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SYNTHESIS AND PROPERTIES OF ARYLETHERSULFONE THERMOSET SYSTEMS

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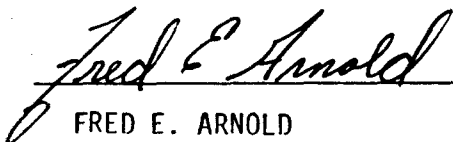
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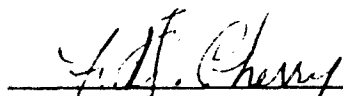


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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. T. E. Helminiak as the Materials Laboratory Project Scientist. Co-authors were P. M. Lindley, L. G. Picklesimer, B. Evans, and F. E. Arnold (AFWAL/MLBP) and J. J. Kane of Wright State University.

This report covers research conducted from April 1983 to April 1984.

The authors wish to thank Mr. E. J. Soloski for the determination of glass transition temperatures and isothermal aging studies of the polymers.

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SECTION I

INTRODUCTION

A substantial effort in our laboratory has been directed toward the synthesis and characterization of acetylene-terminated (AT) matrix resins. The most significant feature and driving force for the effort is that the thermal induced addition reaction provides a moisture insensitive cured product. This technology offers a wide variety of thermoset resins for various high temperature applications. Backbone structural design for use temperature capabilities, processing characteristics and mechanical performance has demonstrated the versatility of the AT type systems.

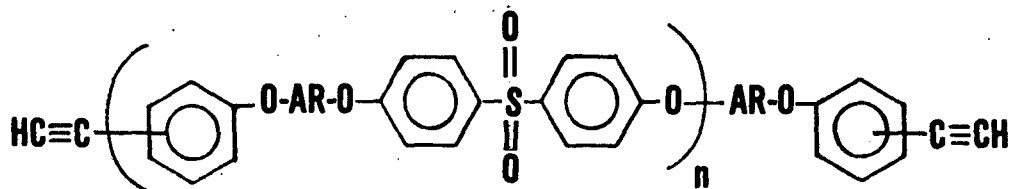
A variety of aromatic and aromatic heterocyclic oligomers with terminal acetylene units have been synthesized and reported (References 1-3) in recent years. Long term use temperatures for these materials are in the range of 250-550°F with short term usage at 600-650°F depending on the specific molecular structure between acetylene cure sites. These materials can be classified into rigid (high Tg) and flexible (low Tg) systems. For higher use temperatures, the rigid aromatic heterocyclic backbones are employed to exhibit higher Tg's after cure. Materials which process similarly to the state-of-the-art epoxides require the more flexible Phenylene R type systems, where R refers to the functional group which imparts the flexibility to the oligomeric backbone.

The rigid high Tg systems are prepared by the formation of a heterocyclic low molecular weight oligomeric species followed by endcapping with an appropriate aromatic acetylene. These heterocyclic systems which have been prepared include the quinoxalines (References 4-6), imides (Reference 7) and N-phenylbenzimidazoles (Reference 8). The formation of the heterocycle is generally a polymer forming polycondensation reaction in which the molecular weight of the oligomer can be controlled by adjusting the stoichiometry of the reactants.

The most convenient method of preparing the flexible (low Tg) system is to employ the Ullmann ether reaction of dibromobenzene and aromatic bis-diols followed by catalytic replacement of the bromine atoms by terminal acetylene groups. A host of commercially available bis-diols have been used in the synthesis with both meta and para dibromobenzene. Low Tg arylether oligomers have been prepared containing sulfone,

sulfide, carbonyl, isopropyl and perfluoroisopropyl groups in the backbone (Reference 9).

These flexible systems do offer the advantages of epoxy-type processing; however, the mechanical properties, in particular the lack of toughness of the resulting resins, were drawbacks. Work with the quinoxaline series (Reference 10) had shown that the toughness of AT systems could be affected by decreasing the crosslink density in the polymer network. This was done by increasing the chain length of the units between terminal acetylenes. In an effort to determine whether this finding with the rigid quinoxalines would also apply to the flexible systems, work was undertaken to synthesize higher molecular weight monomer/oligomer systems of the Phenylene R type shown below.



The approach used involved a four step sequence to obtain the desired product. A number of low cost diols and bis-diols were studied, including Bisphenol A, resorcinol and hydroquinone. An Ullmann ether condensation was used in the reaction sequence in an effort to obtain very flexible systems which would have low initial Tg's for ease of processing.

The objectives of this work were to synthesize a series of arylether sulfone oligomers with an increased chain length between reactive sites by the proposed synthetic route. In addition, it was to be determined if the products obtained by this route would have initial glass transition temperatures near or below room temperature while having cured Tg's in the 300-500°F range of epoxides.

SECTION II

RESULTS AND DISCUSSION

The reaction sequence used to synthesize these flexible systems involved four steps which are outlined in Figure 1. The first of these was an aromatic nucleophilic substitution, a polymer forming reaction in which 4,4'-dichlorodiphenyl sulfone reacts with various diols. The second step, an Ullmann ether reaction, gives bromine terminated products in which the bromines can be replaced by ethynyl end groups in the final stages.

Both the substitution and Ullmann reactions provide sources of oligomers, making the final product a mixture of monomeric and oligomeric species. While this was desirable for the overall objective of the work, increasing chain length between crosslink sites, the presence of oligomers did complicate characterization of the products obtained from the various reactions. For this reason, a reaction scheme which would give a pure monomeric product was formulated and used for all of the diol systems to do preliminary evaluations.

