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SYNTHESIS AND THERMOMECHANICAL PROPERTIES OF NEW AT-PHENYLENE R SYSTEMS

J. S. Wallace
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Polymer Branch
Nonmetallic Materials Division

August 1984

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

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A series of high molecular weight (550-700 amu range) bis-phenol based acetylene terminated (AT) resins were synthesized by reacting four moles of 4,4'-dihalodiphenylsulfone (chloro and fluoro) with one mole of a bis-phenol (4,4'-isopropylidinediphenol, 4,4'-thiodiphenol, p,p'-biphenol, and resorcinol were used), end-capping the resulting halo-terminated products with 4-(m-hydroxyphenyl)-2methyl-3butyn-2-ol, and caustically cleaving the terminal acetone protecting groups to give free ethynyl functionalities. This synthesis produces a mixture of monomer and oligomer AT-products which were separated

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by column chromatography. Structural characterization of the systems was based on elemental and spectrographic (infrared and nuclear magnetic resonance (^1H)) analyses.

Pure AT-monomers and the monomer/oligomer mixtures produced by the outlined stoichiometry were cured at 288°C (550°F) for 8 h in air. Glass transition temperatures (Tgs) of the cured (by thermomechanical analysis) and uncured (by differential scanning calorimetry) AT-systems were measured. Thermo-oxidative stability of the resins was evaluated by isothermal aging (ITA) in air at 315°C (600°F) for 200 h.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Research to Define the Structure Property Relationships," Task No. 2303Q3, Work Unit Directive 2303Q307, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. T. E. Helminiak as the ML Project Scientist. Co-authors were Capt. J. S. Wallace and Dr. F. E. Arnold, Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from September 1982 to November 1983.

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SECTION I

INTRODUCTION

In recent years acetylene terminated resins (AT-resins) have shown promise in the area of high temperature applications and are possible replacements for state-of-the-art epoxy resin systems where humidity exposure is expected. Acetylene terminated resins have two important advantages over previously developed systems: 1) cured products have high thermal stability and exhibit good mechanical properties after exposure to humidity, and 2) the resins are cured through an addition reaction so no volatile by-products are evolved giving a voidless final matrix (Reference 1).

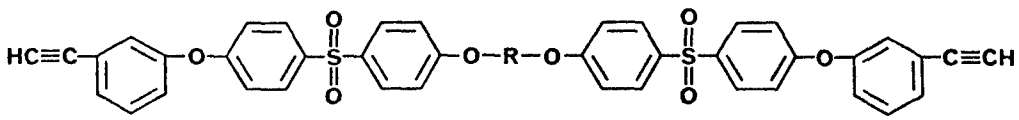
These properties make AT-resins especially attractive for advanced aircraft and aerospace vehicles where material weight is a critical factor and high temperatures as well as humidity are likely to be encountered.

In an effort to optimize mechanical and processing properties many different molecular systems have been inserted between terminal acetylene groups, with each system imparting its own unique properties to the final resin. The first of these systems to demonstrate good mechanical properties were the quinoxalines. These systems, with their large flexible molecular structures, did not however meet epoxy processing standards (i.e., melt processability and room temperature tack and drape (Reference 2) because of a high initial Tg (Reference 3). Two approaches were taken to resolve this problem. The first approach, which is presently still under investigation, was to incorporate reactive plasticizers into the quinoxaline resins. Preliminary data shows that this has the effect of lowering the initial Tg, but further study is required before effects on mechanical properties can be completely evaluated (Reference 4). The second approach involves the substitution of rigid low molecular weight groups into the resin backbone. The first group tried, the diphenyl sulfone linkage, led to resins (commonly known as ATS) with good processing properties but which were brittle in nature (Reference 1). Other AT-resins with groups similar in size, but more flexible than the diphenyl sulfone linkage have been synthesized. Complete mechanical properties evaluations of these systems have not been accomplished. Recent efforts have been directed at the development of an AT-resin for use at 350°F (177°C) with improved toughness.

A factor which has been associated with resin toughness is crosslink density of the matrix. This density can be controlled by increasing or decreasing the molecular

weight of the monomer and oligomer molecules which make up the resin. Reducing the crosslink density in a matrix has been shown to yield improved toughness (Reference 5). In an effort to improve the mechanical properties of a 177°C type AT-resin, monomers and oligomers of higher molecular weight, with various back-bones, are currently being synthesized. This work is centered at the Polymer Branch of the Materials Laboratory and is the basis for the research presented here. The combination of a semiflexible backbone and lower crosslink density should provide an AT-resin with superior mechanical properties. The objectives of this research therefore were:

1. The synthesis of higher molecular weight (550-700 amu range), semi-rigid AT-resins, with the general formula 1 with the potential of improved mechanical properties.



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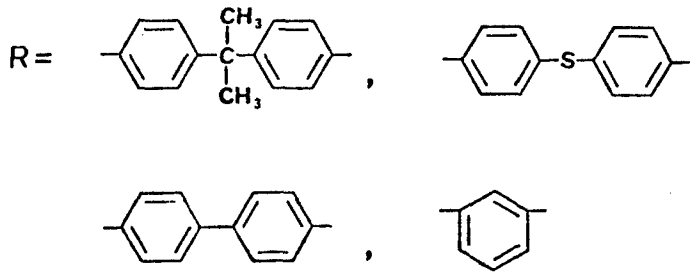


The diol and bis-diols used in these systems were chosen because of their low cost and ready availability. Meta- rather than para-AT end-capped systems were synthesized because the former generally have lower uncured Tgs which are desirable for easy processing.

2. Development of a new acetylene terminating procedure to facilitate the synthesis of the aforementioned systems.

SECTION II

EXPERIMENTAL

1. REAGENTS

The following were purchased from Aldrich Chemical Company and used without additional purification: p,p'-biphenol, 4,4'-thiodiphenol (99%), 4,4'-difluorodiphenylsulfone (99%), 2-methyl-3-butyn-3-butyn-2-ol, and tetrakis(triphenylphosphine) palladium(0) supported on polystyrene with 2% DVB crosslinking. Also purchased from Aldrich Chemical Company were 4,4'-dichlorodiphenylsulfone (98%) and 4,4'-isopropylidinedi-phenol (bisphenoll-A) which were further purified by recrystallization from toluene. The m-bromophenol used was purchased from Aldrich Chemical Company (97%) and Eastman Kodak Company (purity unknown) and was further purified by distillation. Resorcinol was purchased from Matheson, Coleman, and Bell. Dichlorobis(triphenylphosphine)passadium(II) and triphenylphosphine were purchased from Strem Chemicals, Inc., and used without further purification. Potassium methoxide (95-99%) and copper(I) iodide (98%) were purchased from Alfa Products and used without additional purification. All solvents and inorganic acids and bases were reagent grade. The N-methyl-2-pyrrolidone used was further purified by distillation. Silica gel (Woelm Dcc) was purchased from ICN Nutritional Biochemicals. Thin layer chromatography (TLC) strips coated with silica gel containing UV-254 indicator were purchased from Brinkman Instruments, Inc.

2. INSTRUMENTATION

Infrared (IR) spectra were recorded with Beckman Model IR-33 and Perkin-Elmer Model 457 spectrometers. Solid sample spectra were obtained from potassium bromide (KBr) films at concentrations of 2% by weight. Liquid sample spectra were obtained employing sodium chloride (NaCl) cells (with 5% chloroform solutions).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian EM-360A spectrometer using 10% weight/volumn solutions in deuterochloroform (99.6% gold label) with tetramethylsilane as an internal standard.

Melting points were obtained using a Büchi capillary melting point apparatus.

Elemental analyses were performed by the Analytical Laboratories, Wright-Patterson Air Force Base, Ohio.

Differential scanning calorimetric (DSC) data was obtained with a Dupont Model 900 thermal analyzer equipped with a differential scanning calorimetric cell at a heating rate of $10^{o}C$/min.

Thermomechanical analyses (TMA) were performed on a DuPont Model 900 thermal analyzer equipped with a DuPont Model 942 thermomechanical analyzer at a heating rate of $10^{o}C$/min.

Isothermal aging (ITA) studies were performed on a System Research Laboratory (SRL) Model 633-1 multisample ITA apparatus at $600^{0}F$ for 200 h.

3. SYNTHESIS OF THE END-CAPPING AGENT 4-(m-Hydroxyphenyl)-2-methyl-3-butyn-2-ol 2

a. Preparation of 2 Using a Homogeneous Palladium Catalyst

A three-necked 500 mL round-bottom flask was fitted with a reflux condenser, magnetic stir bar, stopper, and gas inlet/outlet adapters. Under dry nitrogen the flask was charged with m-bromophenol (10.0g, 57.8 mmol), 2-methyl-3-butyn-2-ol (5.0g, 59.4 mmol) and 250 mL of distilled triethylamine resulting in a pale yellow solution. The mixture was heated at reflux for 15 min while a nitrogen atmosphere was maintained. After the reflux period the catalyst system consisting of dichlorobis(triphenylphosphine) palladium II (0.1g), triphenylphosphine (0.2g) and cuprous iodide (0.1g) was added. Addition of the catalyst system caused the reaction mixture color to deepen to yellow-orange. After heating at reflux for 25 h, light-colored salts formed. Reaction progress was followed by gas chromatography (GC) using phenol as a standard. GC samples were taken as infrequently as possible to limit reaction mixture exposure to air. After cooling to $25^{o}C$, the reaction mixture was filtered under nitrogen through a glass frit packed with celite. The remaining light gray precipitate was rinsed with additional triethylamine and the filtrates combined, concentrated (rotary evaporator) and the resulting yellow oil dissolved in 200 mL of toluene which was washed with 120 mL of 8% hydrochloric acid. The hydrochloric acid washing was extracted with three 50 mL portions of ethyl acetate which were combined, concentrated (rotary evaporator) and the resulting residue dissolved in 25 mL of toluene. The toluene fractions were combined and dried (magnesium sulfate). The dry toluene solution was treated with ethylene diamine (brown solution) and stirred with heating ($50-60^{o}C$) under nitrogen for 15 min which resulted in a blue precipitate. After cooling to room temperature, the solution was filtered to remove the precipitate and the filtrate was extracted with 250 mL of distilled water and three 125 mL portions

of 10% potassium carbonate. The base extract was stirred in an ice/water both the neutralized with 50% hydrochloric acid (addition was continued until the pH was slightly acidic). The aqueous solution was extracted with one 250 mL portions of ethyl acetate which were combined, dried and evaporated. The resulting dark yellow-orange oil was induced to crystallize by dissolving in methylene chloride, adding n-hexane until slightly cloudy, seeding and cooling by refrigeration for 24 h. The resulting solid was recrystallized from n-hexane/methylene chloride (2/3) to yield 4.1g (41%) of a white solid: mp 94-95°C; IR (KBr) 3380, 3160 cm^{-1} (O-H), 3000, 1575 cm^{-1} (aromatic), 2930 cm^{-1} (aliphatic), 2210 cm^{-1} (C≡C), 1215, 940 cm^{-1} (C-OH) (Figure 1);

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.91; H, 6.81.
Found: C, 74.52; H, 6.96.
Cu and Pd Analysis: Cu, 3ppm; Pd, 3ppm.

b. Preparation of 2 Using a Polymer Supported Palladium Catalyst

With the exception of the catalyst system, the same quantities of reactants and reaction procedures as previously employed for 2 were followed. In place of the standard catalyst system tetrakis(triphenyl-phosphine)palladium(0) supported on polystyrene with 2% DVB crosslinking (0.5g), triphenylphosphine (0.2g) and cuprous iodide (0.054g) were used. The reaction was followed by TLC with ethyl acetate/hexanes (2/3) as the eluent and GC. After 7 h no product formation could be detected. Additional polymer supported catalyst (0.5g) and triphenylphosphine (0.2g) were added to the mixture. After 22.5 h only a small amount of product was observed to have formed. A side product of higher concentration was found to be present by GC and TLC analyses. After 30 h, with the side product concentration increasing and little change in product concentration, the reaction was stopped. No workup of the reaction mixture was attempted.

4. PREPARATION OF HALO-TERMINATED INTERMEDIATE MONOMER/OLIGOMER MIXTURES

1,1'-(1-Methylethylidene)bis[4-[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene] 3

and

α-[4-[1-[4-[4-[(4-Fluorophenyl)sulfonyl]phenoxy]phenyl]-1-methyl-ethyl]phenyl]-W-[4-[(4-fluorophenyl)sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 4

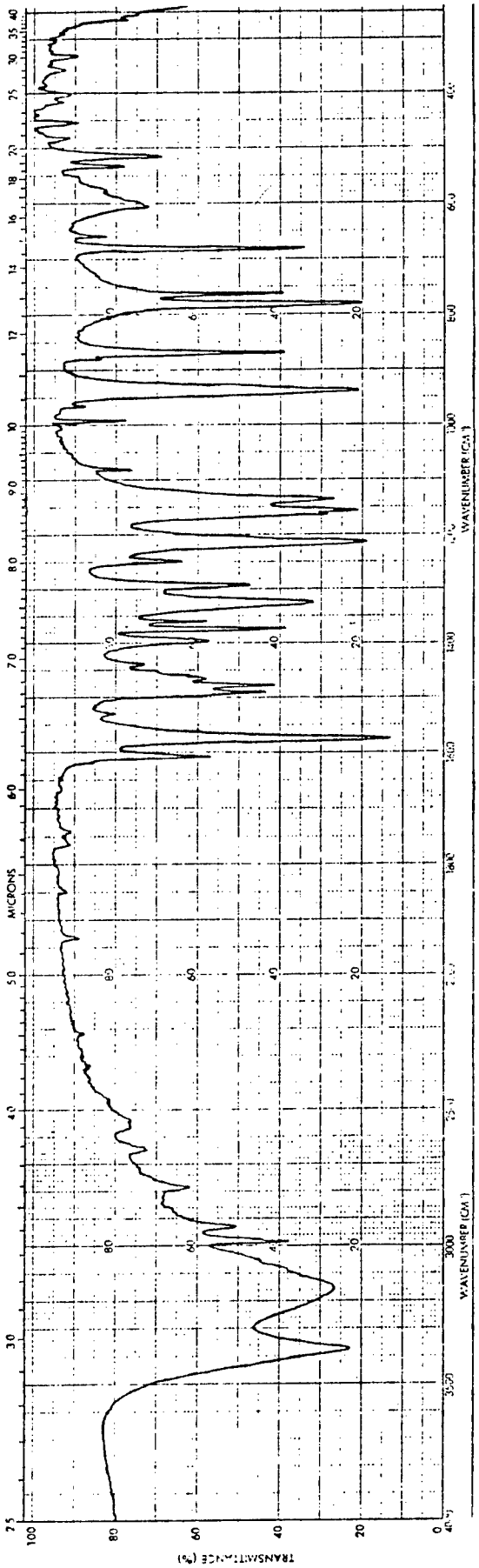


Figure 1. Infrared Spectra of 4-(m-Hydroxyphenyl)-2-methyl-3-butyn-2-ol 2

A three-necked 250 mL round-bottom flask, was equipped with a magnetic stir bar, reflux condenser, Dean-Stark trap, and a gas inlet/outlet adapter. The following mixture was added: 4,4'-iospropylidene-dephenol (3g, 13.2 mmol), difluorodiphenyl sulfone (13.43g, 52.8 mmol), anhydrous potassium carbonate (1.91g, 13.8 mmol), 25 mL of freshly distilled N-methyl-2-pyrrolidone and 25 mL of benzene. The reaction mixture was heated at reflux (100°C) and stirred rapidly under dry nitrogen until all water (a reaction side product) was removed by azeotropic distillation with benzene. The reaction (dark purple color) temperature was then raised and maintained at 135°C for 5 h. The mixture darkened during this period. After cooling to room temperature, the reaction mixture was diluted with 100 mL of methylene chloride and washed with three 200 mL portions of 10% hydrochloric acid, one 200 mL portion of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (460g). Unreacted difluorodiphenyl sulfone was eluted with methylene chloride/petroleum ether (1/4), monomer 3 was eluted with methylene chloride/petroleum ether (1/2) to yield 6.61g of a white crystalline solid: mp 120-122°C; IR(KBr) 3070, 1575, 1480 cm^{-1} (aromatic), 1230 cm^{-1} (ArF), 1320, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{38}H_{31}F_2\ S_2\ O_6$: C, 67.20; H, 4.30; S, 9.20; F, 5.45.
Found: C, 67.21; H, 4.58; S, 9.05; F, 5.44.

