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POLYMERIC MATERIALS CONTAINING AROMATIC ENYNE LINKAGES.(U)
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POLYMERIC MATERIALS CONTAINING AROMATIC ENYNE LINKAGES

Polymer Branch
Nonmetallic Materials Division

December 1978

TECHNICAL REPORT AFML-TR-78-141

Final Report for Period September 1977 to September 1978

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AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

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This technical report has been reviewed and is approved for publication.

F.E. Arnold

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Project Scientist

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FOR THE DIRECTOR

J. M. Kelble, Chief
Nonmetallic Materials Division

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
⑭ 1. ~~REPORT NUMBER~~ AFML-TR-78-141	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE ~~(and Subtitle)~~ ⑥ Polymeric Materials Containing Aromatic Enyne Linkages.		5. ~~TYPE OF REPORT & PERIOD COVERED~~ ⑨ Final Technical Report. Sep 1977 — Sep 1978
		6. ~~PERFORMING ORG. REPORT NUMBER~~
7. ~~AUTHOR(s)~~ ⑩ Mr. B. A. Reinhardt Dr. F. E. Arnold		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS ⑯ 24190415 ⑰ 04
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		12. ~~REPORT DATE~~ ⑪ December 1978
		13. ~~NUMBER OF PAGES~~ 22
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) ⑫ 29p.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Polysulfone
Intramolecular Cyclization
Enyne
Thermoplastic

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

High molecular weight polysulfones containing 1, 3-enyne linkages within the polymer backbone were prepared by the reaction of the potassium salts of (E)-3, 3' -(1-buten-3-ynylene) diphenol and 4,4'-dihydroxybiphenyl with 4,4'-dihalosulfones in DMSO-sulfolane solvent mixtures. The polymers were soluble in methylene chloride and exhibited inherent viscosities as high as 0.74 (0.5% solution in DMAC at 30°C) with glass transition temperatures ranging from 179 to 214°C. It was postulated that the polymers upon heating would cure via an intramolecular cycloaddition reaction to form a 2-phenylnaphthalene fused ring

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system along the polymer backbone. Preliminary thermal analytical data and studies on cured films indicate that the primary curing reaction is <u>inter</u>-molecular in nature rather than intramolecular. Additional data indicate that the enyne polysulfones have suitable properties for use as high temperature thermoplastic composite materials.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials", Task No. 241904, Work Unit Directive 24190415, "Structural Resins". It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were Mr. B. A. Reinhardt and Dr. F. E. Arnold, Air Force Materials Laboratory, (AFML/MBP).

This report covers research conducted from September 1977 to September 1978.

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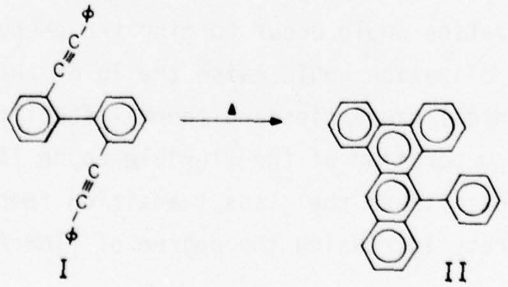
SECTION I

INTRODUCTION

In recent years a totally new approach has been developed for the curing of heterocyclic matrix resins. The approach involves the curing of such materials by intramolecular cycloaddition reactions (IMC) and has been demonstrated with the quinoxaline (Reference 1) and imide (Reference 2) classes of polymers. This type of cure involves starting with a linear, relatively mobile polymer chain which when heated reacts via an IMC reaction to form a cyclic aromatic system within the polymer backbone. The addition reaction transforms the polymer from a fairly flexible chain to a rigid backbone structure, thereby advancing the Tg of the polymer. The IMC cure is primarily dependent upon rotational movement of the polymer backbone, which requires substantially less molecular mobility than the translational movement needed for intramolecular curing reactions. A curing reaction of this type can continue long after the resin has vitrified and the resultant use temperature, depending on the particular system, should be substantially higher than the cure temperature.

Previous IMC systems (Reference 2) were based on the thermal conversion of 2,2'-di(phenylethynyl)-biphenyl(I) to a 9-phenyl-dibenz[a,c]-anthracene structure (II). This reaction had been reported previously (Reference 3) to proceed in high yield either thermally or photochemically. Incorporation of the 2,2' (diphenylethynyl)-biphenyl linkage into a polymer backbone showed substantial advancement in Tg above the cure temperature. Unfortunately,

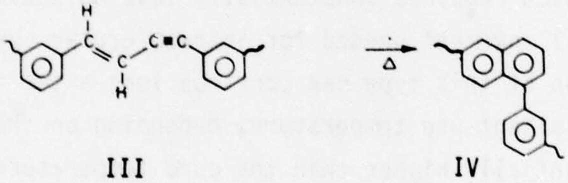


I

II

the extent of flow of the uncured polymers was insufficient for satisfactory processing (References 1,2).