1. MONOMER SYSTEMS

The first step in the synthesis of the model monomeric systems required formation of a mono(bromophenoxy)phenol (I) system by the Ullmann reaction outlined in Figure 2. Here, meta or para dibromobenzene was reacted with the appropriate diol under either of two sets of Ullmann conditions. The first method involved using pyridine, potassium carbonate and cuprous iodide, while the second entailed using 2,4,6-collidine and cuprous oxide. Both of these syntheses will give a small amount of dibrominated material as well as the desired product since two hydroxy linkages are present in the diol, but by controlling the stoichiometry of the reaction the predominant product can be directed toward the mono-bromo material. This Ullmann reaction was done without regard to yield or to optimize conditions, but rather to get enough of the mono(bromophenoxy)phenol product to continue on in the sequence.

Through the use of one of the methods outlined above, all five of the diols shown in Figure 2 were reacted with an isomer of dibromobenzene. The products obtained from this reaction were carried through the sequence shown in Figure 3. The

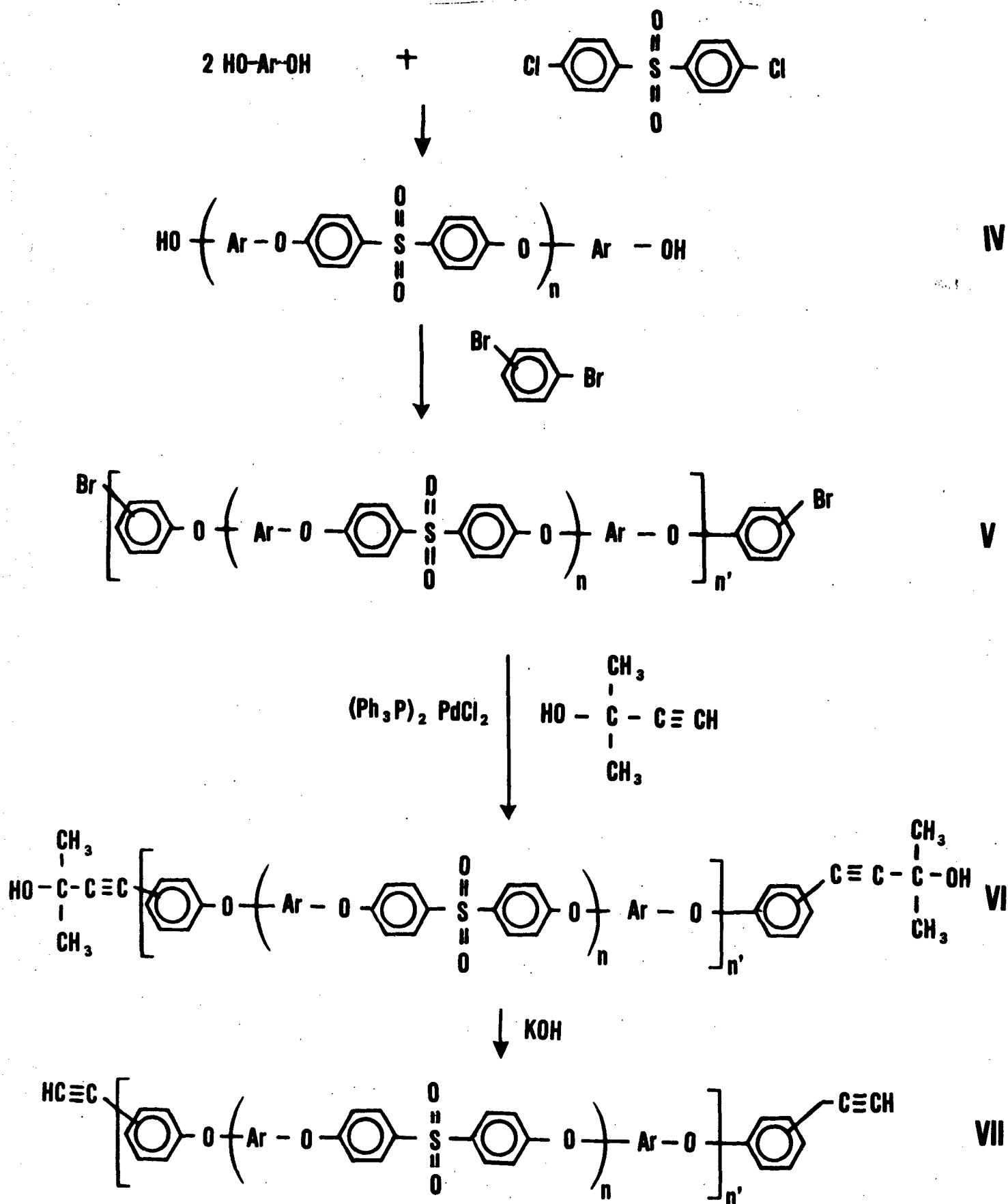


Figure 1. Reaction Sequence Used for the Synthesis of the Monomer/Oligomer Systems