Oligomer 4 was eluted with methylene chloride to yield 1.39g of a clear viscous oil: IR (NaCl film) 3070, 1570, 1475 cm^{-1} (ArF), 1320, 1150 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr). Total yield was 8.00g (87.3%, if based on pure monomer theoretical yield).

1,1'-(1-Methylethylidene)bis[4-[4-[(4-chlorophenyl)sulfonyl]phenoxy]benzene] 5

and

α-[4-[1-[4-[4-[(4-Chlorophenyl)sulfonyl]phenoxy]phenyl]-1-methylethyl] phenyl]-W-[4-[(4-chlorophenyl)sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 6

A three-necked, 250 mL round-bottom flask, was equipped with magnetic stir bar, reflux condenser, Dean-Stark trap, and a gas inlet/outlet adapter. The following mixture was added: 4,4'-isopropylidene-diphenol (bisphenol-A) (5.0g, 22.0 mmol), dichlorodiphenyl sulfone (25.23g, 88.0 mmol), anhydrous potassium carbonate (3.04g, 23.0 mmol), 35 mL of freshly distilled N-methyl-2-pyrollidone and 30 mL of benzene. The reaction mixture was heated at reflux (100°C) and stirred rapidly under dry

nitrogen until all water (a reaction side product) was removed by azeotropic distillation with benzene. The reaction (light green color) temperature was stabilized and maintained at 150°C for 5 h. After cooling to room temperature, the reaction mixture was diluted with 150 mL of methylene chloride and washed with three 200 mL portions of 10% hydrochloric acid, one 300 mL portion of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (514g). Unreacted dichlorodiphenyl sulfone was eluted with hexanes/methylene chloride (4/1). Monomer 5 was eluted with hexanes/chloroform (3/2) to yield 7.29g of a white solid: mp 170-174°C; IR(KBr) 3070, 1575, 1480 cm^{-1} (aromatic), 1380, 1360 cm^{-1} (gem di-methyl), 1315, 1340 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr) 1075 cm^{-1} (ArCl); ^1H NMR 6.95-8.22 (m, aromatic, 32H), 1.71 (s, methyl, 6H);

Anal. Calcd. for $C_{38}H_{31}S_2Cl_2O_6$: C, 64.20; H, 4.13; S, 8.79; Cl, 9.71.
Found: C, 64.15; H, 4.18, S, 8.09; Cl, 10.22.

Oligomer 6 was eluted with chloroform to yield 5.14g of a pale yellow crystalline solid: IR(KBr) 3070, 1580, 1475 cm^{-1} (aromatic), 1380, 1365 cm^{-1} (gem di-methyl), 1320, 1340 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr), 1080 cm^{-1} (ArCl).

Total yield was 12.43g (78% based on pure monomer theoretical yield).

1,1'-Thiobis[4-[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene 7

and

α-[4-[[4-[4-[(4-Fluorophenyl)sulfonyl]phenoxy]phenyl]thio]phenyl]-W-[4-[(4-fluorophenyl)sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 8

A three-necked 250 mL round-bottom flask, was equipped with magnetic stir bar, reflux condenser, Dean-Stark trap, and a gas inlet/outlet adapter. The following mixture was added: 4,4'-thiodiphenol (4.0g, 18.0 mmol), difluorodiphenyl sulfone (18.61g, 73.0 mmol), anhydrous potassium carbonate (2.53g, 18.0 mmol), 35 mL of freshly distilled N-methyl-2-pyrollidone and 30 mL of benzene. The reaction mixture was heated at reflux (100°C) and stirred rapidly under dry nitrogen until all water (a reaction side product) was removed from the system by azeotropic distillation with benzene. The reaction (light purple color) temperature was then raised and maintained at 120°C for 4 h. The mixture darkened slightly during this period. After cooling to 40°C, the reaction mixture was diluted with 100 mL of methylene

chloride, washed with three 200 mL portions of 10% hydrochloric acid, one 400 mL portion of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (500g). Unreacted difluorodiphenyl sulfone was eluted with n-hexane/chloroform (1/1) to yield 6.18g of a white crystalline solid: mp 116-118°C; IR(KBr) 3100-3000, 1590 cm^{-1} (aromatic), 1350-1020 cm^{-1} (ArF), 1340-1300, 1160-1135 cm^{-1} (SO_2), 1275-1070 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{36}H_{24}O_6S_3F_2$: C, 62.92; H, 3.50; S, 14.01; F, 5.54.
Found: C, 62.74; H, 3.57; S, 13.95; F, 5.58.

Oligomer 8 was eluted with chloroform to yield 5.07g of a light yellow viscous oil: IR(NaCl solution) 3070, 1575, 1480 cm^{-1} (aromatic), 1230 cm^{-1} (ArF), 1320, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr); ^{1}H NMR 6.9-8.2 (m, aromatic).
Total yield was 11.25g (89.4% based on pure monomer theoretical yield).

1,1'-Thiobis[4-[4-[(4-chlorophenyl)sulfonyl]phenoxy]benzene 9

and

α-[4-[[4-[4-[(4-Chlorophenyl)sulfonyl]phenoxy]phenyl]thio]phenyl]-W-[4-[(4-chlorophenyl)sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 10

A three-necked 250 mL round-bottom flask, was equipped with magnetic stir bar, reflux condenser, Dean-Stark trap, and a gas inlet/outlet adapter. The following mixture was added: 4,4'-thiodiphenol (5.0g, 22.9 mmol), dichlorodiphenyl sulfone (26.30g, 91.6 mmol), anhydrous potassium carbonate (3.16g, 22.9 mmol), 40 mL of freshly distilled N-methyl-2-pyrollidone and 24 mL of benzene. The reaction mixture was heated at reflux (100°C) and stirred rapidly under dry nitrogen until all water (a reaction side product) was removed from the system by azeotropic distillation with benzene. The reaction (light green color) temperature was then raised and maintained at 160°C for 5 h. After cooling to room temperature the reaction was diluted with 100 mL of methylene chloride, washed with three 20 mL portions of 10% hydrochloric acid, one 400 mL portion of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (500g). Unreacted dichlorodiphenyl sulfone was eluted with n-hexane/ methylene chloride (4/1). Monomer 9 was eluted with n-hexane/chloroform (3/1) to yield 9.18g of a dense white crystalline solid: mp 118-120°C; IR(KBr) 3100-3050, 1575 cm^{-1} (aromatic), 1320, 1150-1140 cm^{-1} (SO_2), 1095 cm^{-1} (ArCl);

Anal. Calcd. for $C_{36}H_{24}O_6S_3Cl_2$: C, 60.05; H, 3.34.
Found: C, 59.42; H, 3.36.

Oligomer 10 was eluted with chloroform/hexanes (1/1) to yield 3.43g of a white fluffy solid: IR(KBr) 3070, 1575, 1475 cm^{-1} (aromatic), 1315, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr), 1080 cm^{-1} (ArCl).
Total yield was 12.61g (76.5% based on pure monomer theoretical yield).

4,4'-Bis[4-[(4-fluorophenyl)sulfonyl]phenoxy]-1,1-biphenyl 11

To a 250 mL round-bottom flask equipped with magnetic stir bar, Dean-Stark trap, nitrogen inlet/outlet adapters, and condenser, 40 mL of distilled N-methyl-2-pyrollidone and 35 mL of dry benzene were added. While stirring under nitrogen, p,p'biphenol (4.0g, 21.5 mmol), difluorodiphenyl sulfone (21.87g, 86.0 mmol), and anhydrous potassium carbonate (2.97g, 21.5 mmol) were added. The mixture was distilled to near dryness and then maintained at 120°C for 7 h while the reaction progress was followed by TLC. When the reaction was complete, the mixture was cooled to room temperature and diluted with 150 mL of methylene chloride. The solution was extracted with three 300 mL portions of 10% hydrochloric acid and one 300 mL portion of distilled water. The methylene chloride solution was dried (magnesium sulfate), filtered, and concentrated (rotary evaporator) to yield a clumpy light-brown product. The crude product was chromatographed on a quartz column filled with activated silica gel (500g). Unreacted difluorodiphenyl sulfone was eluted with n-hexane/methylene chloride (5/1). The product 11 was eluted with n-hexane/methylene chloride (1/1) to yield 11.96g (85%) of white needle-like crystals: mp 180-181°C; IR (KBr) 3065, 1570, 1480 cm^{-1} (aromatic), 1220 cm^{-1} (ArF) 1, 1320, 1150 cm^{-1} (SO_2), 1105 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{36}H_{24}O_6S_2F_2$: C, 66.01; H, 3.67; S, 9.80.
Found: C, 65.44; H, 3.77; S, 9.72.

This reaction procedure produced only a very small amount of oligomer product (~2%). No attempt was made to purify or analyze this material. It was however, separated from the monomer product.

1,3-Bis[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene 12

and

α-[4-[(4-Fluorophenyl)sulfonyl]phenyl]-W-[3-[4-[(4-fluorophenyl)sulfonyl]phenoxy] phenoxy]poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 13

A three-necked, 250 mL round-bottom flask, was equipped with magnetic stir bar, reflux condenser, Dean-Starktrap, and a gas inlet/outlet adapter. The following mixture was added: resorcinol (3.0g, 27.3 mmol), difluorodiphenyl sulfone (27.76g, 109.2 mmol), anhydrous potassium carbonate (3.96g, 28.7 mmol), 30 mL of freshly distilled N-methyl-2-pyrollidone and 30 mL of benzene. The reaction mixture was heated at reflux (100°C) and stirred rapidly under dry nitrogen until all water (a reaction side product) was removed from the system by azeotropic distillation with benzene. The reaction temperature was then raised and maintained at 125°C for 4 h. The mixture was purple in color. After cooling to room temperature, the reaction mixture was diluted with 100 mL of methylene chloride and washed with three 200 mL portions of 10% hydrochloric acid and one 200 mL portion of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (475g). Unreacted difluorodiphenyl sulfone was eluted with hexanes/methylene chloride (3/1). Monomer 12 was eluted with hexanes/methylene chloride (1/1) to yield 9.1g of a white crystalline solid: mp 80-82°C; IR(KBr) 3070, 1575, 1455 cm^{-1} (aromatic), 1225 cm^{-1} (ArF), 1320, 1150 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{30}H_{20}O_6S_2F_2$: C, 62.20; H, 3.50; S, 11.03; F, 6.57.
Found: C, 62.25; H, 3.67; S, 10.58; F, 6.92.

Oligomer 13 was eluted with methylene chloride to yield 4.4g of a light amber viscous oil: IR (NaCl film) 3075, 1575, 1475 cm^{-1} (aromatic), 1225 cm^{-1} (ArF), 1320, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr). Total yield was 13.5g (85.6%, based on pure monomer theoretical yield).

5. PREPARATION OF ACETONE PROTECTED AT-PRODUCTS

a. Monomer Products

4,4'-[(1-Methylethylidene)bis(4,1-Phenyleneoxy-4,1-Phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 14

To a 50 mL, three-necked, round-bottom flask equipped with magnetic stir bar and nitrogen inlet/outlet was added 40 mL of dry DMSO. While stirring under

nitrogen, 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (1.67g, 9.48 mmol) and potassium methoxide (0.67g, 9.48 mmol) were added. The mixture was stirred at 40°C for 1 h to complete generation of the potassium salt. A 250 mL three-necked round-bottom flask, equipped with a gas inlet/outlet, addition funnel, and magnetic stir bar was charged with 16 (3.0g, 4.31 mmol) dissolved in 40 mL of dry DMSO. Under nitrogen, the solution was heated to 90°C with stirring. The potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 was transferred (under nitrogen) to the addition funnel and added to the solution of 3 over a period of 1 h. After addition was complete, the reaction mixture was maintained at 90°C for an additional 3 h, cooled to room temperature and diluted with 150 mL of methylene chloride which was washed with three 200 mL portions of 10% hydrochloric acid and one 300 mL portion of distilled water. The methylene chloride solution was dried (magnesium sulfate), filtered, and concentrated (rotary evaporator) to yield a pale brown product. The crude product was chromatographed on a quartz column filled with activated silica gel (160g). The product was eluted with hexanes/ethyl acetate (3/1) to yield 3.82g (87.9%) of white solid: mp 179-181°C; IR(KBr) 3480 cm^{-1} (COH), 3060, 1570, 1475 cm^{-1} (aromatic), 1380, 1360 cm^{-1} (gem dimethyl), 1315, 1145 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{61}H_{52}S_2O_{10}$: C, 72.70; H, 5.21; S, 6.35.

Found: C, 72.14; H, 5.49; S, 6.01.

4,4'-[Thiobis(4,1-phenyleneoxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 15

A three-necked, 50 mL round-bottom flask, was equipped with magnetic stir bar and gas inlet/outlet adapters. Under dry nitrogen the flask was charged with 4-(m-hydroxyphenyl)-2-methyll-3-butyn-2-ol 2 (1.63g, 9.2 mmol) and 40 mL of dimethylsulfoxide. To this solution, potassium methoxide (0.65g, 9.2 mmol) was added. The mixture was stirred for 1 h at 25°C, transferred to an addition funnel under nitrogen, and added over a period of 1 h to a solution of 7 (3g, 4.4 mmol) in 40 mL of dimethylsulfoxide stirred at 85°C. When addition was complete, the temperature of the reaction mixture was maintained at 85°C and stirred overnight under nitrogen. The reaction mixture was diluted with 150 mL of methylene chloride and washed with three 300 mL portions of 10% hydrochloric acid, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatogrpahed on a quartz column filled with activated silica gel (180g). The product was eluted with ethyl acetate/chloroform (1/9) to yield 3.16g (68.7%) of a white solid: mp 156-157°C;

IR(KBr) 3480 cm^{-1} (COH), 3060, 1570, 1475 cm^{-1} (aromatic), 1315, 1145 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr), 680 cm^{-1} (ArSAr);

Anal. Calcd. for $C_{58}H_{46}O_{10}S_3$: C, 69.68; H, 4.61; S, 9.63.
Found: C, 67.33; H, 4.64; S, 9.26.

4,4'-[[1,1'-Biphenyl]-4,4'-diylbis(oxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 16

To a 50 mL, three-necked, round-bottom flask equipped with magnetic stir bar and nitrogen inlet/outlet was added 40 mL of dry DMSO. While stirring under nitrogen, 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (2.06g, 12.0 mmol) and potassium methoxide (0.82g, 12.0 mmol) were added. The mixture was stirred at 40°C for 1 h after which generation of the potassium salt was judged complete. A 250 mL, three-necked, round-bottom flask was equipped with gas inlet/outlet, addition funnel, and magnetic stir bar and charged with 24 (3.5g, 5 mmol) dissolved in 40 mL of dry DMSO. Under nitrogen the solution was heated to 90°C while stirring. The potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 was transferred (under nitrogen) to the addition funnel and added to the solution of 11 over a period of 1 h. After addition was complete, the reaction mixture was maintained at 90°C for an additional 3 h, cooled to room temperature and diluted with 150 mL of chloroform. The chloroform solution was washed with three 300 mL portions of 10% hydrochloric acid and one 300 mL portion of distilled water. The distilled water wash was extracted with 50 mL of ethyl acetate and the chloroform and ethyl acetate layers combined, dried (magnesium sulfate), filtered, and concentrated (rotary evaporator) to yield an off-white product. The crude product was chromatographed on a quartz column filled with activated silica gel (180g). The product was eluted with ethyl acetate/chloroform (1/9) to yield 3.7g (72%) of white solid: mp 221-223°C; IR(KBr) 3510 cm^{-1} (COH), 3060, 1575, 1475 cm^{-1} (aromatic), 1317, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{58}H_{46}O_{10}S_2$: C, 71.98; H, 4.76; S, 6.63.
Found: C, 71.76; H, 4.86; S, 6.68.