Two other systems which exhibited glass transition temperature after cure in excess of the cure temperature were the acetylene terminated quinoxaline oligomers (Reference 4) and the acetylene terminated polyimide oligomers (Reference 5) (Thermide). These systems were thought to undergo propagation followed by cyclization upon cure to form aromatic rings. The process by which cyclization takes place can follow many mechanistic pathways (Reference 4) one of which involves the initial formation of an enyne (III) linkage followed by rearrangement and aromatization to form a phenylnaphthalene structure (IV). Studies on the pyrolysis of enyne model compounds showed small amounts of phenylnaphthalene as one of the identifiable products.



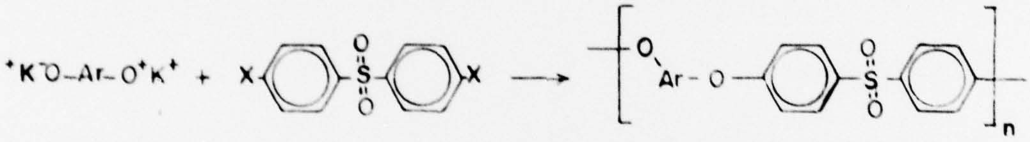
III IV

It was postulated that if a linkage such as III was incorporated into a high molecular weight polymer and that polymer cured at elevated temperature, cyclization would occur forming the phenylnaphthalene structure IV. Such a cyclization would raise the Tg of the material and also optimize the mechanical properties and thermal stability. It was also postulated that incorporation of the flexible enyne linkage into a polymer backbone would tend to lower the glass transition temperature of the uncured polymer, thereby increasing the degree of flow for processing.

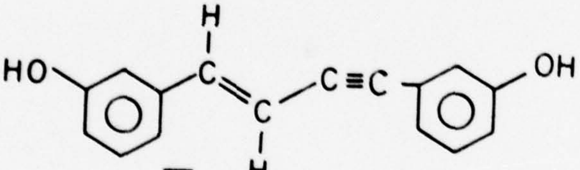
It was our intention in the present work to synthesize a high molecular weight polymer system containing an enyne linkage which could be easily fabricated and upon curing would react via an IMC reaction to form fused aromatic linkages.

SECTION II
RESULTS AND DISCUSSION

The aromatic sulfone polymer backbone was chosen to test the IMC potential for the enyne linkage. The phenylene-R system incorporates ether and sulfone flexible groups which would provide the required chain mobility for processing. It has been demonstrated that the system is insensitive to absorbed moisture both as a thermoplastic (Reference 6) and thermoset (Reference 7) matrix resin. Aromatic polysulfones are prepared by the condensation polymerization of alkali metal salts of bisphenols with aromatic dihalosulfones.



The simplest route to the incorporation of the enyne linkage in an aromatic sulfone polymer appeared in this case to be the synthesis of the diol monomer V.

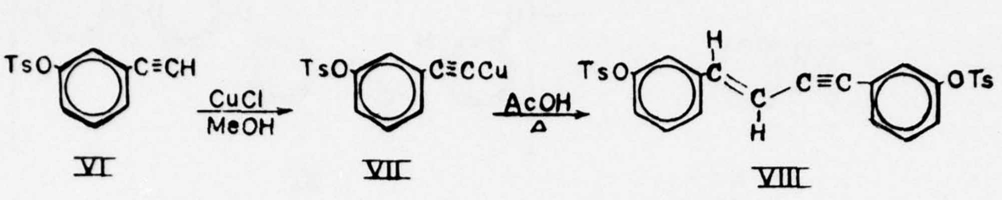


V

1. SYNTHESIS

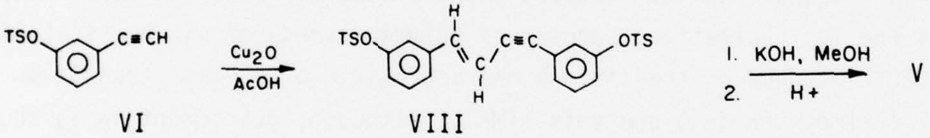
a. Monomers

The enyne diol monomer V was initially synthesized via the Strauss Coupling of the corresponding cuprous salt of 3-ethynylphenyl (p-toluene sulfonate)(VI) in refluxing acetic acid followed by basic hydrolysis according to the reaction scheme illustrated below.