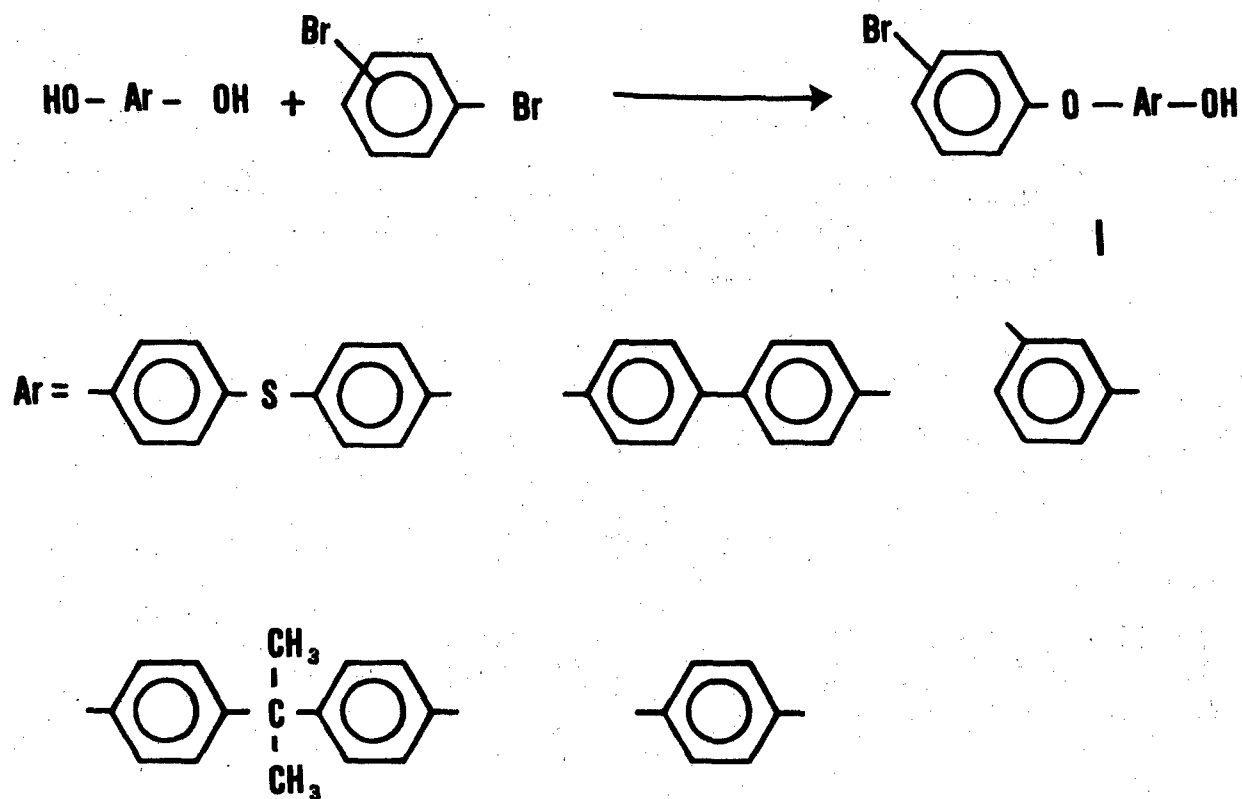


Figure 2. Synthesis of Mono(Bromophenoxy)phenols

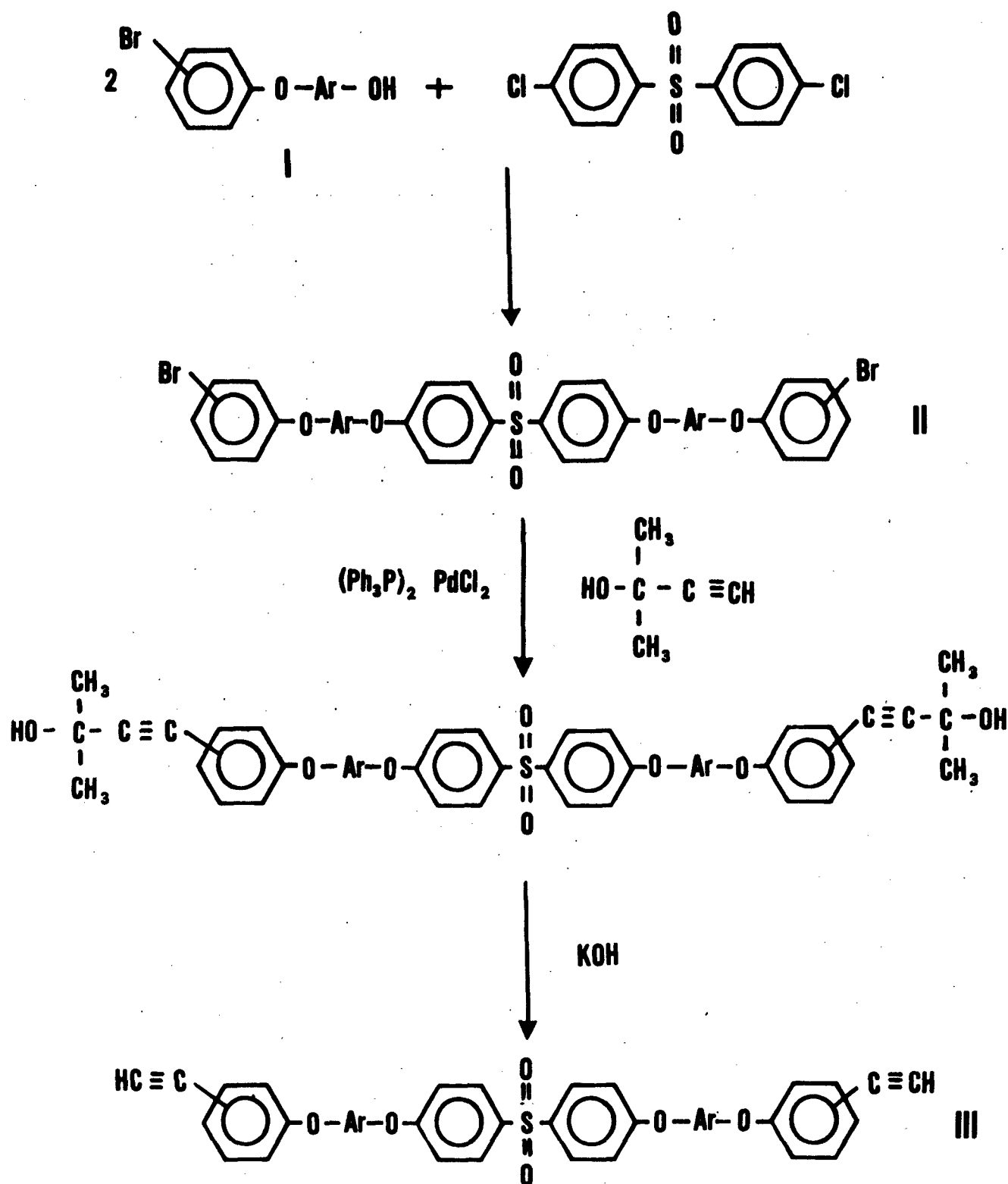


Figure 3. Synthesis of the Model Monomeric Systems

mono(bromophenoxy)phenol was reacted with 4,4'-dichlorodiphenyl sulfone in a nucleophilic aromatic substitution using 1-methyl-2-pyrrolidinone (NMP) as a solvent and potassium carbonate as base. The reaction was run using a 2:1 ratio of bromo compound to sulfone, and since the substitution is a polymer forming reaction under normal circumstances, good conversion to the dibromo product was observed with no oligomer formation.

The second and third steps in the monomer synthesis involve the replacement of bromine with an acetylene protected by an acetone adduct, followed by cleavage of the adduct. These steps will be discussed in more depth later as they are the same for systems containing only monomer or a monomer/oligomer mixture.

2. EVALUATION OF MONOMERS

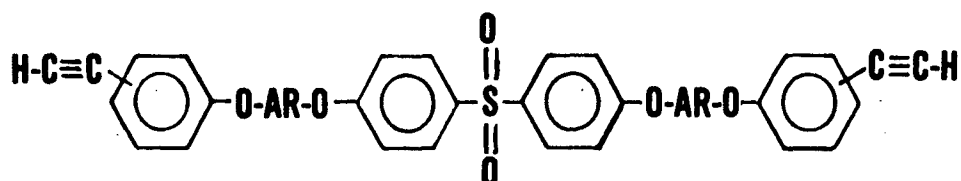
Following the completion of this sequence of reactions, the monomeric models (III) for all of the diol systems were formed. The products were then evaluated for initial and final Tg's and the results compiled in Table 1.

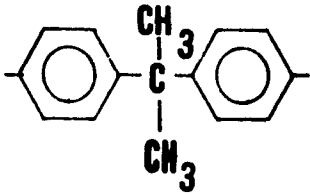
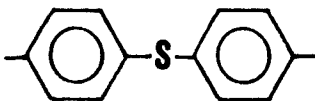
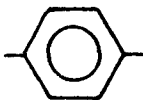
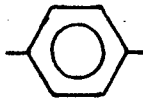
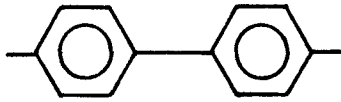
The initial Tg's found in column three of the table were determined by differential scanning calorimetry at a scan rate of 10°C/min. Final Tg's were determined by TMA on samples which had been cured in air at 550°F for 8 h. No residual exotherm was found in any of the samples when scanned by DSC following this cure cycle.