4,4'-[1,3-Phenylenebis(oxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 17

To a 50 mL, three-necked, round-bottom flask equipped with magnetic stir bar and nitrogen inlet/outlet was added 40 mL of dry DMSO. While stirring under nitrogen, 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (2.02g, 11.5 mmol) and potassium

methoxide (0.80g, 11.5 mmol) were added. The mixture was stirred at 40°C for 1 h after which generation of the potassium salt was complete. A 250 mL, three-necked, round-bottom flask was equipped with gas inlet/outlet, addition funnel, and magnetic stir bar and charged with 25 (3.0g, 5.2 mmol) dissolved in 40 mL of dry DMSO. Under nitrogen the solution was heated to 90°C while stirring. The potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 was transferred (under nitrogen) to the addition funnel and added to the solution of 12 over a period of 1 h. After addition was complete, the reaction mixture was maintained at 90°C for an additional 3 h, cooled to room temperature and diluted with 150 mL of methylene chloride. The methylene chloride solution was washed with three 300 mL portions of 10% hydrochloric acid and one 300 mL portion of distilled water. The methylene chloride solution was dried (magnesium sulfate), filtered, and concentrated to yield a pale yellow product. The crude product was chromatographed on a quartz column filled with activated silica gel (170g). The product was eluted with hexanes/ethyl acetate (2/3) to yield 3.4g (73.6%) of off-white solid: mp 120-106°C; IR(KBr) 3490 cm^{-1} (COH), 3060, 1570, 1475 cm^{-1} (aromatic), 1315, 1145 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr);

Anal. Calcd. for $C_{52}H_{44}O_{10}S_2$: C, 70.10; H, 4.90; S, 7.20.

Found: C, 69.57; H, 5.00; S, 6.90.

b. Monomer/Oligomer Products

α-[3-(3-Hydroxy-3-methyl-1-butynyl)phenyl]-W-[4-[[4-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 18

(Pure Oligomer)

The potassium salt of the end-capping agent 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (2.00g, 11.25 mmol) was reacted with 4 (4.0g). The same reaction and purification procedures as used for the synthesis of the monomer 14 were followed. The resulting crude product was chromatographed on a quartz column filled with activated silica gel (150g). The product was eluted with hexanes/ethyl acetate (1/1) to yield 4.1g (82.8% based on pure dimer theoretical yield) of a pale yellow solid: IR(KBr) 3480 cm^{-1} (COH), 3060, 1570, 1475 cm^{-1} (aromatic), 1380, 1360 cm^{-1} (gen dimethyl), 1315, 1145 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr).

15 and α-[3-(3-Hydroxy-3-methyl-1-butynyl)phenyl]-W-[4[[4-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 19

A mechanical mixture consisting of 60% 7 (2.4g) and 40% 8 (1.6g) was prepared. The mixture was then reacted with excess potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (2.14g, 12.1 mmol). The same reaction and purification procedures as used for the synthesis of the monomer 28 were followed. The resulting product mixture was chromatographed on a quartz column filled with activated silica gel (170g). The product was eluted with hexanes/ethyl acetate (1/1) to yield 4.22g (83% based on pure monomer theoretical yield) of an off-white solid mixture of 15 and 19: IR(KBr) 3500 cm^{-1} (COH), 3060, 1575, 1475 cm^{-1} (aromatic) 1317, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr), 680 cm^{-1} (ArSAr).

17 and α-[4-[[4-[3-(3-Hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl]phenyl]-W-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 20

A mechanical mixture consisting of 70% 12 (2.1g) and 30% 13 (0.9g) was prepared. The mixture was then reacted with excess potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (2.00g, 11.35 mmol). The same reaction and purification procedures as used for the synthesis of the monomer 30 were followed. The resulting product mixture was chromatographed on a quartz column filled with activated silica gel (160g). The product was eluted with hexanes/ethyl acetate (2/3) to yield 3.9g (84% based on pure monomer theoretical yield) of a pale yellow solid mixture of 17 and 20: IR(KBr) 3480 cm^{-1} (COH), 3060, 1575, 1475 cm^{-1} (aromatic), 1315, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr).

6. CLEAVAGE OF AT-PRODUCT ACETONE PROTECTING GROUPS

a. Monomer Products

1,1'-(1-Methylethylidene)bis[4-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene] 21

from 14

A solution of 14 (2.0g 2.0 mmol) in 150 mL of dry toluene was formed with heating under nitrogen in a three-necked, 250 mL, round-bottom flask which was equipped with a Dean-Stark trap, reflux condenser, magnetic stir bar and a gas inlet/outlet

adapter. Dry, powdered potassium hydroxide (2.0g) was added and the mixture stirred and heated at reflux for 1 h. Acetone formed as the reaction progressed was removed by azeotropic distillation with toluene. The toluene was replaced and the distillation procedure repeated two more times. The progress of the reaction was followed by TLC on silica gel (methylene chloride). After 3 h the reaction mixture was cooled to room temperature, filtered through celite and washed with three 200 mL portions of distilled water, dried (magnesium sulfate), and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silical gel (160g). The product was eluted with hexanes/methylene chloride (3/1) to yield 1.56g (83%) of a white solid: mp 80-82°C; IR(KBr) 3300 cm^{-1} (C≡H), 3050, 1570, 1475 (aromatic), 1380, 1360 (gem di-methyl), 1315, 1340 (SO_2), 1100 cm^{-1} (ArOAr) (Figure 2); ^{1}H NMR 6.85-8.20 (m, aromatic, 32H), 3.15 (s, acetylene, 2H), 1.71 (s, methyl, 6H) (Figure 3);

Anal. Calcd. for $C_{55}H_{40}S_2O_8$: C, 74.00; H, 4.53; S, 7.18.
Found: C, 74.36; H, 4.83; S, 7.02.

1,1'-(1-Methylethylidene)bis[4-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene] 21

from 5

To a 50 mL, three-necked, round-bottom flask equipped with a magnetic stir bar and nitrogen inlet/outlet was added 40 mL of dry DMSO. While stirring under nitrogen, 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 (1.45g, 8.2 mmol) and potassium methoxide (0.58g, 8.2 mmol) were added. The mixture was stirred at 40°C for 1 h after which generation of the potassium salt was complete. A 250 mL, three-necked, round-bottom flask was equipped with a gas inlet/outlet, addition funnel, and magnetic stir bar and charged with 5 (3.0g, 4.1 mmol) dissolved in 40 mL of dry DMSO. While stirring under nitrogen, the solution was heated to 150°C. The potassium salt of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 was transferred (under nitrogen) to the addition funnel and added to the solution of 5 over a period of 1 h. After addition was complete, the reaction mixture was maintained at 150°C for an additional 4 h. Reaction progress was followed by TLC (methylene chloride) which showed six separate spots. After cooling to room temperature, the reaction mixture was diluted with 150 mL of methylene chloride and washed with three 200 mL portions of 10% hydrochloric acid and one 300 mL portion of distilled water. The methylene chloride solution was dried (magnesium sulfate), filtered, and concentrated (rotary evaporator) to yield a

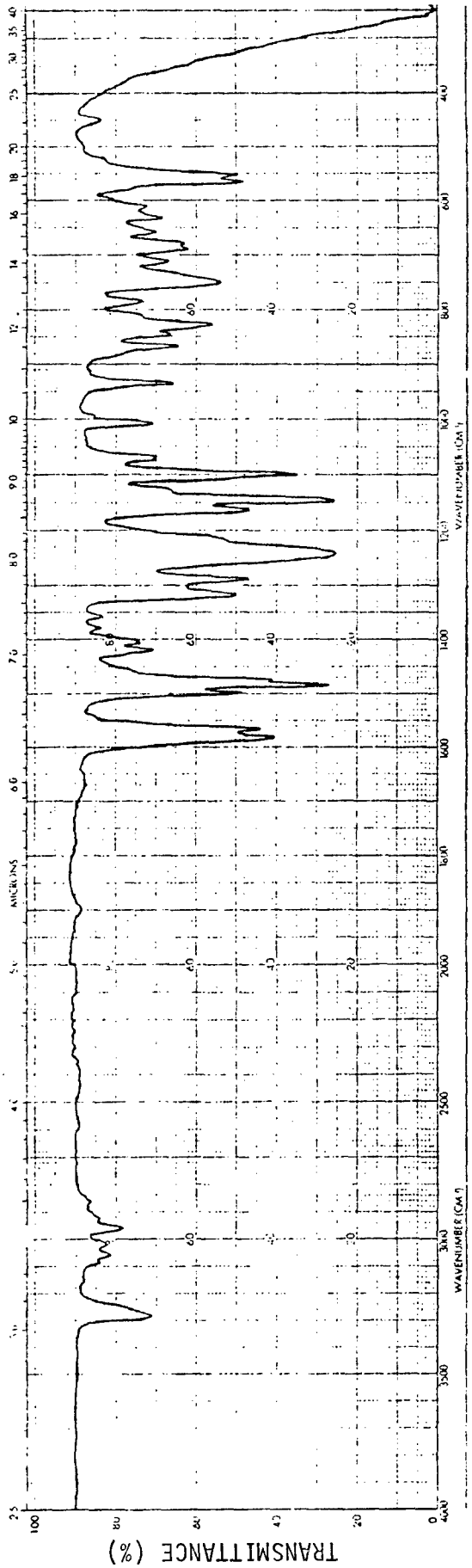


Figure 2. Infrared Spectra of 1,1'-(1-Methylethylidene)bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene] 21

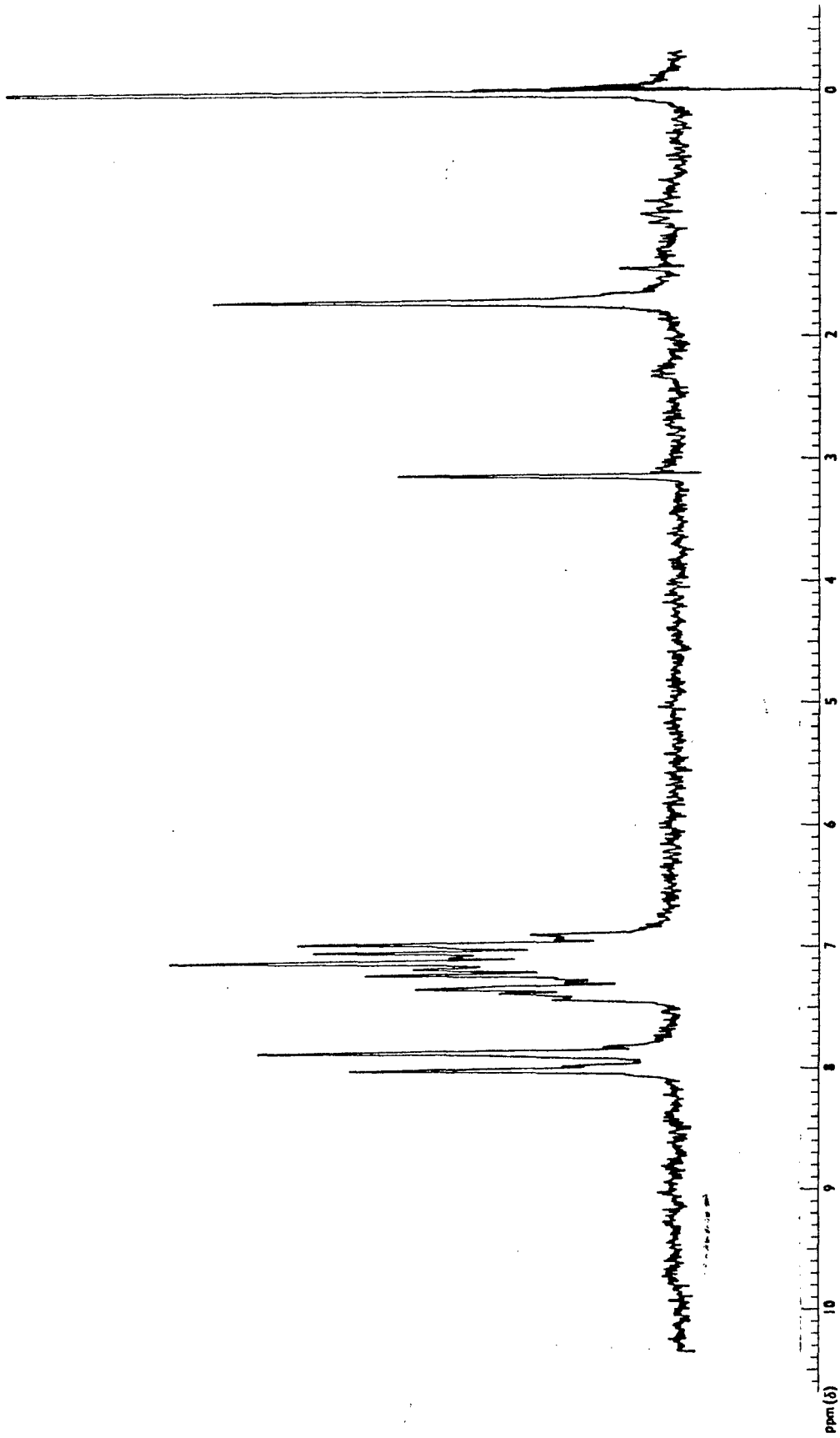


Figure 3. ^{1}H NMR Spectra of 1,1'-(1-Methylethylidene)bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene] 21

dark yellow oil. TLC of the crude product showed several components. The mixture was chromatographed on a quartz column filled with activated silica gel (180g). The first band was eluted with hexanes/methylene chloride (2/1) to yield 1.7g (43.1%) of 21 a yellow solid: mp 79-83°C; IR(KBr) 3300 cm^{-1} (C≡CH), 3045, 1570, 1480 cm^{-1} (aromatic), 1380, 1360 cm^{-1} (gem di-methyl), 1315, 1340 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr); ^{1}H NMR 6.85-8.20 (m, aromatic, 32H), 3.15 (s, acetylene, 2H), 1.71 (s, methyl, 6H);

Anal. Calcd. for $C_{55}H_{40}S_2O_8$: C, 73.99; H, 4.48.

Found: C, 71.80; H, 4.50.

Bis[p-[p-[[p-(m-ethynylphenoxy)phenyl]sulfonyl]phenoxy]phenyl]sulfide 22

A solution of 15 (2.0g, 2.0 mmol) in 60 mL of dry benzene was formed with heating under nitrogen in a three-necked, 250 mL, round-bottom flask which was equiped with a Dean-Stark trap, reflux condenser, magnetic stir bar and a gas inlet/outlet adapter. A 10% methanolic potassium hydroxide solution (50 mL) was added and the mixture stired and heated at reflux for 1 h. Acetone formed as the reaction progressed was removed by azeotropic distillation with benzene. Benzene was replaced and the distillation procedure repeated three times. The progress of the reaction was followed by TLC on silica gel with methylene chloride. After 4 h, the reaction mixture was cooled to 25°C, filtered through celite and washed with three 100 mL portions of distilled water, dried (magnesium sulfate) and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (160g). The product was eluted with hexane/chloroform (1/1) to yield 1.39g (79%) of a fluffy white solid: mp 92-94°C; IR(KBr) 3280 cm^{-1} (C≡CH), 3050, 1570, 1475 cm^{-1} (aromatic), 1315, 1140 cm^{-1} (ArOAr), 685 cm^{-1} (ArSAr), (Figure 4); ^{1}H NMR 6.8-8.20 (m, aromatic, 32H), 3.15 (s, acetylene, 2H) (Figure 5);
Anal. Calcd. for $C_{52}H_{34}S_2O_8$: C, 70.69; H, 3.85; S, 10.89.