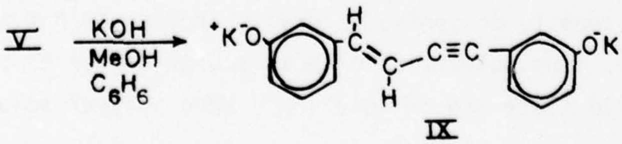
$$\text{VIII} \xrightarrow[\text{MeOH}]{\text{KOH}} \xrightarrow[H_2O]{H^+} \text{V}$$

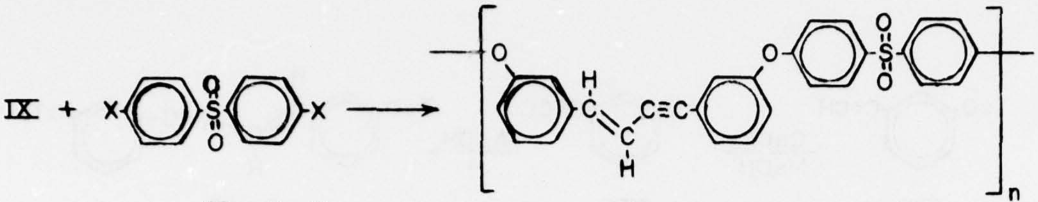
The reaction scheme was shortened, thus improving the yield, when VI was allowed to react with cuprous oxide in acetic acid to give VIII in 65% yield. Hydrolysis of VIII followed by acidification gave V in 80% yield.



b. Polymers

The enyne containing polysulfone polymer XI was prepared by the addition of either of two 4-4'-dihalodiphenyl sulfones (X a,b) to a solution of the potassium salt of V in a mixture of DMSO and sulfolane at 145°C.





Xa. X = F
b. X = Cl

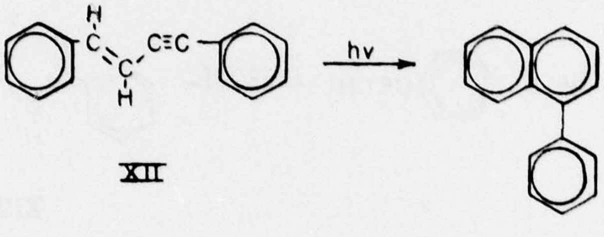
XI

The polymer XI was precipitated by dropwise addition of the reaction into MeOH. The polymers were soluble in methylene chloride in concentrations greater than 20% and tough, transparent films could be cast from 1-3% solutions of the polymer in the same solvent. Intrinsic viscosities of polymers in DMAC ranged from 0.38 to 0.67.

The DSC thermogram (Δ = 20°C/min) of the enyne polysulfone shows an initial base line shift characteristic of a glass transition at 170°C and a strong exotherm beginning at 200°C and reaching a maximum at 302°C. In all cases, the extrapolated onset of the DSC baseline shift was taken as the Tg. Pelletized samples of polymer cured for six hours at 343°C (650°F) showed no transitions characteristic of a glass transition by DSC or Thermomechanical analysis (TMA). Although advancement in Tg above the cure temperature took place, samples of thin films when cured at temperatures as low as 250°C were very brittle and insoluble in organic solvents. The thermal reaction of the polymer film can be monitored by observing the infrared absorption at 948 cm^{-1} as a function of time. When film samples are heated at 265°C, under nitrogen, the absorption at 948 cm^{-1} decreases continuously until a limiting value is reached after approximately two hours. Such behavior is characteristic of a highly crosslinked material, thus <u>inter</u>chain reaction seems to be taking place to a great extent. The data collected seem to be contradictory to whether or not an IMC reaction is taking place. The polymer also shows a high degree of photoreactivity in both the solid state and in solution. When polymer solutions are exposed to fluorescent or UV light for a period of time precipitation of material results. Similarly the polymers in the solid state are rendered partially insoluble on extended exposure to fluorescent or light.

c. Model Compounds

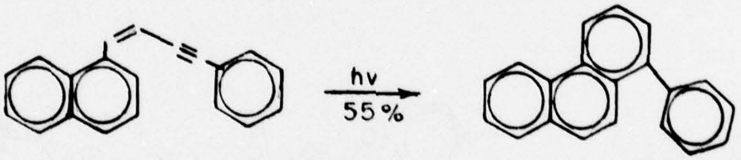
In an attempt to understand the thermal curing reaction, and the photoreactivity of the sulfone polymer a model compound study was initiated. Previous studies have been carried out on the photocyclization of enynes (Reference 8). The reaction of 1,1'(1-buten-3-yne-1,4-diyl) bisbenzene (XII) with UV light produces the cyclization product XIII in only 2% yield (Reference 6). The reaction was also reported not to occur thermally at any temperature.



XII

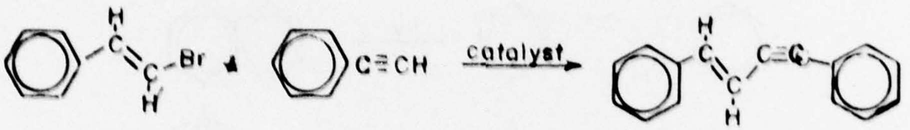
XIII

When the ring system involved in the cyclization was changed from phenyl to naphthyl the reaction proceeded in 55% yield photochemically (Reference 6).