The second column in the table indicates whether the dibromobenzene used was the meta or the para isomer. In order to provide more flexibility for the rigid diols, 4,4'-dihydroxybiphenyl and hydroquinone, the meta isomer of dibromobenzene was used in preference to para. It was postulated that the meta isomer would increase the free volume of the chain thus lowering the initial Tg. The hydroquinone system was synthesized with both para and meta dibromobenzene isomers to provide a comparison between the effects of the variation in structure.

The variation in the initial Tg's show the effect on processability of the structures of the diol and the dibromobenzene. Two of the systems, those based on thiodiphenol and dihydroxybiphenyl, gave crystalline products which could not be made amorphous upon heat treatment. This effect on chain flexibility of dibromobenzene

TABLE 1
THERMOMECHANICAL PROPERTIES OF THE MONOMERIC SYSTEMS



AR	m/p AT - ISOMER	^a T _g INITIAL	^b T _g CURED	^c
	p	58°C	271°C	
	p	33° (T _m =74°C)	174°C	
	p	20°C	240°C	
	m	12°C	185°C	
	p	59°C	230°C	
	m	59° (T _m =186°C)	241°C	

a. DETERMINED BY DSC (10°C/MIN)

b. DETERMINED BY TMA (10°C/MIN)

c. CURED AT 550°F, 8HR

structure could be seen with the two hydroquinone systems. In this case, the meta isomer gave an initial Tg of 12°C while the more rigid para system had a Tg of 59°C. Variation of diol structure shows a parallel effect as shown with the resorcinol/p-dibromobenzene system. This material has a softening temperature of 20°C.