Found: C, 69.39; H, 3.95; S, 10.75.

4,4'-Bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]-1,1'-biphenyl 23

A solution of 16 (2.2g, 2.28 mmol) in 150 mL of dry toluene was formed with heating under nitrogen in a three-necked, 250 mL, round-bottom flask which was equipped with a Dean-Stark trap, reflux condenser, magnetic stir bar and a gas inlet/outlet adapter. A 10% methanolic potassium hydroxide solution (50 mL) was added and the mixture stirred and heated at reflux for 1 h. Acetone formed as the reaction progressed was removed by azeotropic distillation with toluene. Toluene was

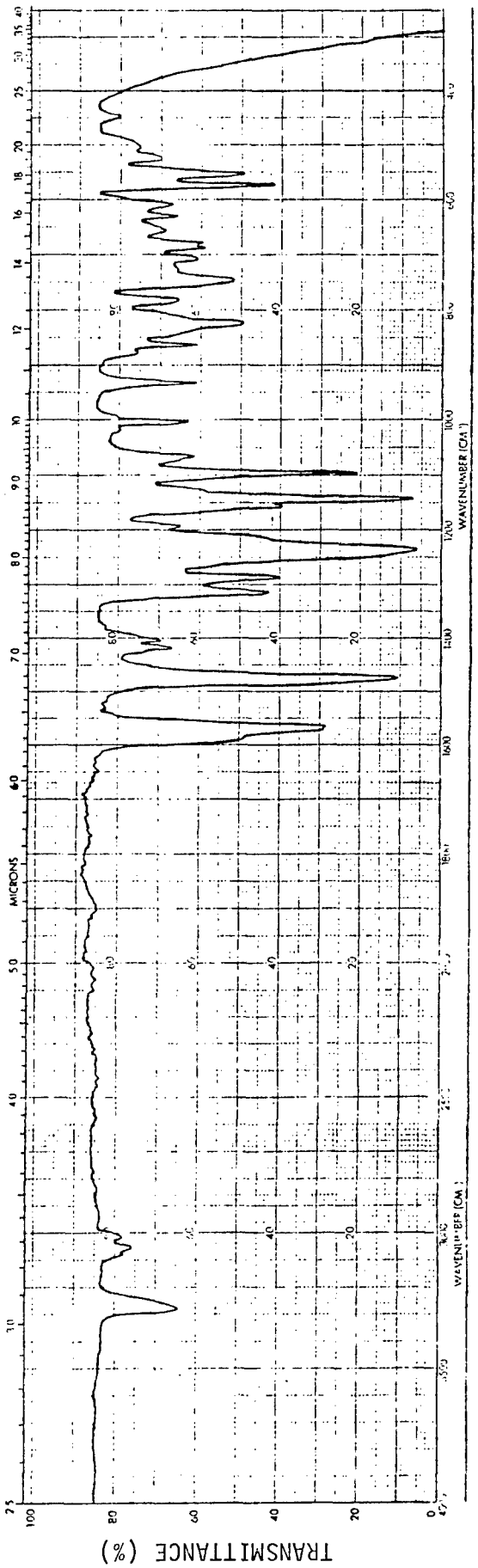


Figure 4. Infrared Spectra of Bis[p-[p-[[p-(m-ethynylphenoxy)phenyl]sulfonyl]phenoxy]phenyl]sulfide 22

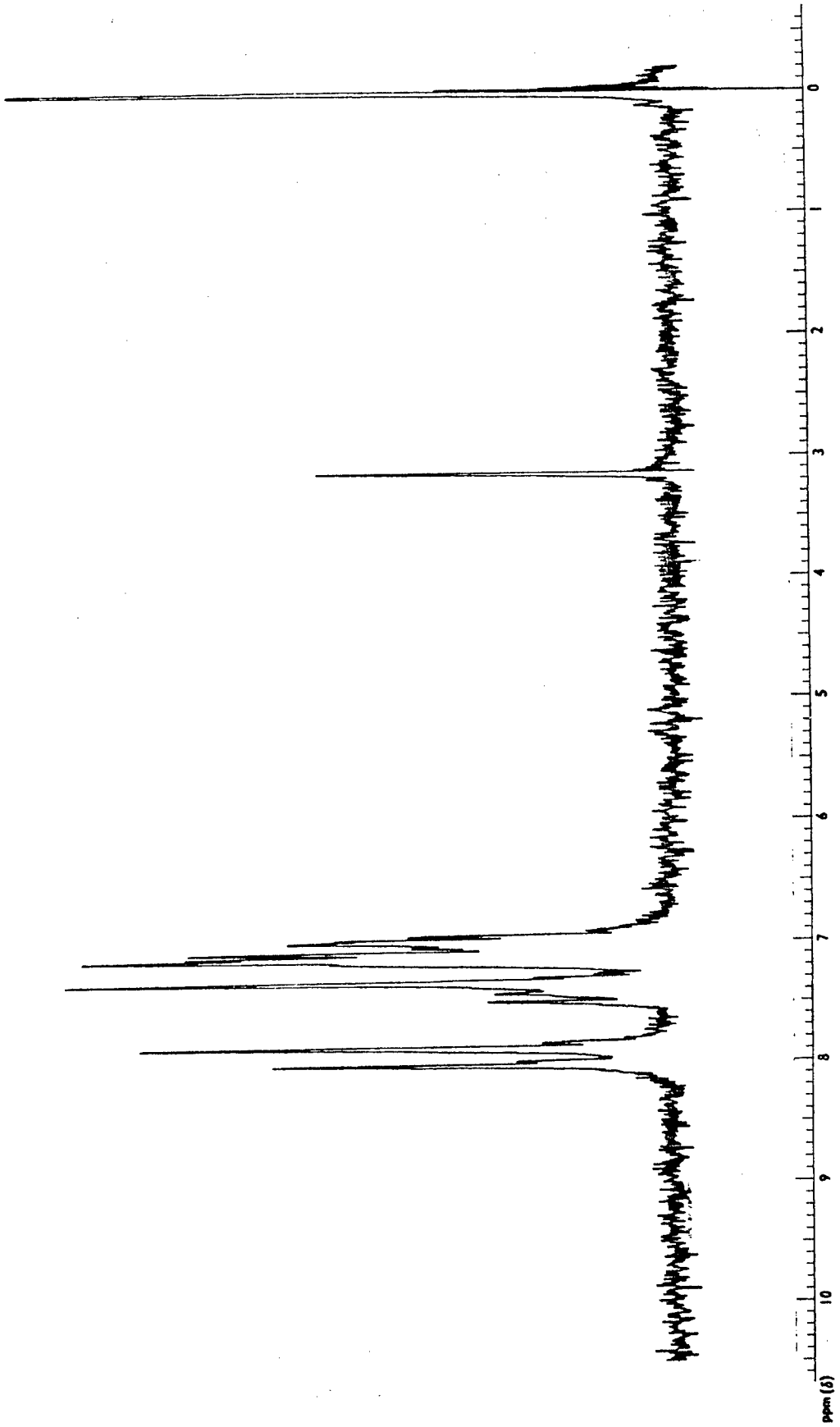


Figure 5. ^{1}H NMR Spectra of Bis[p-[p-[[p-(m-ethynylphenoxy)phenyl]sulfonyl]phenoxy]phenyl]sulfide 22

replaced and the distillation procedure repeated two more times. The progress of the reaction was followed by TLC on silica gel (methylene chloride). After 3 h, the reaction mixture was cooled to 25°C, filtered through celite and washed with three 200 mL portions of distilled water, dried (magnesium sulfate), and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (170g). The product was eluted with hexanes/methylene chloride (1/1) to yield 1.57g (80.9%) of a dense white solid: mp 187-190°C; IR(KBr) 3280 cm^{-1} (C≡CH), 3050, 1575, 1480 cm^{-1} (aromatic), 1315, 1140 cm^{-1} (ArOAr) (Figure 6); ^1H NMR 6.90-8.10 (m, aromatic, 32H), 3.15 (s, acetylene, 2H) (Figure 7);

Anal. Calcd. for $C_{52}H_{34}S_2O_8$: C, 73.4; H, 4.00; S, 7.54.

Found: C, 72.1; H, 4.38; S, 7.20.

1,3-Bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene 24

A solution of 17 (3.0g, 3.37 mmol) in 150 mL of dry toluene was formed with heating under nitrogen in a three-necked, 250 mL, round-bottomed flask which was equipped with a Dean-Stark trap, reflux condenser, magnetic stir bar and a gas inlet/outlet adapter. Dry powdered potassium hydroxide (2g) was added and the mixture stirred and heated at reflux for 1 h. Acetone formed as the reaction progressed was removed from the system by azeotropic distillation with toluene. Toluene was replaced and the distillation procedure repeated three more times. The progress of the reaction was followed by TLC on silica gel (methylene chloride). After 3 h, the reaction mixture was cooled to room temperature, filtered through celite and washed with three 200 mL portions of distilled water, dried (magnesium sulfate), and filtered. The filtrate was concentrated (rotary evaporator) and chromatographed on a quartz column filled with activated silica gel (160g). The product was eluted with hexanes/methylene chloride (1/2) to yield 2.21g (85%) of a fluffy white solid: mp 63-67°C; IR(KBr) 3270 cm^{-1} (C≡CH), 3050, 1570, 1475 cm^{-1} (SO_2) 1100 cm^{-1} (ArOAr) (Figure 8); ^1H NMR 6.75-8.45 (m, aromatic, 28H), 3.15 (s, acetylene, 2H), (Figure 9);

Anal. Calcd. for $C_{46}H_{30}S_2O_8$: C, 71.33; H, 3.87; S, 8.28.

Found: C, 70.90; H, 4.07; S, 8.29.

b. Monomer/Oligomer Products

α-(3-Ethynylphenyl)-W-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy] poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 25

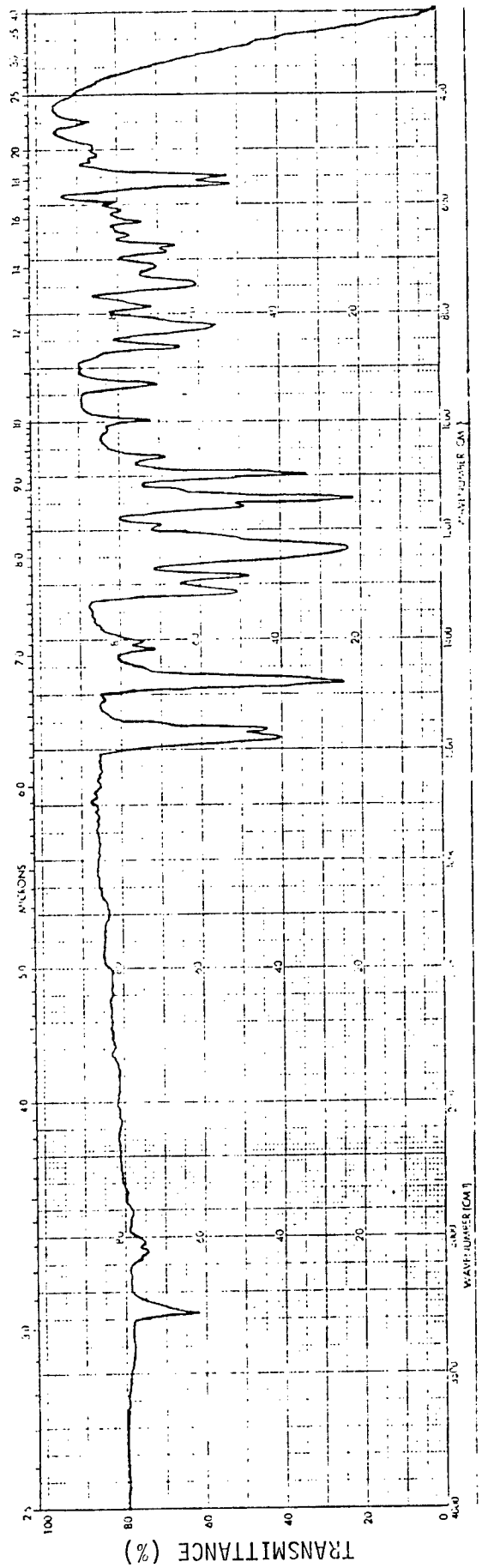


Figure 6. Infrared Spectra of 4,4'-Bis[4-[[4-(3-ethynylphenoxy) phenyl]sulfonyl]phenoxy]-1,1'-biphenyl 23

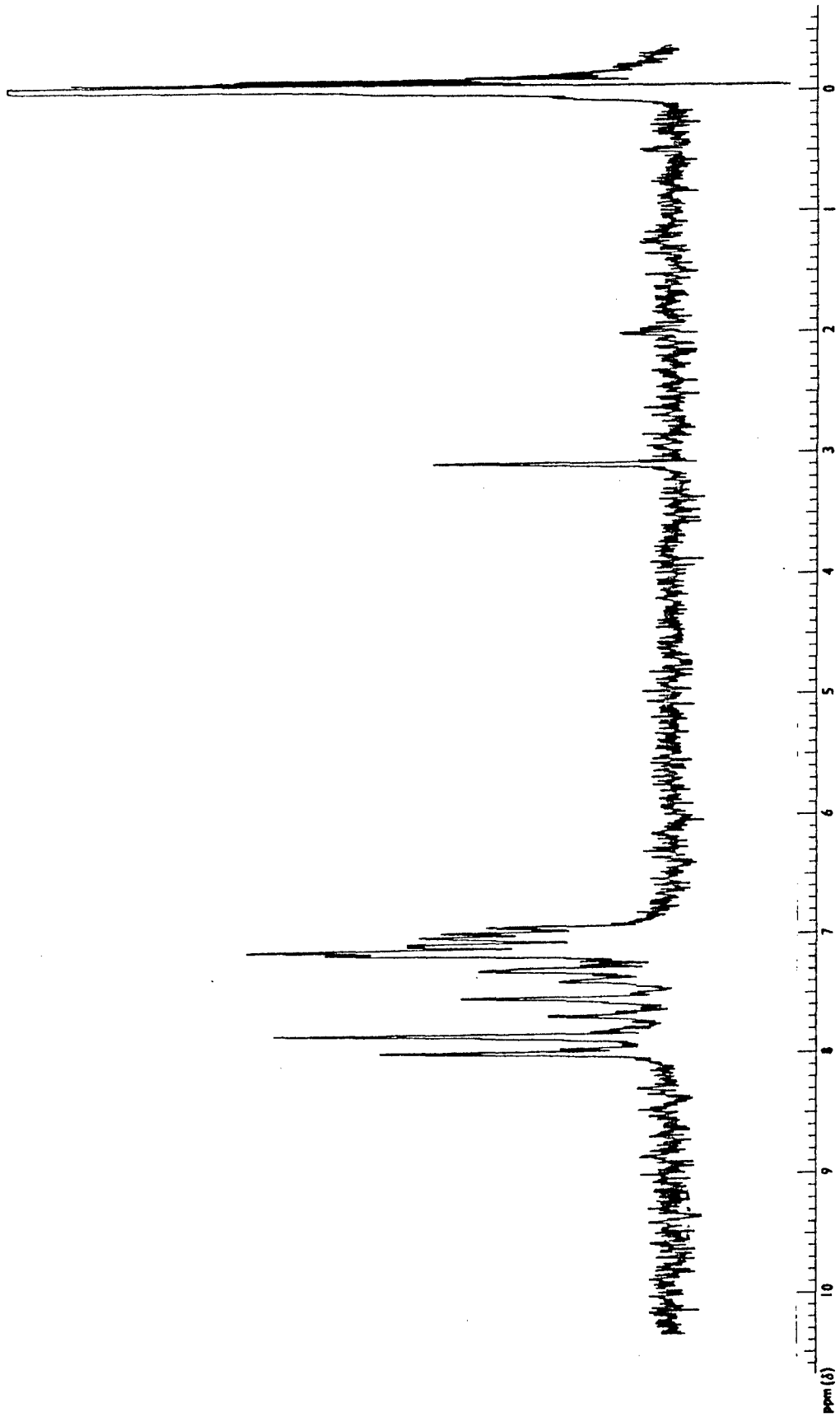


Figure 7. ^{1}H NMR Spectra of 4,4'-Bis[4-[[4-(3-ethynylphenoxy) phenyl]sulfonyl]phenoxy]-1,1'-biphenyl 23