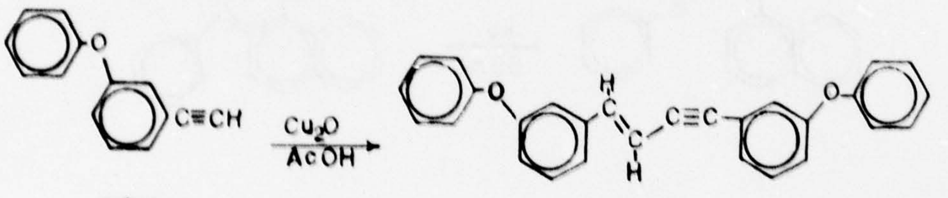
In some cases it was reported that substitution on the phenyl ring involved in the cyclization improved the yield but in general only low yields are obtained when the aryl group involved contains only one aromatic ring. This behavior has been attributed to the low reactivity of the phenyl group in the radical additions (Reference 9).

The thermal reactions of enynes to form cyclic products have been observed and only in the gas phase (Reference 10). In this study an attempt was made to reinvestigate model compounds pertaining to the polymer to determine if any cyclic products were obtained under the specified cure conditions, either thermally or photochemically. The two model compounds were synthesized as described below. The reaction of (E)-β bromostyrene with phenyacelylene in the presence of bis (triphenylphosphine) palladium dichloride and cuprous iodide in triethylamine gave the model compound (E)-1,1'-(1-buten-3-yne-1,4-diyl) bisbenzene XIV in 85% yield (Reference 11).



XIV

An additional enyne model compound XVI, this one containing pendant phenoxy groups was synthesized by the cuprous oxide catalyzed dimerization of 3-phenoxyphenylacetylene XV in acetic acid according to the following scheme:



XV

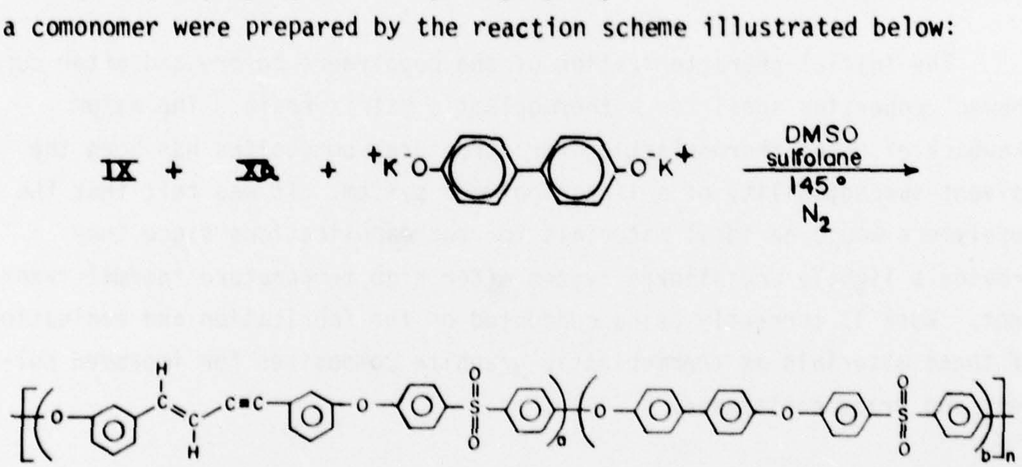
XVI

Both solutions and neat samples of XIV and XVI when heated at 210°C in solution and 250°C under nitrogen gave only polymer and recovered starting materials as the major products. Traces of cyclic products could be detected in minute amounts by thin layer chromatography but could not be obtained in sufficient amounts for characterization. Almost identical results were obtained when dilute solutions of the two compounds were exposed to UV light, in benzene solution under nitrogen. Again only polymeric products and unreacted starting material were isolated in reasonable amounts.

Although cyclization does not appear to be a major reaction in the photolysis or thermalysis of the two enyne model compounds investigated, the possibility exists that the electronic and steric characteristics of a high molecular weight polymeric backbone could favor ring closure over interchain reaction, thus allowing the polymer to react at least partially via an IMC mechanism.

d. Copolymers

Since the interchain reaction of the enyne sulfone polymer appeared to be so facile, it was postulated that enyne sulfone copolymers could be made which would be soluble in common organic solvents, easily processible, and which could be lightly crosslinked at high temperature. Such materials after crosslinking would be insoluble and possess optimum solvent resistance as thermoplastic matrix resins. Enyne sulfone copolymers (XVII) employing 4,4'-dihydroxybiphenyl in various concentrations as a comonomer were prepared by the reaction scheme illustrated below:



XVII

The copolymers were isolated by precipitation of the reaction mixture into methanol. The solubilities and film forming characteristics of copolymers were very similar to those of the enyne homopolymer. Thermal characterization data for copolymers and enyne hemopolymer are summarized in Table 1.