A similar trend was postulated for final Tg's of the cured materials. This result was observed in some cases, as with the hydroquinone systems where the more flexible meta product gave a significantly lower final Tg. The highest cured Tg's were seen in the Bisphenol A, dihydroxybiphenyl and resorcinol systems. The lowest final Tg was observed with the thiodiphenol product, at 174°C, less than 350°F.

The fact that the incorporation of thiodiphenol into the backbone produced both undesired crystallinity and a low final Tg led to a decision not to synthesize the monomer/oligomer mixture for this system.

3. MONOMER/OLIGOMER SYNTHESIS

The first two steps in the four step reaction sequence of Figure 1 are capable of producing both monomer and oligomer. The first step, aromatic nucleophilic substitution, is a polymer forming reaction under the correct stoichiometric conditions. In order to favor the formation of monomer with a small amount of oligomer, the substitution was carried out at a 4:1 ratio of diol to dichlorodiphenyl sulfone. This led to a predominantly monomeric product (IV) with only the requirement that the excess diol be removed from the product to eliminate the potential presence of low molecular weight species in later reactions.

It should be noted that one of these diols, the hydroquinone, did not provide any oligomer in the first step. This was due to the formation of the quinone structure which made it impossible to use hydroquinone directly in the substitution reaction. An alternate method was used to overcome this problem which involved the use of 4-methoxyphenol to obtain the sulfone product, followed by cleavage of the methyl ether to the diol (VIII) with boron tribromide. This set of reactions is outlined in Figure 4.

All of the sulfone diols were able to form oligomers in the second step of the reaction sequence, the Ullmann ether synthesis. As with the synthesis of the

