated.

### Nature of Char

Elemental analyses were carried out on two sets of polymers before and after pyrolysis at 700 and 900°C. The results are shown in Table 5. They are very similar to those for "normal" phenol-formaldehyde resins reported by Lochte et al. [5]. It is reasonable to suggest that the phenyl ether linkage is not destroyed but is incorporated into a continuous network of fused aromatic and heterocyclic rings similar to that postulated by Bruck [6]. An idealized structure is presented in Fig. 2.



Table 4. Effect of t-Butyl Group on Char Yields

Composition		Char yield (%)	Decrease in char yield (%)	t-Butyl group in cured resin (%)
Diphenol (II) (V)	Methylol-diphenol (VI)			
1.5 —	1.0	65.4	—	—
0.5 1.0	1.0	54.0	11.4	10.3
2.0	1.0	60.3	—	—
1.0 1.0	1.0	50.6	9.7	8.7

Table 5. Analysis of Polymers Before and After Pyrolysis

Sample	Pyrolysis temp., °C	% C	% H	% O <sup>a</sup>
A	Original	81.4	5.52	13.04
	700	93.2	2.41	4.39
	900	94.5	1.19	4.31
B	Original	79.9	5.59	14.51
	700	93.9	1.89	4.21
	900	94.9	1.49	3.61

<sup>a</sup>Determined by neutron activation analysis.

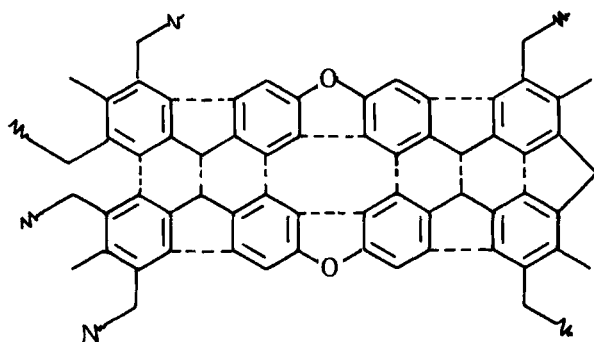


Fig. 2. Possible char structure.

**Polymer with Filler**

The effect of filler in the polymer system was briefly examined. Carbon fibers were incorporated into the polymer matrix. The properties of this system are shown in Table 6. The data suggest that improved properties may be obtained by incorporation of heat-stable fillers.

Table 6. Properties of Polymer-Containing Carbon Fibers

Composition	45% 1/4-in. carbon fibers 55% Polymer (III/VI = 1.5/1.0)
Density	85 lb/ft <sup>3</sup>
Average tensile strength	
Perpendicular to axis	3760 psi
Parallel to axis	305 psi
Char yields	
Polymer with fibers	77%
Polymer only (calculated)	59%
Polymer only (actual)	61%

## EXPERIMENTAL

### Analytical Methods

Gel-permeation chromatography was carried out with a Water's Associates gel permeation chromatograph. The column consisted of five 4-ft sections connected in a series. The permeability limit of the gel packing in the first two sections was 10,000 Å; in the next section 1000 Å; and in the last two sections, 100 Å. Tetrahydrofuran was used as solvent. The flow rate was maintained at 0.7 ml/min. The concentrations of different molecular species were measured by differential refractometer. The relationship between molecular weight and elution count is assumed to be linear due to the similarity of molecular structure involved.

NMR spectra were recorded with a Varian Associates A-60 spectrometer.

Thermogravimetric analyses were carried out with an automatic recording thermobalance. The pressure was 1 mm Hg and the temperature was increased at the rate of 12°C/min. The char yields were obtained from actual weighing of samples.