Samples of enyne polysulfone polymers and copolymers were cured at 343°C(650°F) for six hours and then exposed to an air environment at 600°F for a number of hours. The results of the isothermal aging studies are illustrated in Figure 1. In general, the thermal stability in air for the polymers decreases as the amount of enyne linkage increases.

The DSC and TMA data of the copolymers indicate between a 20-96°C advancement, depending on the uncured copolymer composition, in Tg when pelletized samples were cured at 343°C(650°F) for six hours. When film samples of the copolymers were cured at 265°C for four hours, tough insoluble films were obtained which were very flexible. Again, the intensity of the infrared band at 948 cm^{-1} reached a limiting value after approximately two hours of thermal treatment. The flexibility increased as the amount of enyne in the copolymer was reduced. This behavior was expected and is characteristic of a decreased crosslink density.

The initial characterization of the copolymers before and after cure showed properties ideal for a thermoplastic matrix resin. The major drawback of using thermoplastics for structural composites has been the solvent susceptibility of a linear polymer system. It was felt that the copolymers would be ideal materials for such applications since they provide a lightly crosslinked system after high temperature thermal treatment. Work is currently being conducted on the fabrication and evaluations of these materials as thermoplastic graphite composites for improved solvent and craze resistance.

SECTION III

EXPERIMENTAL

1. MONOMERS

a. (E)-3,3'-(1-Buten-3-ynylene)diphenol di-p-toluenesulfonate (XIV)

To a two liter, 3-necked round bottom flask, equipped with a nitrogen inlet, condenser, and magnetic stirring bar was added 100 ml glacial acetic acid. The acetic acid was deaerated by bubbling nitrogen through the liquid at reflux for 15 minutes. To the acetic acid at reflux was added 10.6g (0.0740 mol) of Cu_2O and the resulting suspension refluxed for 20 minutes. At the end of this period almost all the Cu_2O had dissolved and a blue green solution had developed. To the solution at reflux was then added 100g (0.368 mol) of 3-ethynyl-p-toluene sulfonate. Upon addition of the tosylate the solution changed to orange in color. Heating was continued an additional 1-1/2 hours. The reaction mixture was cooled, filtered, and added dropwide to a stirring suspension consisting of 25 ml H_2O, 300 gm $NaHCO_3$, and 200 ml CH_2Cl_2. When all the bicarbonate appeared to have reacted additional solid sodium bicarbonate was added as needed until all the acetic acid reaction mixture had been neutralized. The CH_2Cl_2 layer was then separated and the water layer washed with 100 ml additional CH_2Cl_2. The 300 ml CH_2Cl_2 layer was washed with two 500 ml portions of H_2O, dried of M_gSO_4 and reduced in volume to approximately 80 ml of a thick viscous oil which was chromatographed on a 60 x 5 cm dry column (quartz) of silica gel using 2:1 CH_2Cl_2-hexane as the eluent. The solvent is evaporated to give 66.0g(65%) of a white crystalline solid mp 138-139°C.

Anal. Calcd for $C_{30}H_{24}S_2O_6$: C, 66.16; H 4.44; S, 11.78

Found: C, 66.59; H 4.32; S, 11.74

b. (E)-3,3'-(1-Buten-3-ynylene)diphenol (V)

In a 5ℓ, 3-necked round bottom equipped with a nitrogen inlet and a distillation apparatus was added 125.0g (0.23 mol) of 1, 4-bis [phenyl(p-toluene sulfonate)-3-yl-buta-1-ene-3-yne] and 2500 ml of methanol. To the resulting pale yellow suspension was added 51.60g NaOH in 750 ml of H_2O. The reaction mixture was then heated to reflux and approximately 2500 ml of distillate collected. (If during the course of the reaction the tosylate does not go into solution more methanol is added until solution is obtained. This additional methanol is removed along with the original 2500 ml.) After the removal of the methanol 750 ml of water was added and the resulting solution poured into a mixture of 400 ml of H_2SO_4 and 4000g of ice. The reaction mixture was then stirred until all the ice melted and the resulting precipitate filtered, washed with H_2O, air dried for a short time and then dried under high vacuum at room temperature for 24 hours. The solid was recrystallized by stirring in 1000 ml boiling cyclohexane and adding benzene slowly until solution occurred. The purple solution was treated with charcoal, filtered, and cooled. The resulting crystals are filtered, air dried for a short time, and dried for four hours under high vacuum. A 3.0g portion of the dried, off-white solid is dissolved in 20 ml of 4:1 methylene chloride-acetonitrile and chromatographed on a 60 x 5 cm dry column (quartz) using 4:1 chloroform-acetonitrile as the eluent. The elution is followed by UV light and the large second band collected. After removal of the solvent under high vacuum the resulting white solid (2.3g) had a melting point of 146-147°C.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12