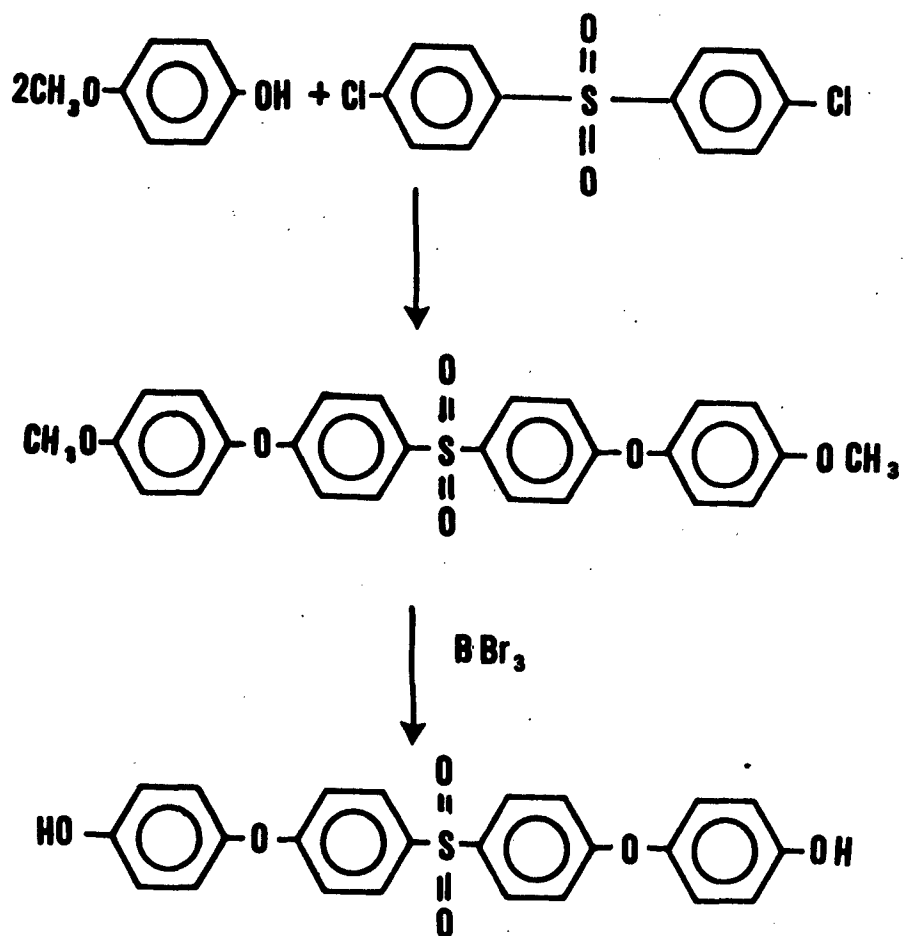


Figure 4. Synthesis of the Hydroquinone Based Diol

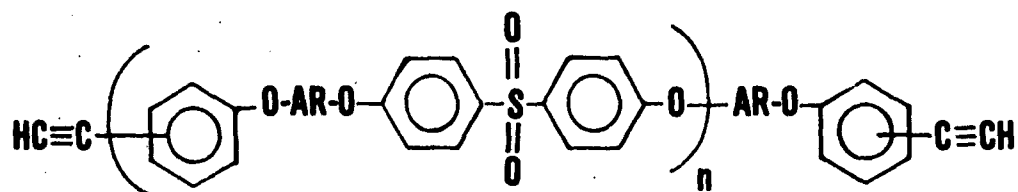
mono(bromophenoxy)phenol products, two methods were used to form the dibromo materials. Method A used pyridine, potassium carbonate and cuprous iodide, while Method B employed collidine and cuprous oxide with the dibromobenzene and higher molecular weight diol (IV). The major difference between the syntheses of the mono(bromophenoxy)phenols described earlier and these lies in the stoichiometry of the reactions. In order to obtain bromo endcapped product and to allow formation of predominantly monomeric species, the reactions were run at a 10:1 ratio of dibromobenzene to diol. This ratio has been found (Reference 11) to form monomer as the major product, while also affording a reasonable amount of higher molecular weight products (V).

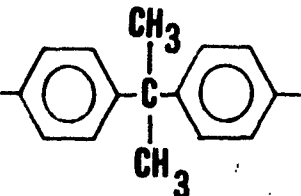
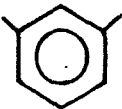
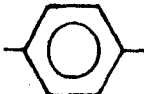
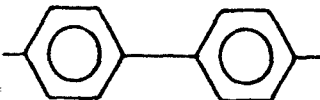
The monomer/oligomer mixtures were used in the third step of the reaction sequence, the replacement of bromine with 2-methyl-3-butyn-2-ol by use of the bis(triphenylphosphine) palladium chloride catalyst system. This reaction used a triethylamine/pyridine solvent system to replace the bromines on the ether sulfone with ethynyl groups protected by acetone adducts. The acetone protecting groups were then removed in a toluene/methanol/potassium hydroxide solvent system.

4. EVALUATION OF OLIGOMERIC SYSTEMS

Completion of the cleavage reactions gave the five acetylene terminated systems (VII) evaluated in Table 2. The third column of the table contains monomer/oligomer ratios for the various systems. These ratios were determined by a column chromatography separation of products, and was based on a weight percent ratio of the amount of monomer to oligomer. The variation in these ratios in the five systems is extreme, ranging from 60% monomer with dihydroxybiphenyl to 95% monomer with hydroquinone/p-dibromobenzene. Since all of the systems were synthesized with the same ratios of reactants in the oligomer forming steps, the differences must be attributed to the identity of the diol and/or the meta or para dibromobenzene isomer. Even eliminating the two hydroquinone systems since they only form oligomers in the Ullmann step, a variation of 60-85% in monomer for the other systems, resorcinol and biphenyl, is significant. The structure of the diol used obviously influences the formation of monomer and oligomer in the first steps of the reaction sequence. The effect of either meta or para dibromobenzene isomers is seen with the two hydroquinone products, where the meta isomer forms more oligomer than the para.

TABLE 2
THERMOMECHANICAL PROPERTIES OF THE OLIGOMERIC SYSTEMS



AR	m/p AT-ISOMER	MONO/OLIG RATIO	a T _g INITIAL	b T _g CURED
	p	75/25	55°C	241°C
	p	85/15	12°C	200°C
	m	85/15	2°C	215°C
	p	95/5	35°C	220°C
	m	60/40	61°C (TM=135°C)	241°C

a. DETERMINED BY DSC (10°C/MIN)

b. DETERMINED BY TMA (10°C/MIN)

c. CURED AT 550°F, 8 HR

The difference between the two dibromobenzene isomers which was noted in the monomeric systems with regards to initial Tg also holds true for the oligomers. The meta system still has a lower initial Tg with the resorcinol system as an intermediate between the two hydroquinone products. The other initial glass transitions are higher than the hydroquinone systems. The dihydroxybiphenyl material exhibits a melting point at 135°C, and though lower than the pure monomer it is still high for the desired room temperature processability. Cured Tg's of all of the systems studied were above 350°F.

Isothermal aging of the samples at 600°F in air is shown in Figure 5. A weight loss of 20-30% was observed for all of the systems over 200 h. There is little difference between the various products since the controlling factor of the thermoxidative stability, the sulfone linkage, is common to each of them.