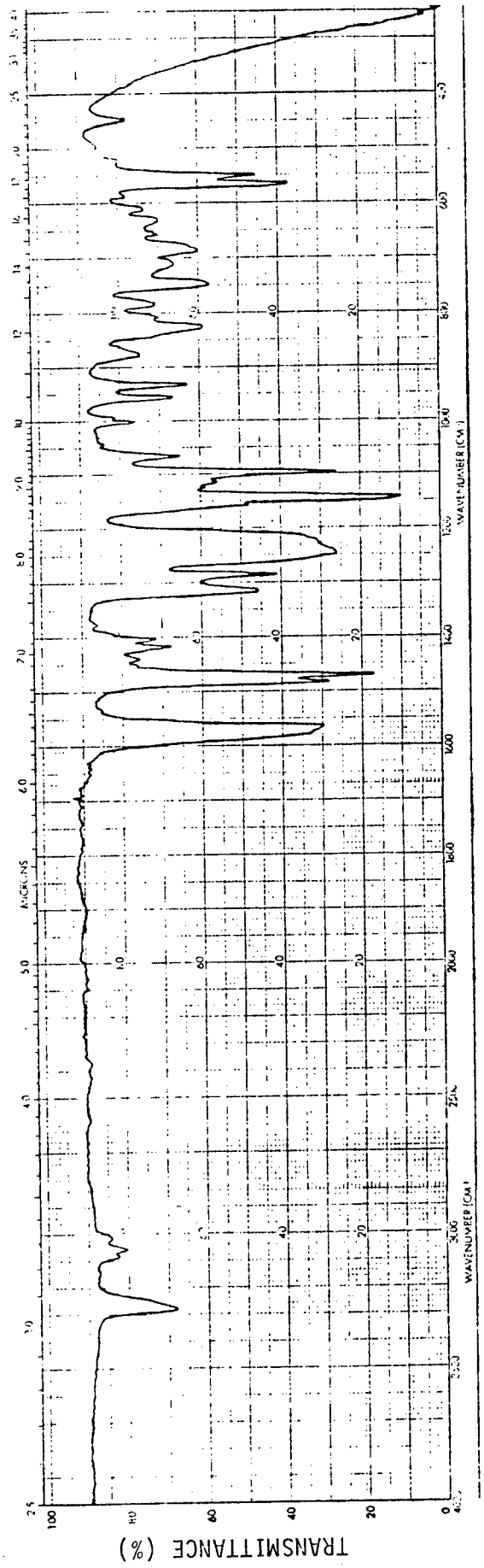


Figure 8. Infrared Spectra of 1,3-Bis[4-[[4-(3-ethynylphenoxy) phenyl]sulfonyl]phenoxy]benzene 24

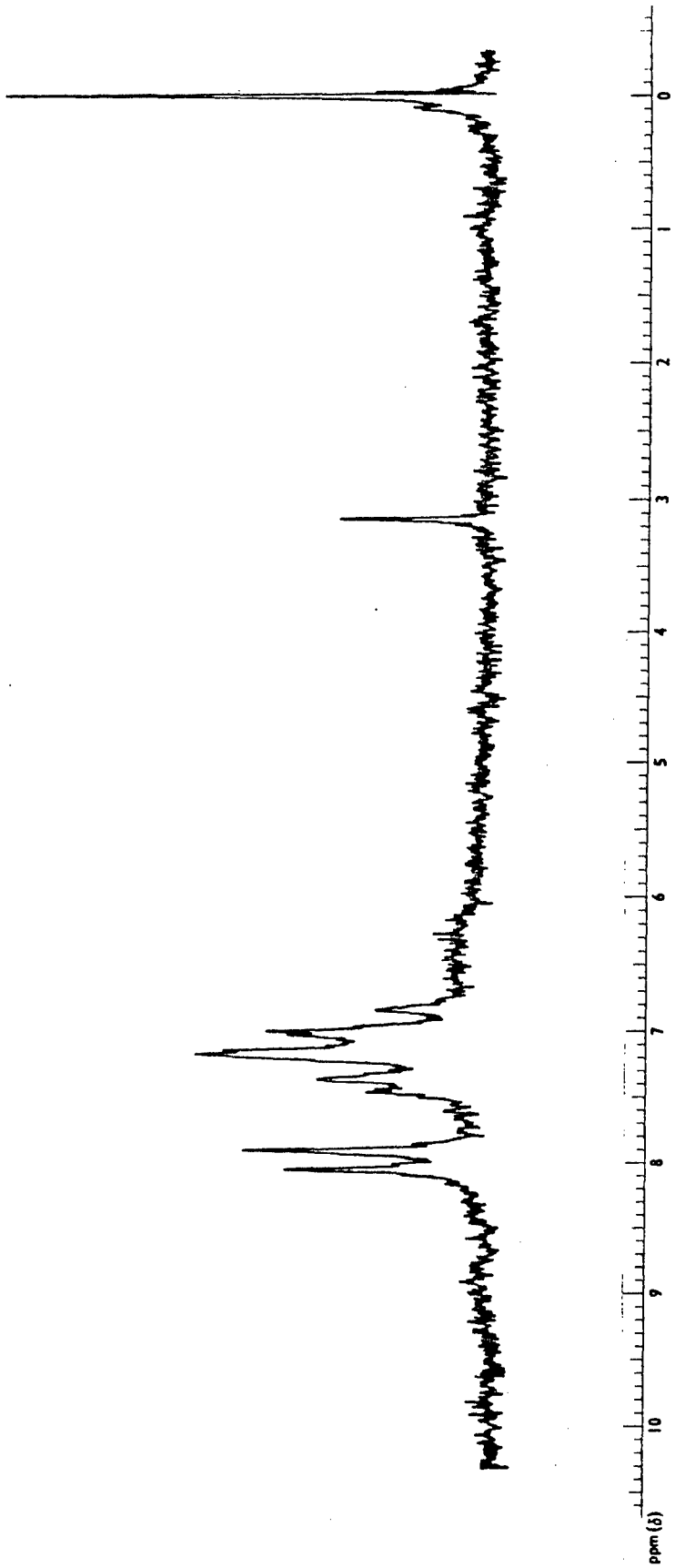


Figure 9. ^{1}H NMR Spectra of 1,3-Bis[4-[[4-(3-ethynylphenoxy) phenyl]sulfonyl]phenoxy]benzene 24

(Pure Oligomer)

Excess dry powdered potassium hydroxide (2g, 11.35 mmol) was reacted with 18 (3.0g) in toluene at reflux. The same reaction and purification procedures as used for the synthesis of the monomer 21 were followed. The resulting crude product was chromatographed on a quartz column filled with activated silica gel (80g). The product, was eluted with methylene chloride to yield 2.37g (86% based on pure dimer theoretical yield) of a yellow solid: IR(KBr) 3290 cm^{-1} (C≡CH), 3050, 1570, 1475 cm^{-1} (aromatic), 1380, 1360 cm^{-1} (gem di-methyl) 1315, 1140 (SO_2), 1100 cm^{-1} (ArOAr); ^1H NMR 6.90-8.21 (m, aromatic, unknown number of H), 3.15 (s, acetylene, unknown number of H), 1.70 (s, methyl, unknown number of H).

22 and α-[3-Ethynylphenyl)-W-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl] phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 26

A portion of the previously synthesized mixture of 15 and 19 (total weight 3g) was reacted with excess dry powdered potassium hydroxide (2g, 11.35 mmol) in toluene at reflux. The same reaction and purification procedures as used for the synthesis of the monomer 22 were followed. The resulting crude product was chromatographed on a quartz column filled with activated silica gel (120g). The product was eluted with hexanes/methylene chloride (1/4) to yield 2.04g (77% based on pure monomer theoretical yield) of a pale yellow solid mixture of 22 and 26: IR(KBr) 3270 cm^{-1} (C≡CH), 3050, 1570, 1475 cm^{-1} (aromatic), 1315, 1140 cm^{-1} (SO_2), 1100 cm^{-1} (ArOAr), 685 cm^{-1} (ArSAr); ^1H NMR 6.8-8.22 (m, aromatic, unknown number H), 3.15 (s, acetylene, unknown number H).

24 and α-[4-[[4- (3-Ethynylphenoxy)phenyl]sulfonyl]phenyl]-W-(3-ethynyl-phenoxy) poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 27

A portion of the previously synthesized mixture of 17 and 20 (total weight 3g) was reacted with excess dry powdered potassium hydroxide (2g, 11.35 mmol) in toluene at reflux. The same reaction and purification procedures as used for the synthesis of the monomer 24 were followed. The resulting crude product was chromatographed on a quartz column filled with activated silica gel (80g). The product ws eluted with methylene chloride to yield 2.19g (84% based on pure monomer theoretical yield) of a white solid mixture of 24 and 27: IR(KBr) 3300 cm^{-1} (C≡CH), 3050, 1570, 1475 cm^{-1} (aromatic), 1320, 1145 cm^{-1} (SO_2), 1095 cm^{-1} (ArOAr); ^1H NMR 6.70-8.50 (m, aromatic, unknown number of H), 3.15 (s, acetylene, unknown number of H).

SECTION III

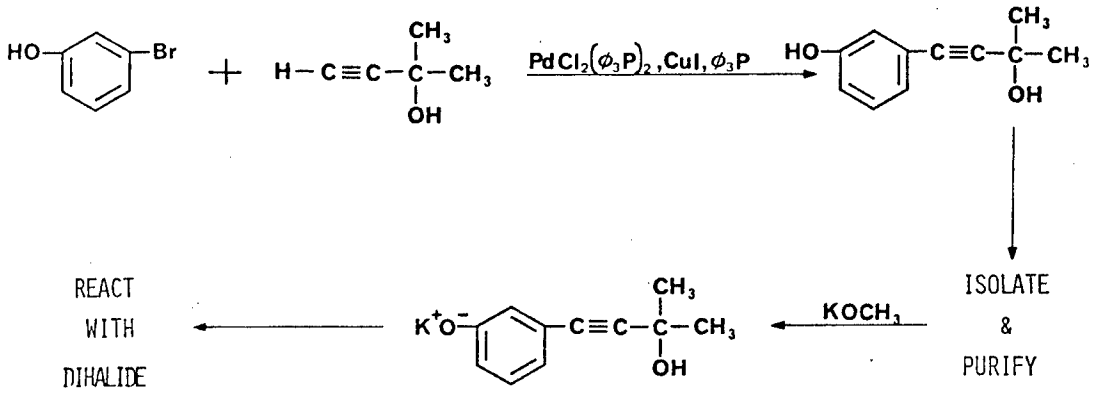
RESULTS AND DISCUSSION

1. RESEARCH APPROACH

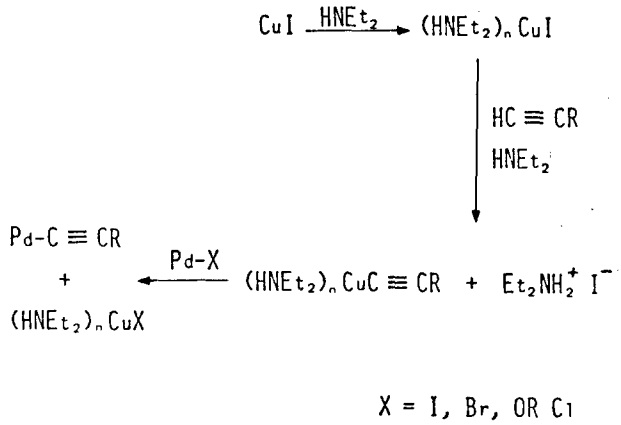
In order to meet a long-term objective of new AT-resin mechanical properties evaluation, research was directed toward the expeditious synthesis and thermomechanical analysis of increased molecular weight AT-systems. Standard reaction conditions were established by adjusting proven synthetic methods to obtain the desired products. An exhaustive study to optimize reaction conditions, purification techniques, and synthetic yields was not attempted. Despite this constraint, most yields were quite acceptable.

2. END-CAPPING AGENT 2

In previously employed end-capping schemes a palladium catalyst was used to directly connect a protected ethynyl group (2-methyl-3-butyn-2-ol) to a bulky intermediate. This procedure results in the entrapment of catalyst metals which must be laboriously removed from the final AT-product. If these metals are not removed, premature curing of the system occurs which narrows the processing window. In extreme cases where large quantities (>100ppm) of palladium remain, curing in the reaction vessel during the cleavage of the acetone protecting group has been observed (Reference 6). The end-capping agent 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 eliminates this problem. The synthesis of 2 is accomplished by using a palladium catalyst to replace the bromine atom of m-bromophenol with a protected ethynyl group. This route results in the preparation of a substituted phenolic acetylene which can be completely isolated from the catalyst metals by an ethylenediamine treatment.



The utility of a palladium catalyst in the synthesis of substituted aryl acetylenes is well established (References 7-10). The end-capping agent 2 was produced by using a standard catalyst system, dichlorobis-(triphenylphosphine)palladium(II)/copper(I) iodide/triphenylphosphine mixture, which has been employed in previously developed ethynylation procedures (Reference 10). The copper(I) iodide is believed to act as a cocatalyst, reducing the palladium(II) complex to the active palladium(0) catalyst as shown below. In the example shown here diethylamine is the solvent (Reference 11). Sonogashira has proposed a catalytic cycle (Figure 10) which shows: 1) the reduction of the palladium complex, 2) coordination of the aryl halide and acetylene with the palladium(0) complex and 3) the reductive elimination of the substituted aryl acetylene and regeneration of the active catalyst (Reference 10). The use of a basic solvent (in this case diethylamine) is important to stabilize acetylenic anions (Reference 9). The third catalyst system component, triphenyl phosphine, is presumably added to help replace lost triphenyl phosphine ligands on the palladium complex and thus prevent metal agglomeration.