Found: C, 81.27; H, 4.95

2. POLYMERS AND COPOLYMERS

a. Poly [(E)-(oxy-1, 4-phenylenesulfonyl-1, 4-phenyleneoxy-1, 3-phenylene-1-buten-3-ynylene-1, 3-phenylene)] (XI)

In a 50 ml polymerization flask equipped with a nitrogen inlet, an addition funnel, and a short path distillation apparatus was added 0.5907g (2.5 mmol) of (E)-3,3'-(1-buten-3-ynylene) diphenol (V) 5.0 ml of 1N potassium hydroxide in methanol, 10 ml methanol and 10 ml benzene. The reaction mixture was heated and the solvent removed until only a few ml remained. At this time 10 ml of additional benzene was added and distilled to remove the last traces of water. To the resulting thick suspension was added 5 ml of dry dimethyl sulfoxide and 15 ml of dry sulfolane. The temperature of the reaction mixture was slowly raised to 130°C during which time all solids in the reaction mixture went into solution. To the brownish-orange solution was added 0.6357g (2.5 mmol) of 4,4'-difluorodiphenylsulfone and the solid washed with 5 ml benzene. The temperature was raised slowly to 140-145°C and maintained there for four hours. The polymerization mixture was then cooled, diluted with 10 ml methylene chloride, and precipitated into 1500 ml of methanol. The white fluffy polymer was washed with methanol, air dried, dissolved in 20 ml methylene chloride, filtered and reprecipitated into methanol. A 0.5% solution of the polymer in DMAC at 30°C gave an intrinsic viscosity of 0.67.

Analytical data for the homopolymers and copolymers are summarized in Table 2.

b. Poly [(E)-(oxy-1,4-phenylenesulfonyl-1,4-phenylene oxy-1,3-phenylene-1-buten-3-ynylene-1,3-phenylene)-CO-(oxy-4,4'-biphenylylenoxy-1,4-phenylsulfonyl-1,5-phenylene)] (XVI) (25 mole percent enyne) (XVIIb)

In a 50 ml polymerization flask equipped with a nitrogen inlet, an addition funnel, and a short path distillation apparatus was added

0.1477g (0.625 mmol) of (E)-3,3'-(1-buten-3-ynylene) diphenol (V), 0.3491g (1.875 mmol) of 4,4'-dihydroxybiphenyl) 5.0 ml of 1N potassium hydroxide in methanol, 10 ml of methanol and 10 ml of benzene. The reaction mixture was heated and the solvent removed until only a few milliliter remained. At this time 10 ml of additional benzene was added and distilled to remove the last traces of water. To the resulting thick suspension was added 10 ml of dry dimethyl sulfoxide and 10 ml of dry sulfolane. The temperature of the reaction mixture was slowly raised to 130°C during which time all suspended solids in the reaction mixture went into solution. To the brownish orange solution was added 0.6357g (2.5 mmol) of 4,4'-difluorodiphenylsulfone and the solid washed with 5 ml dry benzene. The temperature was raised slowly to 140-145°C and maintained there for four hours. The polymerization mixture was then cooled and precipitated into 1500 ml of methanol. The white fluffy polymer was washed with methanol, air dried, dissolved in 20 ml methylene chloride filtered and reprecipitated into methanol. A 0.5% solution of the polymer in DMAC at 30°C gave an intrinsic viscosity of 0.74. The polymer, both dry and in solution must be stored in the absence of light.

Anal. Calcd for $C_{52}H_{34}O_8S_2$: C, 72.77; H, 4.03, S, 7.74

Found: C, 72.38; H, 3.75, S, 8.09

The other copolymers were made using the above procedure except the solvent was changed to 12 ml dimethyl sulfoxide and 6 ml of sulfolane to attain better solubility for the potassium salts at 130°C.

3. MODEL COMPOUNDS

a. 1, 1'-(1-buten-3-yne-1, 4-diyl)bis-benzene (XIV)

This compound was prepared in 85% yield according to the known procedure (Reference 9) mp 96-97°C, lit (Reference 12) 96-97°C.

b. (E)-3,3'(1-buten-3-ynylene)diphenyl bisphenyl ether (XVI)

Acetic acid (50 ml) was degassed by heating to reflux while nitrogen was bubbled through. To the deareated solvent at reflux was added 0.81g of cuprous oxide. The solution was heated at reflux for 30 minutes at which time 5.0g (0.0281 mol) of 3-phenoxyphenylacetylene was added. The color of the reaction mixture went from blue to orange after ten minutes. After 40 minutes the solution went from orange to green in color. The solution was heated at reflux a total of 1.5 hours after which time it was cooled, poured into a mixture of one liter of saturated sodium bicarbonate solution, and 200 ml of dichloromethane. The organic layer was separated, washed with water, dried over anhydrous magnesium sulfate, and filtered through celite. The solvent was removed under reduced pressure to give a viscous oil which was chromatographed on a dry silica gel column using 3:1 hexane-dichloromethane as the eluent. Removal of solvent under reduced pressure produced an oil which became solid upon addition of hexane to yield 2.3g (42%) of an off-white solid, m; 87-88°C.