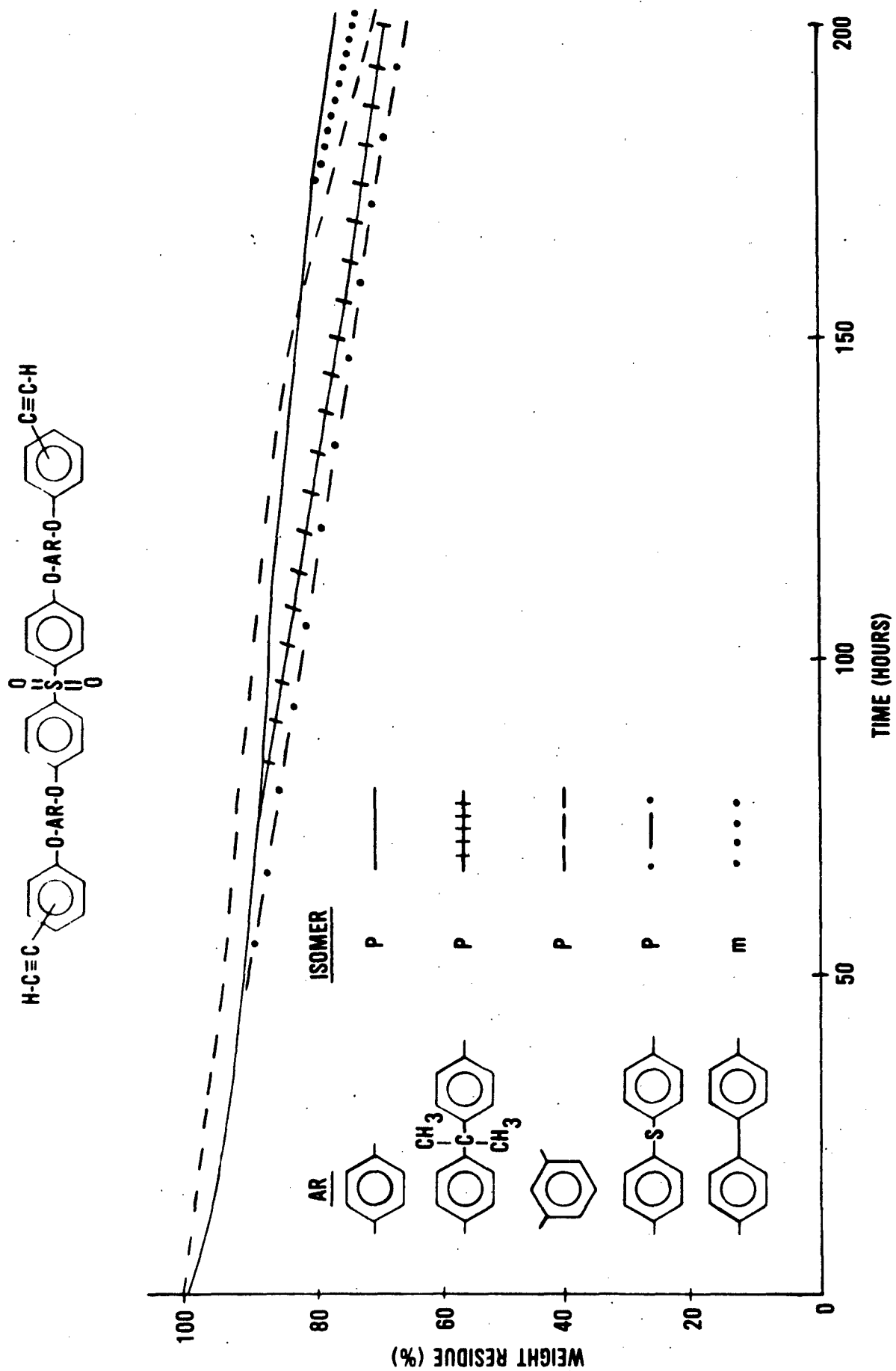


Figure 5. Isothermal Aging in Air at 600°F

SECTION III

EXPERIMENTAL

1. MONO(BROMOPHENOXY)PHENOL (I)

The mono(bromophenoxy)phenols required for the monomeric models were synthesized by two methods. Method A: a mixture of pyridine (90mL), diol (60 mmol), dibromobenzene (56.4g, 240 mmol), anhydrous potassium carbonate (33.3g, 250 mmol) and cuprous iodide (1.62g, 9 mmol) was heated at reflux under nitrogen for 20h. After cooling to room temperature, the reaction mixture was acidified with 1N HCl and the product extracted with chloroform. The chloroform was evaporated and the residue extracted with 10% aq. NaOH. The aqueous phase was acidified, extracted with chloroform, and reduced in volume to an oil that was stirred with 20% aq. NaOH to afford the sodium salt of the product. The salt was isolated and dried to give a white solid. The solid was acidified to pH 1 in water, and the freed mono(bromophenoxy)phenol was washed with water and dried. C-H analysis for products was satisfactory.

Method B: a mixture of diol (50 mmol), dibromobenzene (47.0g, 200 mmol), cuprous oxide (1.97g, 15 mmol) and 2,4,6-collidine (100mL) was heated to reflux under nitrogen for 20h. The product was isolated as in Method A.

2. 1,1'-SULFONYLBIS[4-[MONO(BROMOPHENOXY)PHENOXY]BENZENE] MONOMER (II)

A mixture of dry 1-methyl-2-pyrrolidinone (45mL), benzene (25mL), I (52.8 mmol), 4,4'-dichlorodiphenyl sulfone (7.58g, 26.4 mmol) and anhydrous potassium carbonate (3.83g, 27.7 mmol) was purged with nitrogen for 15 minutes. The mixture was heated to reflux and the benzene azeotrope collected between 80°C and 150°C. When most of the benzene had been removed, the reaction was heated at 165° for 7h. After cooling to room temperature, the mixture was poured into 350mL 10% sulfuric acid and was extracted with chloroform. The organic phase was washed first with 25% sulfuric acid, then with distilled water. After drying over MgSO₄, the chloroform solution was evaporated to dryness affording a 75-85% yield of the monomeric sulfone.