Triethylamine, because of its basic properties was chosen as the solvent for the end-capper 2 synthesis. Reactions were run at reflux for times ranging from 2 to 30 hours. Reaction progress was followed by gas chromatography (GC) using phenol as a standard. All reactions were run under a dry nitrogen atmosphere. Yields rapidly increased with time up to 12 hours, slowly increased with time up to 24 hours, and showed a slow decline thereafter (see Figure 11). The reaction never appears to go to completion regardless of reaction time, and there is always residual m-bromophenol remaining (detected by GC and TLC). Dieck and Heck state that the major limitation of substituted aryl acetylene preparation is that aryl halides with strongly electron-donating substituents have relatively low reactivity toward oxidative addition (Reference 9). The failure of the end-capper reaction to go to completion is most likely associated with the inductive electron-donating effect of the hydroxy group

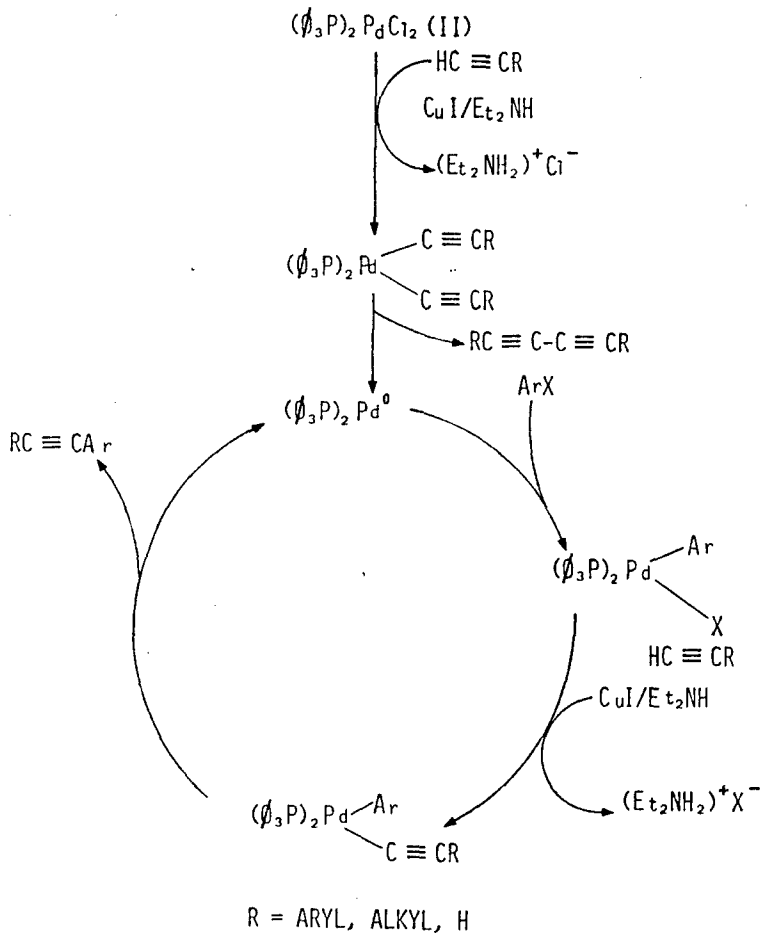


Figure 10. Catalytic Cyclic Proposed by Sonogashira

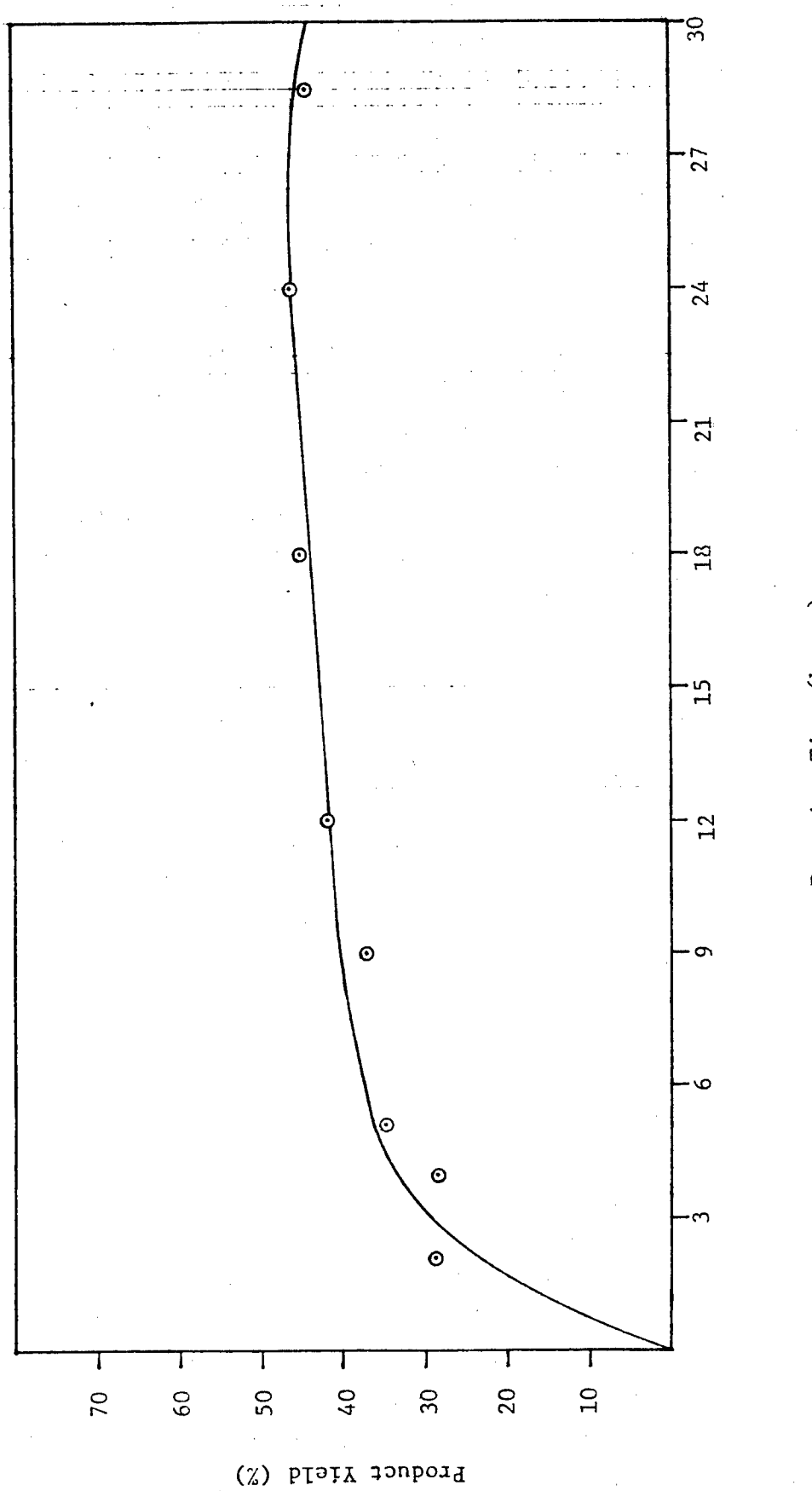


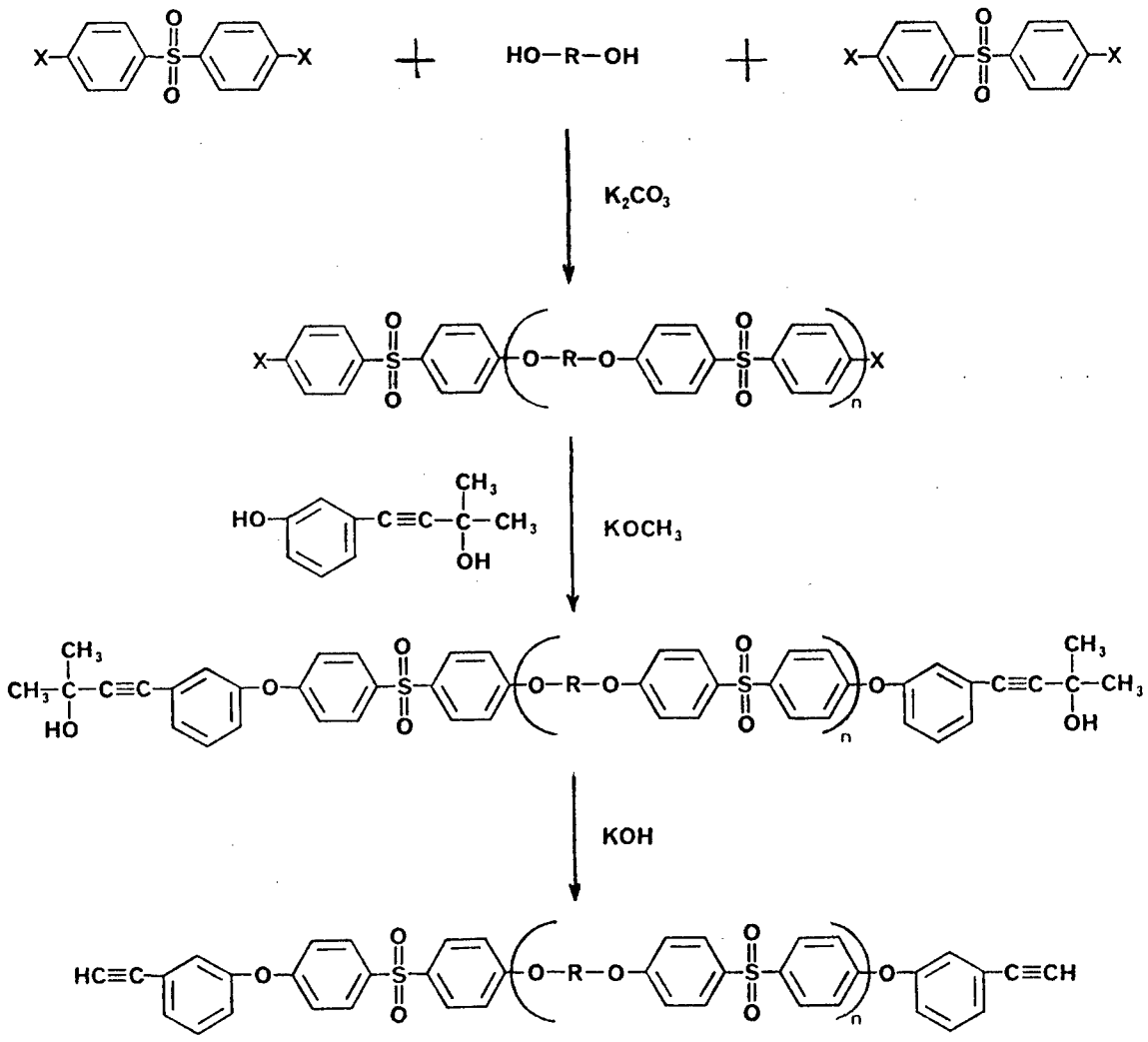
Figure 11. End-Capping Agent (4-(m-Hydroxyphenyl)-2-methyl-3-butyn-2-ol) 2 Yield Versus Reaction Time (Reactions Run at Reflux in Triethylamine)

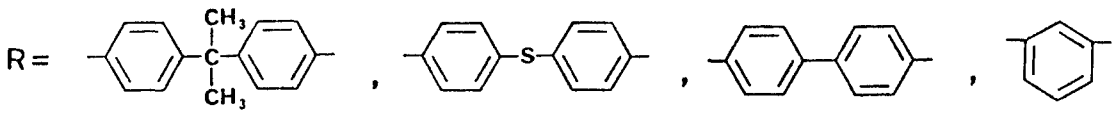
of m-bromophenol. This leads to the unproven hypothesis that the palladium catalyst is involved with a competing deactivation reaction with a relatively fast rate. Thus, a portion of the catalyst is deactivated or destroyed before it can react with m-bromophenol. The acetylenic starting material, 2-methyl-3-butyn-2-ol, was used in slight excess because it was known that some would be lost to side reaction products (Reference 9). Increasing the excess had no observable effect on reaction yield (consistently 40%).

In an attempt to improve the yield, prevent the hypothesized deactivation problem, and possibly recover and reuse the catalyst a new approach was tried. This approach involved the use of a new catalyst, tetrakis(triphenylphosphine)palladium(0) supported on polystyrene with 2% divinyl benzene (DVB) crosslinking. All previously used reaction conditions were repeated with only the catalyst being changed. The reaction was followed by both GC and TLC. At first a small amount of polymer supported catalyst (containing approximately 1/2 of the palladium present in the previously used homogeneous catalyst) was tried. With this quantity of catalyst the reaction appeared to proceed very slowly with barely detectable product formation after three hours. Increasing the quantity of catalyst did increase the product formation rate slightly, but it also greatly increased the formation rate of an unknown high Rf side product. In general, the use of this polymer supported catalyst was not successful. In a study by Terasawa, et al., a noncrosslinked polystyrene palladium supported catalyst was used to synthesize substituted aryl acetylenes (Reference 12). Results from this study show that the reaction rates of the noncrosslinked supported catalyst were as good or better than the similar homogeneous catalysts tried. This suggests that DVB crosslinking may prevent one or both of the reaction substrates (probably the m-bromophenol) from entering the polymer to coordinate with the palladium. Solvent effects undoubtedly also play an important role in opening the polymer support for oxidative addition.

3. AT-MONOMER AND AT-MONOMER/OLIGOMER SYSTEMS

The general approach used to synthesize the AT-monomer and AT-monomer/oligomer products consists of three synthetic steps: 1) synthesis of halo-terminated intermediates, 2) end-capping of the intermediates with end-capping agent 2, and 3) cleavage of the acetone protecting groups to produce the final AT-product. Production of both monomeric and oligomeric products is an inherent part of this synthetic route. Purification by column chromatography is required after each synthetic step.





X = F, Cl

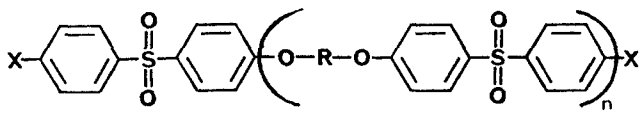
a. Synthesis of the Halo-Terminated Intermediates

A procedure similar to that developed by McGrath, et al., was used to produce halo-terminated products (Reference 13). The use of both 4,4-difluoro and 4,4-dichlorodiphenyl sulfone (chosen for the sulfone's ability to activate the displacement of the terminal halo groups) to end-cap several bis-phenols were

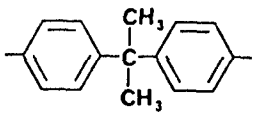
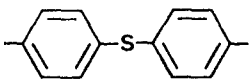
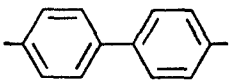
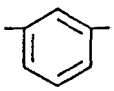
evaluated. In an effort to produce primarily monomer products, dihalodiphenyl sulfone was used in a 4:1 molar excess with respect to the bis-phenols (the four different bis-phenols used were bisphenol-A, 4,4'-thiodiphenol, p,p'-biphenol, and resorcinol). The stoichiometry outlined above produced monomer/oligomer ratios ranging from 100/0 to 60/40 depending on the bis-phenol reactant used (all monomer/oligomer ratios along with total product yields are shown in Table 1). Yields of fluoro-terminated products were generally about 10% higher than chloro-terminated products (only two of the bis-phenols were reacted with 4,4-dichlorodiphenyl sulfone). All reactions were run in N-methyl-2-pyrollidone (NMP) under nitrogen using potassium carbonate as a base. Typical reaction time was 4 hours with reaction progress followed by TLC. A higher reaction temperature was required for chloro displacement (150°C for chloro vs. 100°C for fluoro). The higher temperature in the chloro reaction led to the production of some side products (TLC analyses showed origin Rf material) and is probably the cause for the slightly lower chloro-terminated product yields. Before end-capping, monomer was separated from oligomeric products by column chromatography. Monomer/oligomer ratios were determined by weighing each component after separation.

TABLE 1

HALO-TERMINATED INTERMEDIATE SYNTHETIC YIELDS



X = F or Cl

R	Chloro-Terminated Ratio of Mono./Olig.	Chloro-Terminated Total Yield (%)[a]	Fluoro-Terminated Ratio of Mono./Olig.	Fluoro-Terminated Total Yield (%)[a]
	60/40	78	80/20	87
	70/30	77	60/40	89
	b	b	100/0	85
	b	b	70/30	86

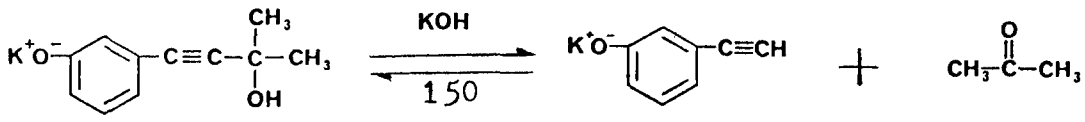
a) Based on pure monomer theoretical yield.
b) Product was not synthesized.

Monomer characterization was accomplished by standard procedures (IR, proton-NMR, and elemental analysis). Oligomer characterization was limited to IR and in some cases IR and proton-NMR analyses, because oligomer composition was not determined, i.e., the oligomer product consists of dimer, trimer, tetramer, etc., in unknown quantities. Therefore, elemental analysis of oligomeric products would provide little useful information. Characterization results proved consistent with proposed product structures. For detailed halo-terminated product characterization results, see Experimental, Preparation of Halo-terminated Intermediate Monomer/Oligomer Mixtures.

b. End-Capping of the Halo-Terminated Intermediates

Reaction conditions developed for ethynylation of the halo-terminated intermediates were based on previously used end-capping schemes (Reference 6) and analysis of the reactivity and stability of the end-capping agent 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2. The general procedure developed involves: 1) the generation of the potassium salt (by reaction with potassium methoxide) of 2 in DMSO, 2) addition (under nitrogen atmosphere) of the salt to a solution of the desired halogenated intermediate, and 3) the maintenance of reaction conditions (temperature, nitrogen atmosphere, etc.) until product formation is judged complete by TLC analyses.