Anal Calcd. for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19

Found: C, 86.67, H, 4.87

4. SPECTRAL PROPERTIES OF MONOMER, MODEL COMPOUNDS AND POLYMERS

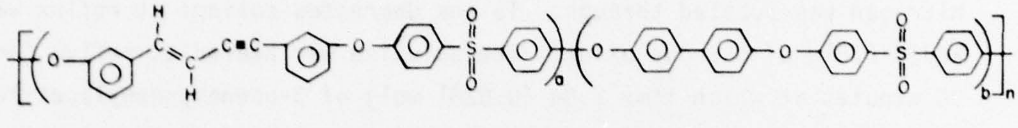
Infrared, proton NMR, and C_{13} NMR spectral results are summarized for all compounds and polymers in Tables 3-5.

5. PHOTO REACTIONS OF MODEL COMPOUNDS

Irradiations were carried out on 5 x 10^{-4}m solutions of the compounds in deareated benzene using an Ace Glass No. 7825-34 Hanovia Immersion Lamp. Irradiations were carried out for ten hours and were monitored by Thin Layer Chromatography on silica gel using hexane and the developing solvent.

TABLE 1

THERMAL ANALYTICAL AND VISCOSITY DATA ENYNE POLYSULFONES



	Compound Structure		[n]^{a}	x	Tg^{b} pred.	Tg^{c}	Ti^{d}	Tg^{e} cured	Tg^{f} pred cured	W^{g}
	%a	%b								
XI	100	0	0.67	F	176	179	200	None Observed	264	17
	100	0	0.38	Cl	"	"	"	"	"	"
	0	100		Cl	-	220	--	--	--	91
XVII a	50	50	0.47	F	196	191	225	287	244	50
b	25	75	0.74	F	207	205	257	255	232	68
c	10	90	0.41	F	214	214	220	234	227	79

a. Intrinsic viscosity measured in DMAC (0.5%).
b. Predicted Tg base on Fox-Flory or Copolymer Equation.
c. Measured by DSC and TMA.
d. Temperature at which curing exotherm begins.
e. Tg measured by DSC and TMA for polymer samples cured at 343°C (650°F) *for six hours.*
f. Tg predicted from Fox-Flory and Copolymer Equation for cyclized polymer.
g. Isothermal Aging - weight retained after 200 hours at 315.6°C (600°F).

TABLE 2

ELEMENTAL ANALYSES FOR ENYNE POLYSULFONE POLYMERS

Polymer	Calcd %	Found %
XI	C 74.64 H 4.03 S 7.12	C 74.06 H 3.68 S 7.15
XVIIa	C 73.47 H 4.03 S 7.51	C 71.52 H 3.83 S 7.88
XVIIb	C 72.77 H 4.03 S 7.74	C 72.38 H 3.75 S 8.09
XVIIc	C 72.31 H 4.03 S 7.90	C 73.09 H 3.91 S 7.66

TABLE 3

INFRARED SPECTRAL DATA

Compound	IR (cm^{-1})	Assignment
XIV	1482(s)	ν aromatic
	940(s)	δ trans CH=CH
XVI	2195(w)	ν C=C
	1488(s)	ν aromatic
	952(s)	δ trans CH=CH
XI	1320(s)	ν SO_2
	1150(s)	"
	1480(s)	ν aromatic
	948(s)	δ trans CH=CH
XVII a,b,c	1480(s)	ν aromatic
	948(m)	δ trans CH=CH
	1150(s)	ν SO_2
	1320(s)	
V	3250(s)broad	ν OH
	1450(s)	ν aromatic
	940(m)	δ trans CH=CH
VIII	1465(s)	ν aromatic
	955(s)	δ trans CH=CH

TABLE 4

NMR SPECTRA H^1

Compound	Solvent	Chemical Shift δ	Coupling Constraint Hz	Description	Assignment
V	$CDCl_3$-$(CF_3)_2CO$	6.3	16.3	1/2 of AB Multiplet	1 = CH
		6.7 - 7.3		Multiplet	9-phenyl H
		8.4		Broad Singlet	1 = CH 2 - OH
XIV	$CDCl_3$	6.4	16.3	1/2 AB Doublet	1 = CH
		7.0	16.3	1/2 AB Doublet	1 = CH
		7.2 - 7.6		Multiplet	10 - phenyl H
XVI	$CDCl_3$	6.3	16.3	1/2 AB Doublet	1 = CH
		6.8 - 7.4		Multiplet	1 = CH 18 - phenyl H