## DIPHENOLS

A solution of 534 g (2 moles) of 4,4'-oxy-bis-(*a*-chloro-*p*-tolyl)ether (I) (mp 64-65°C) in 600 g of chlorobenzene was added slowly with stirring to 2620 g (30 moles) of phenol at 50°C. After the addition, excess phenol and chlorobenzene were removed under reduced pressure. Treatment of the residue with benzene produced a precipitate which was recrystallized from 70% aqueous ethanol to yield 100 g (20%) of 4,4'-oxy-bis-(*p*-phenylenemethylene)-diphenol (II), mp 150-152°C ([7], mp 152-153°C); NMR (CDCl<sub>3</sub>) δ 3.83 (s, 4, Ar-CH<sub>2</sub>-PhOH-*p*) and 7.0 ppm (m, 16, ArH). Other analytical results are shown in Table 2.

The benzene filtrate was evaporated to dryness under reduced pressure 430 g (56%) of a tacky, amber solid, diphenol (III), GPC mol wt 385,660. Results of GLC analysis are shown in Table 1 and elemental analysis in Table 2.

## Diphenol (V)

2,2'-[Oxy-bis-(*p*-phenylenemethylene)]-bis-(4-*t*-butylphenol). Using the same procedure as above except that 4-*t*-butylphenol (mp 98-99°C) was used instead of phenol, (V) was obtained in 66% yield, mp 142-144°C. Analytical results are shown in Table 2.

## Methylol-diphenol (VI)

5,5'-[Oxy-bis-(*p*-phenylenemethylene)]-bis-(2-hydroxy-*m*-xylene-*a,a'*-diol). A mixture of 100 g (0.26 mole) of diphenol (II), 24 g (0.6 mole) of sodium hydroxide, and 300 ml of water was heated to 50-55°C with stirring. When a homogeneous solution was obtained, 220 g (2.66 moles) of 37% formalin solution were added dropwise. After the addition was completed, the mixture was stirred at 50-55°C for 2 hr. The mixture was allowed to cool and 300 ml of ethyl acetate were added. The mixture was then acidified with 60 ml of concentrated hydrochloric acid. The organic phase was washed successively with water, 10% sodium bisulfite, and water. The ethyl acetate solution was then dried over anhydrous sodium sulfate and evaporated to dryness in vacuo at room temperature. The white solid obtained was recrystallized from aqueous acetonitrile to give 60 g (46%) of methylol-diphenol (VI), mp 117-119°C (dec.); NMR (CDCl<sub>3</sub>) δ 3.81 (s, 4, Ar-CH<sub>2</sub>-PhOH), 4.70 (s, 8, ArCH<sub>2</sub>-OH), and 7.0 ppm (m, 12, ArH); other analytical results are shown in Table 2.

### Methylol-Diphenol (VII)

The procedure was similar to that for (VI), except that diphenol (III) was used instead of diphenol (II). The reaction with formaldehyde was carried out under nitrogen atmosphere. The tan solid obtained after the removal of ethyl acetate was not purified further. GPC showed species with molecular weights of 510, 925, and 1200. Other analytical results are shown in Table 2.

## THERMOSETTING POLYMERS

Diphenol and methylol-diphenol in the desired molar ratios were dissolved in methanol and the solution was evaporated to dryness at room temperature in vacuo. The solid mixture was packed into a 10 × 75-mm test tube or similar metal mode. The mixture was allowed to gel under reduced pressure below 90°C in order to remove as much entrapped air as possible. The tube was then placed in a Parr bomb and the curing was carried out under nitrogen pressure of 200 psi. The bleeding of nitrogen continued as the temperature was raised to 200°C over 6 hr and held there for 24 hr. The cooling of the system lasted about 20 hr. The compositions and analyses of the polymers prepared are shown in Table 3.

The same procedure was used for the preparation of polymers containing carbon fibers. The fibers (HITCO carbon fibers) were mixed with the methanolic solution of the desired diphenol and methylol-diphenol mixture. The curing was carried out at 200°C and 400 psi. The properties of the polymer are shown in Table 6.

## CONCLUSION

This class of phenyl ether phenolic polymers exhibits char yields as high as 66% when heated in vacuo to 900°C. Incorporation of thermally stable fillers or substituents on the phenol can produce desired properties without weakening the basic system. The high char yield and char stability of these polymer systems indicate that they could be useful in ablative applications.

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