3. 1,1'-SULFONYLBIS[4-(PHENOLPHENOXY)BENZENE] MONOMER AND OLIGOMER (IV)

A mixture of dry 1-methyl-2-pyrrolidinone (40mL), benzene (20mL), diol (95 mmol), 4,4'-dichlorodiphenyl sulfone (6.79g, 23.7 mmol) and anhydrous potassium carbonate

(3.43 g, 24.8 mmol) was purged with nitrogen for 15 minutes. The mixture was heated to reflux and the benzene azeotrope collected until the reaction temperature reached 190°C. When most of the benzene was removed, the reaction was heated at 190°C for 7h. After cooling to room temperature, the reaction was poured into 400mL 10% HCl. A dark, gummy solid separated and the aqueous solution was decanted from the gum. This solid was dissolved in 100mL glacial acetic acid, and the acid solution was precipitated into 1200mL ice water to give a light solid. The precipitate was dissolved in diethyl ether and filtered over a bed of silica gel to remove a dark impurity. The ether solution was dried giving a light amorphous solid in 75-85% yield.

4. BROMINATED MONOMER/OLIGOMER MIXTURES FROM IV (V)

The brominated sulfone monomer/oligomer mixtures were prepared by two different methods. Method A: a mixture of pyridine (70mL), IV (11.5 mmol), dibromobenzene (26.96g, 115 mmol), anhydrous potassium carbonate (7.94g, 57.5 mmol) and cuprous iodide (0.13g, 0.7 mmol) was heated at reflux under nitrogen for 24h. After cooling to room temperature, the reaction mixture was acidified with 1N HCl and the aqueous solution extracted with ether. The organic phase was reduced in volume to a brown gum which was washed several times with hexane and then dried to give a 75-95% yield of the dibromo product.

Method B: after combining 2,4,6-collidine (9mL), IV (10,25 mmol), dibromobenzene (24.2g, 102.5 mmol) and cuprous oxide (2.95g, 20.51 mmol), the reaction mixture was heated at reflux under nitrogen for 24h. When the reaction had cooled to approximately 80°C, the mixture was filtered, then diluted with chloroform. The organic phase was warmed to 60°C with 100mL conc. HCl, washed with water and then was filtered through a short bed of silica gel. The product, a light amorphous solid, was obtained in 75-90% yield.

5. ACETONE PROTECTED ACETYLENE MONOMER/OLIGOMER FROM V (VI)

A solution of V (5.5 mmol), 2-methyl-3-butyn-2-ol (2.76g, 32.9 mmol), pyridine (15mL), triethylamine (30mL), bis(triphenylphosphine) palladium chloride (0.10g), cuprous iodide (0.10g) and triphenylphosphine (0.20g) was degassed with nitrogen for 15 minutes. The reaction was heated at reflux for 24h, cooled and filtered, then acidified with 1N HCl. The product was extracted with toluene. The organic phase

was washed with 1N HCl and then was heated for 1/2h at 60°C with ethylene diamine. After washing well with water, the toluene solution was dried over MgSO_4 and chromatographed on silica gel using chloroform as eluent. The chloroform was removed to give a light, amorphous solid in 70-85% yield.

6. ETHYNYL TERMINATED MONOMER/OLIGOMER MIXTURES FROM VI (VII)

A mixture of the bis-butynol adduct, VI (3.9 mmol), toluene (40mL) and 10% methanolic KOH (40mL) was heated to reflux under nitrogen. The methanol and toluene were removed by distillation, adding more toluene as needed to maintain the reaction volume at 40mL. After 4h, the reaction was cooled to room temperature and filtered over a bed of packed Celite. The toluene solution was washed with water, dried over MgSO_4 , and reduced in volume to give the ethynyl product (VII) a light colored solid, in 80-95% yield. Monomer/oligomer ratios were determined by column chromatography as weight % monomer: weight % oligomer.

7. 4,4'-[SULFONYLBIS(BIS(4,1-PHENYLENEOXY)]BIS[PHENOL] (VIII)

A dry flask containing 1,1'-Sulfonylbis[4-(4-methoxyphenoxy)benzene] (10.0g, 22 mmol) was cooled in a dry ice - acetone bath for 15 minutes. After cooling, a 1.0M solution of Boron tribromide in methylene chloride (16.5g, 66 mmol) was added and the reaction was allowed to reach room temperature. After stirring for 18h, the solution was slowly added to 300mL water and stirred for several hours until a light solid could be filtered. The solid was washed with water and dried to give the product in 95% yield.

8. CHARACTERIZATION

Differential scanning calorimetry and thermal mechanical analysis data were obtained on a DuPont 990 thermal analyzer coupled with a DuPont DSC or TMA cell. Isothermal aging studies were carried out with an automatic multisample apparatus.

SECTION IV

CONCLUSIONS

The synthesis of Phenylene R type systems via the proposed route afforded two materials which had both final Tg's above the 350°F limit and initial Tg's which were at or below room temperature. The two systems which offered the most desirable properties were those based on resorcinol/p-dibromobenzene and hydroquinone/m-dibromobenzene. Of the two, the hydroquinone system offered a lower initial softening temperature while also providing a cured Tg above 200°C. For this reason the product from hydroquinone and m-dibromobenzene was chosen as the candidate system for future work.

A scale-up of the reaction sequence to obtain enough of the material for mechanical testing is in progress. Following completion of the synthetic work, evaluation of the mechanical properties of the chosen system will be carried out to determine whether increasing chain length between reactive sites will indeed bring an improvement in toughness of acetylene terminated Phenylene R systems.

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