An unexpected problem was encountered with the end-capping of the chloro-terminated intermediates. As in the previous step (halo-terminated product synthesis) a high temperature (150°C) was required to accomplish chlorine displacement. The combination of high temperature and basic conditions produced interestingly, the final unprotected AT-monomer and AT-monomer/oligomer systems in low yield (20-40%), see Experimental, Cleavage of AT-Product Acetone Protecting Groups. Evaluation of the stability of the potassium salt of 2 (using sodium nitro-prusside as an indicator for acetone - limit of identification ~10 micrograms) (Reference 14) was accomplished by bubbling nitrogen gas, which had been previously passed over a DMSO solution of the end-capper 2, into a standardized amount of indicator and noting any color changes (bright-red indicates presence of acetone). Tests were conducted at ten minute intervals using fresh indicator and clean glassware each time. Results from this procedure showed that 2 was completely stable in DMSO at temperatures as high as 160°C. The addition, however, of even a very small amount of base (2-3 drops of 20% methanolic potassium hydroxide) at high temperatures (~150°C) caused an immediate strong red color change in the indicator. This positive test result leads to the conclusion that the equilibrium reaction shown below is occuring.



2

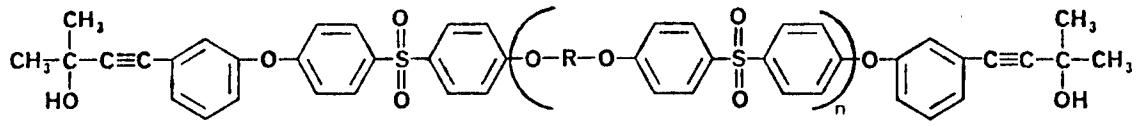
When the salt of the end-capping agent was formed at low temperature (40-50°C) no acetone was detected. As the solution was slowly heated, acetone began being detected at approximately 130°C. The loss of the protecting group was clearly occuring below the 150°C temperature required for chlorine displacement. Weaker bases such as potassium carbonate were tried, but gave similar results. Solvents other than DMSO (NMP and sulfolane) were also tried, but the salt of 2 was only slightly soluble in them making addition to the chloro-terminated intermediate difficult. Running the reaction at greater than atmospheric pressure might allow the acetone adduct to remain in solution at higher temperatures and give the desired product, the protected AT-systems. Testing this idea was not attempted. Thin-layer-chromatography (TLC) analysis of the reaction mixture always showed the presence of many side products. These compounds were probably formed as a result of the loss of the acetone protecting group.

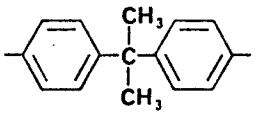
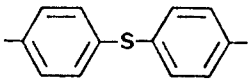
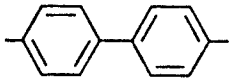
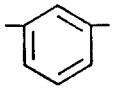
Reaction of the fluoro-terminated systems with 2 proceeded very smoothly and gave good yields (70-85%) of the protected AT-products. Displacement of the fluorine atoms (detected by TLC analyses) was accomplished at 85-90°C and 2 retained its protecting group. Table 2 shows the yields of acetone protected AT-systems obtained from end-capping monomer and monomer/oligomer mixtures of fluoro-terminated intermediates.

Characterization of products produced from both the fluoro- and chloro-terminated precursors were accomplished in the same way as previously described. Proposed product structures were found to be consistent with characterization results (see Experimental, Preparation of Acetone Protected AT-Products for detailed results).

TABLE 2

ACETONE PROTECTED AT-MONOMER/OLIGOMER SYNTHETIC YIELDS



R	Ratio Monomer/Oligomer	Synthetic Yield (%)
	100/0 0/100	87 83[a]
	100/0 60/40	69 83[b]
	100/0	72
	100/0 70/30	74 84[b]

a) Based on pure dimer theoretical yield.
b) Based on pure monomer theoretical yield.

c. Cleavage of the Acetone Protecting Groups

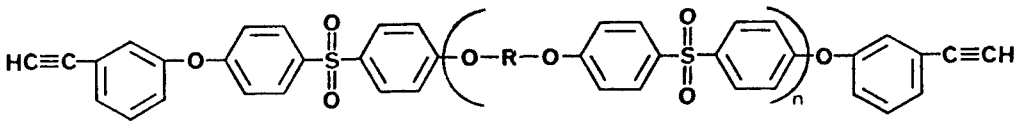
Caustic conditions were used to cleave the protecting acetone groups and give the final AT-monomer and AT-monomer/oligomer products in yields ranging from 77 to 85%. Published procedures for acetone protecting group cleavage follow the general route: 1) the protected AT-compound is dissolved in either benzene or toluene, 2) while stirring, excess methanolic potassium hydroxide is added to the solution, and 3) the reaction mixture is heated to reflux and methanol, along with a specified amount of aromatic solvent, is distilled from the system removing the acetone adduct. Reaction progress is followed by thin-layer-chromatography (TLC) (Reference 18).

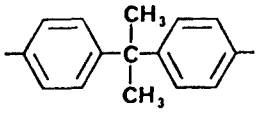
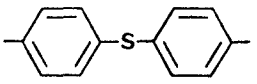
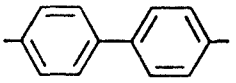
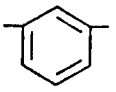
The procedure outlined above was followed for the synthesis of several of the products reported here. There was however, a problem with the formation of some

high Rf side products. Using column chromatography these high Rf products were separated (a yellowish solid) and analyzed by proton-NMR, IR, and high performance liquid chromatography (HPLC) which showed at least one and possibly two methoxy functionalities present in the sample. High performance liquid chromatography indicated that the unknowns were in the 300-400 molecular weight range. This evidence points to the possibility that the methanol (the only source of a methoxy group) used to disperse the potassium hydroxide was participating in the reaction and causing the formation of high Rf side products. The exact structures of the side products were not determined, but spectrographic analyses (NMR, IR) indicated that a sulfone functionality was also present. To prevent the formation of the side products all remaining cleavage reactions were conducted without methanol. The base was finely powdered, dried, and added directly to the reaction mixture. Thin-layer-chromatography (TLC) results showed that none of the previously described side products was generated using this procedure. Table 3 shows the yields obtained for

TABLE 3

AT-MONOMER/OLIGOMER SYNTHETIC YIELDS



R	Ratio Monomer/Oligomer	Acetone Cleavage Yield (%)	Overall Yield (%)
	100/0 0/100	83[a] 86[a]	63 62[b]
	100/0 60/40	79 77	49 57[c]
	100/0	80	49
	100/0 70/30	85[a] 84[a]	54 61[c]

a) Cleavage Rxn run without methanol.
b) Based on pure dimer theoretical yield.
c) Based on pure monomer theoretical yield.

the cleavage step and also the overall synthetic yields for the AT-systems. Final products were characterized as previously described (see Experimental, Cleavage of AT-Product Acetone Protecting Groups).

4. AT-RESIN THERMOMECHANICAL PROPERTIES

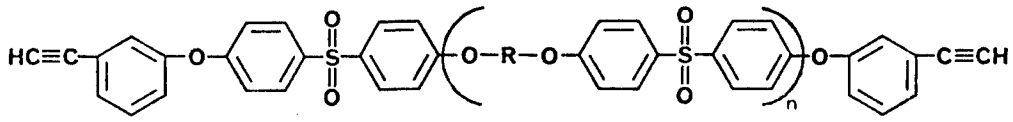
After final chromatographic purification, samples of the AT-systems were cured in air at 288°C (550°F) for eight hours. Samples chosen for curing included pure monomers, monomer/oligomer mixtures produced by the stoichiometry outlined in the previous section, and in one case (the bisphenol-A based resin) pure oligomer. This set of samples was selected to provide data showing the effect of oligomer concentration on thermomechanical properties.

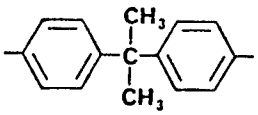
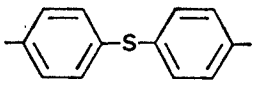
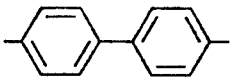
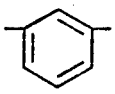
Preparation of the samples for curing proved somewhat difficult because the large AT-systems tended to retain work-up solvents (toluene, ethyl acetate, water, etc.) even after extended periods of drying (50°C) under vacuum. This led to the formation of gas bubbles and finally voids (after the volatiles escaped during curing) in the final cured resins. These cured samples showed very irregular surfaces and were not suitable for thermomechanical properties study. This sample preparation problem was overcome by first melting the material to fill a sample cup and then exposing the filled cup to high vacuum (0.1mm Hg) at 150°C for 15 minutes. This procedure effectively removed all retained solvents and gave smooth voidless samples after final curing in air at 288°C.

Differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were used to measure the glass transition temperatures (Tgs) of the uncured and curved AT-resins respectively (Table 4). It has been shown that increased oligomer content in a resin generally depresses the final cured Tg (Reference 15). The cured Tg values for the AT-resins prepared for this research follow this trend with one exception, the 4,4'-thiodiphenol based resin exhibits a slight increase in Tg. The cause for this exception is not known but may be associated with experimental error ($\pm$5%) which is inherent in TMA measurements on very small samplers. For composite applications and a 350°F use temperature, cured resins must exhibit a minimum Tg of 220°C. A review of the cured Tg values shows that only the bisphenol-A based resin does not meet this criteria. For easy processing, an initial Tg of ~20°C is required; this gives the uncured resin the necessary tack and drape for practical handling. Initial Tgs for the synthesized resins fall between 45 and 60°C which is too high for conventional process techniques. The p,p'-biphenol based resin has, in addition to a

TABLE 4

AT-RESIN INITIAL AND CURED GLASS TRANSITION TEMPERATURES (TGS)



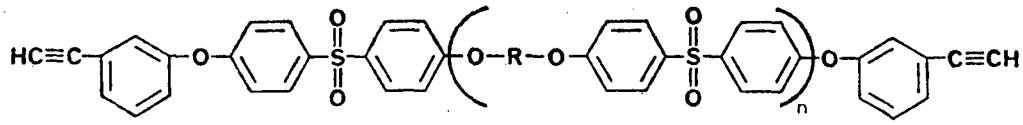
R	Ratio Monomer/Oligomer	a Tg Initial (°C)	b c Tg Cured (°C)
	100/0	55	191
	80/20	55	168
	0/100	46	140
	100/0	54	232
	60/40	50	240
	100/0	50	275
	100/0	53	269
	70/30	45	246

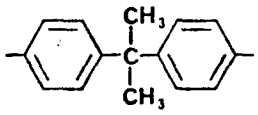
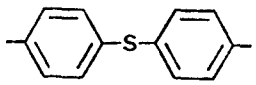
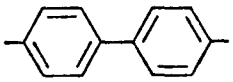
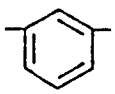
a) Determined by DSC (10°C/min).
b) Determined by TMA (10°C/min).
c) Cured at 550°F, 8H, in air.

high initial Tg, a Tm of 180°C (Table 5). Most AT-systems cure rapidly at temperatures over 175°C. As soon as the p,p'-biphenol system melts, rapid curing begins and no time is available for processing. The lack of a processing window makes this system almost impossible to handle by standard methods. The most attractive AT-systems seem to be the 4,4'-thiodiphenol and resorcinol based resins. Even though these systems have initial Tgs of ~50°C, they all show adequate cured Tgs and have wide processing windows (Tables 4 and 5). To investigate the possibility of lowering the initial Tgs of these systems reactive diluents were mixed with the 60/40 monomer/oligomer ratio 4,4'-thiodiphenol based resin. The diluents chosen for the test were 1-(3-ethynyl-phenoxy)-3-phenoxybenzene commonly known as mono-ATP (initial Tg = -49°C) and 1,3-bis-(3-ethynyl-phenoxy)benzene commonly known as ATP (initial Tg = -39°C).

TABLE 5

ONSET AND PEAK OF AT-RESIN POLYMERIZATION



R	Ratio of Mono./Olig.	Tm (°C)[a]	Tpoly Onset(°C)[a]	Tpoly Max (°C)[a]
	100/0	80	160	250
	80/20	77	160	245
	0/100	--	110	270
	100/0	--	145	240
	60/40	--	150	230
	100/0	180	185	230
	100/0	70	130	230
	70/30	--	135	235

a) Determined by DSC (10°C/min).

Using the Fox-Flory series (Reference 15) (Equation 1) shown below, it was calculated that 20% mono-ATP would be required to drop the 4,4'-thiodiphenol based resin's initial Tg from 50°C to 23°C.

$$\frac{1}{Tgm} = \frac{\%A}{TgA} + \frac{\%B}{TgB} + \frac{\%C}{TgC} + \ldots \text{ etc.} \qquad (1)$$

where

Tgm = Tg of the mixture (°K)

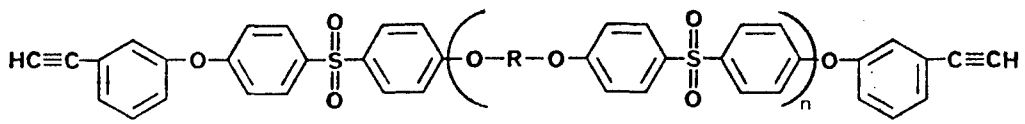
TgA, TgB, TgC, ... etc. = Tg of component A, B, C, ... etc. (°K)

% A, % B, % C, ... etc. = Decimal % of component A, B, C, ... etc. present in the mixture

The initial Tg of the mixture as measured by DSC was 10°C. This corresponds well with the predicted value and provides the desired room temperature tack and drape. To determine the effect of mono-ATP on the cured Tg of the resin some samples of the mixture were cured in air for five hours at 150°C (low initial temperture to prevent any evaporation of mono-ATP) and then for eight hours at 288°C. The cured Tg of the mixture (TMA measurement) was 168°C. It can be seen that the mono-ATP diluent is effective for lowering the initial Tg of the 4,4'-thiodiphenol based resin but it drops the final cured Tg well below the 220°C required for 177°C (350°F) applications. The use of ATP as a diluent was next tested. A mixture of 20% ATP and 80% 4,4'-thiodiphenol based resin was prepared. The initial Tg of the mixture was measured to be 10°C (DSC) and the final cured Tg 236°C (TMA). The same cure cycle as used for the mono-ATP mixture was employed. It appears that ATP makes an excellent diluent for the 4,4'-thiodiphenol based system providing a low initial Tg and yet only slightly lowering the final cured Tg. Although not evaluated, the use of ATP with the resorcinol based resin would probably also be effective because of the system's structural similarity. The results of the diluent tests are shown in Table 6.

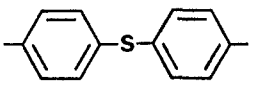
TABLE 6

INCORPORATION OF REACTIVE DILUENTS WITH 4,4'-THIODIPHENOL BASED RESINS



Diluent	%	Uncured Tgcal[a] °C	Uncured Tg°C	Cured Tg°C
--	0	--	50	240
mon-ATP	20	23	10	168
ATP	20	27	10	236

a) Calculated using the Fox-Flory equation.

R = 

Thermo-oxidative stability of the resins was evaluated by isothermal aging (ITA) in air for 200 hours. A plot (Figure 12) of system weight loss versus aging time shows the results of the aging study for the cured pure monomer resins. All the systems showed good thermal stability with weight losses ranging from 28% to 38% after 200 hours. The comparable monomer/oligomer mixtures of the resins generally showed slightly greater weight losses.