TABLE 5

C-13 NMR OF ENYNE POLYSULFONES

COMPOUND	δC_{13}	CARBON ASSIGNMENT
V	89.0	C≡
	91.9	C≡
	108.0	C=
	113.3	C=
	116.4 - 157.9	Phenyl C
XI	90.0	C≡
	91.0	C≡
	109.0	C=
	117.7 - 161.2	Phenyl C

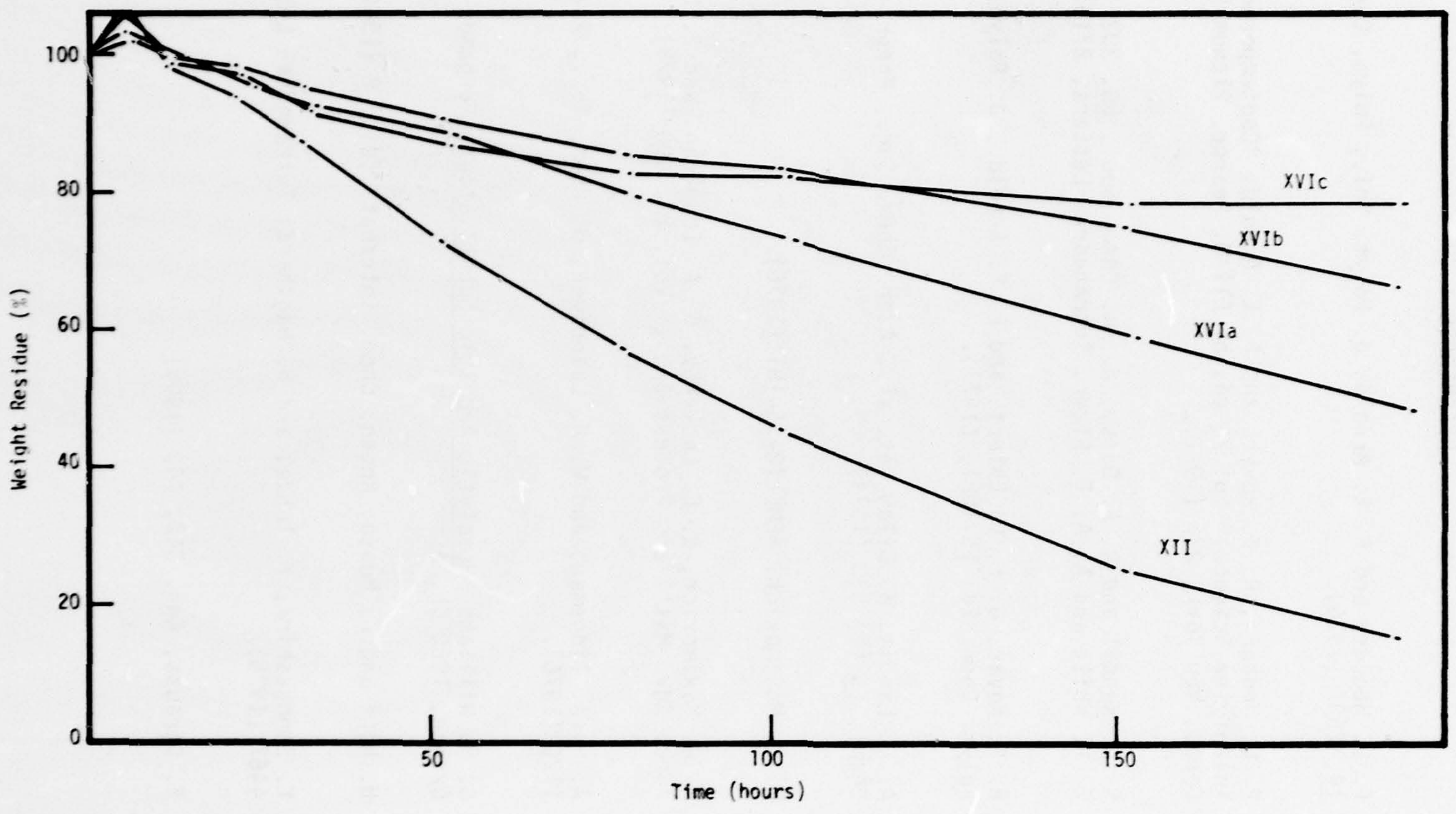


Figure 1. Isothermal Aging Curves for Enyne Polymers and Copolymers in Air at 315.6°C(600°F)

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