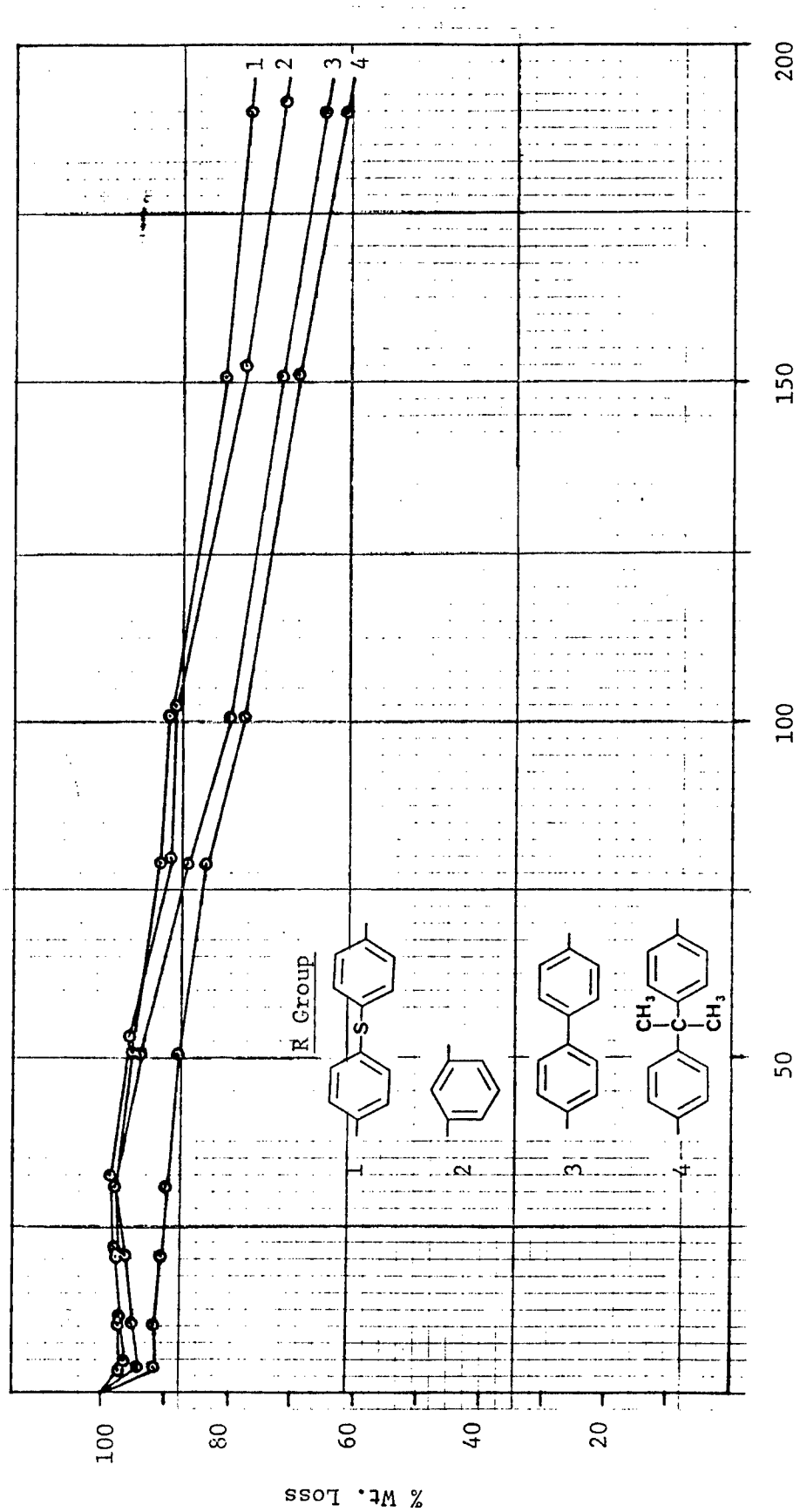


Figure 12. Isothermal Aging Study on Cured Bis-phenol Based AT-Resins Preformed at 600°F (315°C) for 200 Hours in Air

SECTION IV

CONCLUSIONS

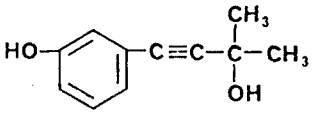
The use of 4-(m-hydroxyphenyl)-2-methyl-3-butyn-2-ol 2 as an acetylene end-capping agent has the significant advantage of simplifying the task of catalyst metals removal which is a difficulty encountered with other end-capping approaches. Further study is required to improve the synthetic yield of 2. An effort directed at achieving a better yield would be best focused on the development of a recoverable polymer supported palladium catalyst for ethynylation of bromophenol. In addition to improving the yield, such a system would lower the synthetic cost and make large scale reactions possible.

All the AT-resins synthesized by the new procedure showed good thermal stability and several exhibited excellent cured Tgs. The high initial Tgs of the systems remain a problem. The investigation of ATP as a reactive diluent gave promising results and might provide a solution to this problem. It is clear that some type of diluent must be incorporated with these systems to make conventional processing possible. What effect this might have on the synthesized resins' mechanical properties remains to be seen. Scale-up of the resins to the 50g level would provide material for mechanical properties characterization and determine if these increased molecular weight systems have improved toughness.

APPENDIX

SIGNIFICANT STRUCTURES

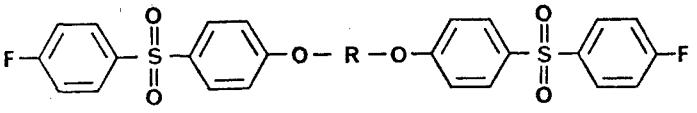
End-Capping Agent



4-(m-Hydroxyphenyl)-2-methyl-3-butyn-2-ol 2

Halo-Terminated Intermediates

Monomers



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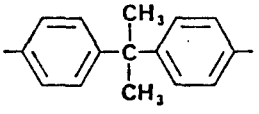
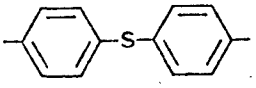
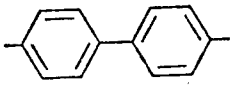
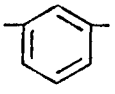
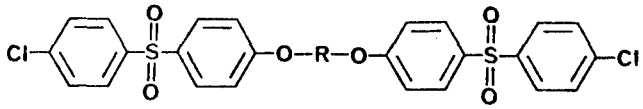
	1,1'-(1-Methylethylidene)bis[4-[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene] 3
	1,1'-Thiobis[4-[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene 7
	4,4'-Bis[4-[(4-fluorophenyl)sulfonyl]phenoxy]-1,1-biphenyl 11
	1,3-Bis[4-[(4-fluorophenyl)sulfonyl]phenoxy]benzene 12



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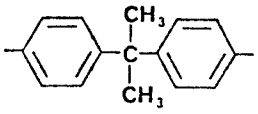
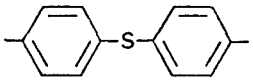
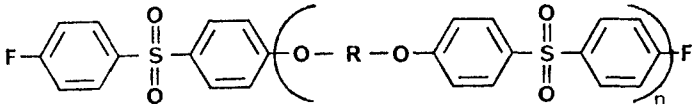
	1,1'-(1-Methylethylidene)bis[4-[4-[(4-chlorophenyl)sulfonyl]phenoxy]benzene] 5
	1,1'-Thiobis[4-[4-[(4-chlorophenyl)sulfonyl]phenoxy]benzene 9

Oligomers



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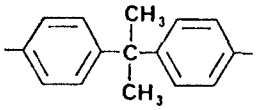
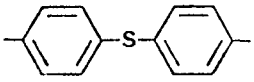
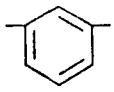
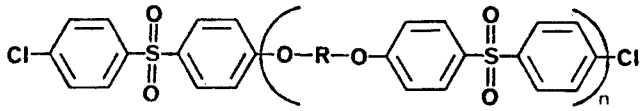
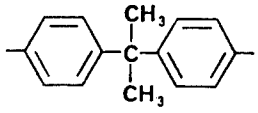
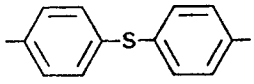
	α-[4-[1-[4-[4-[(4-Fluorophenyl)sulfonyl]phenoxy]phenyl]-1-methylethyl]phenyl]-W-[4-[(4-fluorophenyl)sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 4
	α-[4-[[4-[4-[(4-Fluorophenyl)sulfonyl]phenoxy]phenyl]thio]phenyl]-W-[4-[(4-fluorophenyl)sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 8



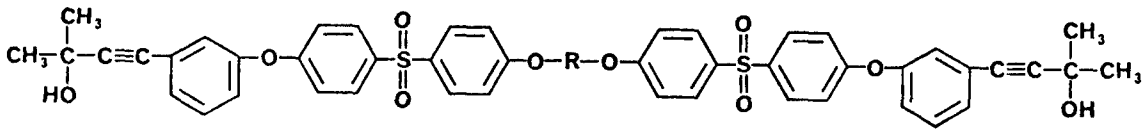
α-[4-[(4-Fluorophenyl)sulfonyl]phenyl]-W-[3-[4-[(4-flurorphenyl)sulfonyl]phenoxy]phenoxy]poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 13



R	Name
	α-[4-[1-[4-[4-[(4-Chlorophenyl)sulfonyl]phenoxy]phenyl]-1-methylethyl]phenyl]-W-[4-[(4-chlorophenyl)sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 6
	α-[4-[[4-[4[(4-Chlorophenyl)sulfonyl]phenoxy]phenyl]thio]phenyl]-W-[4-[(4-chlorophenyl)sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 10

Acetone Protected AT-Systems

Monomers



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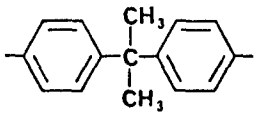
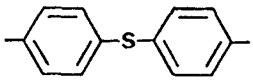
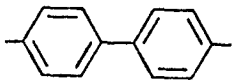
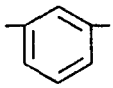
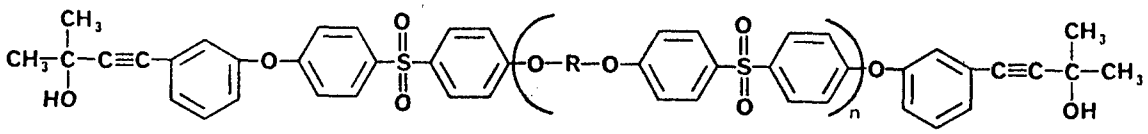
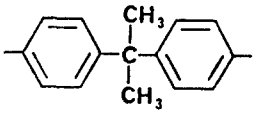
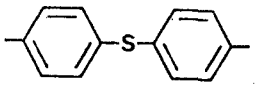
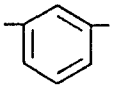
	4,4'-[(1-Methylethylidene)bis(4,1-phenyleneoxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 14
	4,4'-[Thiobis(4,1-phenyleneoxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 15
	4,4'-[[1,1'-Biphenyl]-4,4'-diylbis(oxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 16
	4,4'-[1,3-Phenylenebis(oxy-4,1-phenylenesulfonyl-4,1-phenyleneoxy-3,1-phenylene)]bis[2-methyl-3-butyn-2-ol] 17

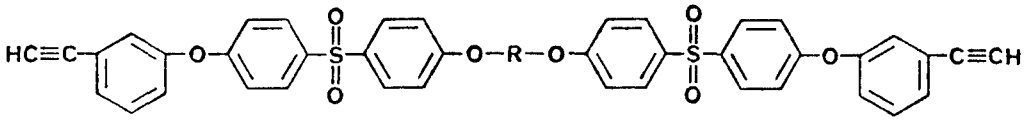
Oligomers

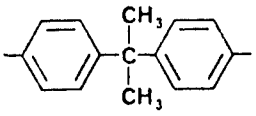
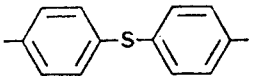
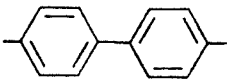
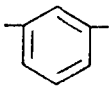


R	Name
	α-[3-(3-Hydroxy-3-methyl-1-butynyl)phenyl]-W-[4-[[4-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 18
	α-[3-(3-Hydroxy-3-methyl-1-butynyl)phenyl]-W-[4[[4-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 19
	α-[4-[[4-[3-(3-Hydroxy-3-methyl-1-butynyl)phenoxy]phenyl]sulfonyl] phenyl]-W-[3-(3-hydroxy-3-methyl-1-butynyl)phenoxy]poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 20

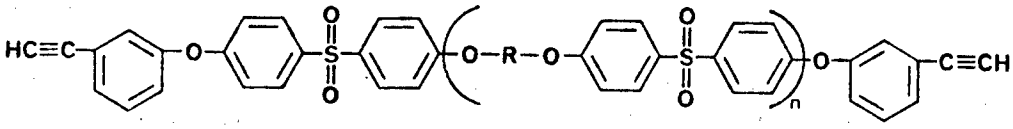
Unprotected AT-Systems

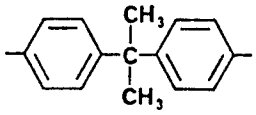
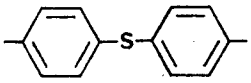
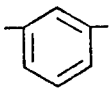
Monomers



R	Name
	1,1'-(1-Methylethylidene)bis[4-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene] 21
	Bis[p-[p-[[p-(m-ethynylphenoxy)phenyl]sulfonyl]phenoxy]phenyl]sulfide 22
	4,4'-Bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]-1,1'-biphenyl 23
	1,3-Bis[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]benzene 24

Oligomers



R	Name
	α-(3-Ethynylphenyl)-W-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene(1-methylethylidene)-1,4-phenylene] 25
	α-[3-Ethynylphenyl)-W-[4-[[4-(3-ethynylphenoxy)phenyl]sulfonyl]phenoxy]poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylenethio-1,4-phenylene) 26
	α-[4-[[4-(3-Ethynylphenoxy)phenyl]sulfonyl]phenyl]-W-(3-ethynylphenoxy)poly(oxy-1,3-phenyleneoxy-1,4-phenylenesulfonyl-1,4-phenylene) 27

REFERENCES

1. C. Y-C. Lee, I. J. Goldfarb, T. E. Helminiak, F. E. Arnold, Soc. Adv. Matr. Proc. Eng. Ser., 28, 699, 1983.

2. J. Gamble, "The Effects on Rigidity as a Function of Para Ethynylphenoxy Linkages in an Acetylene Terminated Thermosetting System", (M.S. Dissertation), Wright State University, 1981.

3. C. Y-C. Lee, I. J. Goldfarb, F. E. Arnold, T. E. Helminiak, Org. Coat. Appl'd Polym. Sci. Preprints, 48, 1983.

4. S. Sikka and I. J. Goldfarb, Org. Coat. Plast. Preprints, 45, 138, 1981.

5. T. E. Helminiak and W. B. Jones, Org. Coat. and Plast. Preprints, 48, 221, 1983.

6. E. T. Sobourin, The Synthesis of Polymer Precursors and Exploratory Research Based on Acetylene Displacement Reaction, Materials Laboratory, Wright-Patterson AFB, Ohio 45433, AFWAL-TR-80-4151, 1980.

7. E. T. Sobourin, Preprints Div. Petr. Chem., 24, 233, 1979.

8. L. Cassar, J. Organomet. Chem., 93, 253, 1975.

9. H. A. Dieck and R. E. Heck, J. Organomet. Chem., 93, 259, 1975.

10. K. Sonagashira, Y. Tohda, N. Hagihara, Tet. Letter, 4467, 1975.

11. K. Sonagashira, T. Yatake, Y. Tohda, S. Takahashi, and N. Hagihara, J.C.S. Chem. Comm., 291, 1977.

12. M. Terasawa, K. Kaneda, T. Imanada, and S. Teranishi, J. Organomet. Chem., 162, 403, 1978.

13. D. Mohanty, J. Hedrick, K. Gobetz, B. Johnson, K. Yilgor, E. Yilgor, R. Yang, and J. McGrath, Polym. Preprints, 23(1), 284, 1982.

14. F. Feigl, Spon Tests in Organic Analysis, Elsevier Publishing Co., New York, 1966.

15. P. Flory, Principles of Polymer Chemistry, Cornell University Press, New York, 1953.

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