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# Phenylthiazyl Polymers with Flexible Spacers: Synthesis and Electrical Properties

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ABSTRACT: A series of polymers with (phenylthio)phenyldithiazyl (PTPD series) and phenylenedithiobis(phenyldithiazyl) (PDBPD series) segments have been synthesized by using a novel route involving the in situ chlorinolysis of a benzyl-protected precursor monomer. These polymers can be transformed from an insulating to a semiconducting state upon oxidation with bromine. The PTPD polymer made with a triethylene glycol spacer is soluble and fusible, while the ones with shorter spacers are insoluble. The polymers attain conductivities in the range of $10^{-3}$–$10^{-5}$ ($\Omega$ cm)$^{-1}$ on doping with bromine.

## Introduction

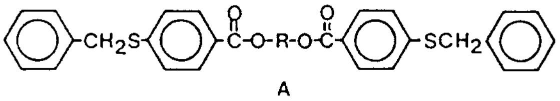
In the 1970s, polythiazyl, $(SN)_x$, received considerable attention due to its superconducting behavior.[1] But $(SN)_x$ is both insoluble and infusible. There have been various attempts[2–7] to introduce organic groups in the SN backbone with the objective of obtaining soluble derivatives but without success. In our previous paper[9] we described the synthesis of some model phenylthiazyl compounds (RPhSNSNSPhR and RPhSNSNSPhSNSNSPhR) which have elongated and planar structures. These compounds formed semiconducting complexes upon doping with bromine. The central purpose of this work is to synthesize and characterize polymers with (phenylthio)phenyldithiazyl (PTPD = –PhSNSNSPh–) or phenylenedithiobis(phenyldithiazyl) (PDBPD = –PhSNSNSPhSNSNSPh–) segments along with flexible spacers, to obtain soluble polymers. The properties of these polymers are compared with their respective model compounds.

## Experimental Section

**Materials and Methods.** All manipulations, unless mentioned otherwise, were carried out under a dry nitrogen atmosphere. Elemental analyses were performed by the University of Massachusetts Microanalysis Laboratory. NMR spectra were recorded with either a Varian XL 200 or a Varian XL 300 spectrometer. ESR spectra were recorded with a Varian E-9 X-band spectrometer. *g* values were determined by using $\alpha,\alpha'$-diphenylpicrylhydrazyl (DPPH) as a marker, and spin concentrations were determined by using tetramethylpiperidinyloxy as a standard.

Solvents were purified by using the usual techniques under inert atmosphere.[8] $SO_2Cl_2$ was fractionally distilled immediately prior to use. Bis(trimethylsilyl)sulfur diimide was synthesized by using the modified procedure of Kuyper et al.[6] $NaN(SiMe_3)_2$ was purchased from Petrarch Chemical and used as received. Synthesis of *N,N′*-bis(trimethylsilyl)phenylenebis(dithiazyl), $Me_3SiNSNSPhSNSNSiMe_3$, has been previously described.[9]

**Synthesis of *p*-(Benzylthio)benzoyl Chloride.** *p*-(Benzylthio)benzoic acid was synthesized from *p*-aminobenzoic acid by using the procedure of Pettit and Sherrington.[10] (Benzylthio)benzoyl chloride was synthesized by using a procedure similar to that of Barry and Finnar.[11] To a slurry of (benzylthio)benzoic acid (15 g) in 150 mL of dry benzene was added 16 g of $SOCl_2$, and the mixture was refluxed until all the acid dissolved to form a clear light yellow solution (ca. 5 h). The volume of the solution was then reduced to about 50–60 mL, and about 150 mL of *n*-heptane was added to it. The solution was cooled in a freezer to promote crystallization. The very fine white crystals formed were filtered, washed with dry Skelly F (bp 40–60 °C), and dried. The yield was 80% (13 g), mp 100–102 °C: $^1H$ NMR ($CDCl_3$) $\delta$ 4.27 [s, 2 H, $SCH_2Ph$], 7.26–7.41 [m, 7 H, aromatic (2 H), benzyl (5 H)], 7.98 [d, 2 H, aromatic].



A

**Diesters. Decanediol Diester A-1, R = $(CH_2)_{10}$.** 1,10-Decanediol (2.50 g, 14.34 mmol) and (benzylthio)benzoyl chloride (8.28 g, 31.5 mmol, 10% excess) were mixed with 150 mL of $CH_2Cl_2$ and 2.5 mL of pyridine. The solution was refluxed for 24 h and washed successively with dilute HCl, water, $NaHCO_3$ solution (5%), and finally distilled water. The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent stripped off. Recrystallization of the solid residue from $CH_2Cl_2$/ethanol produced 7.37 g of the diester for a yield of 82% with mp 96–98 °C.

**Diethylene Glycol Diester A-2, R = $CH_2CH_2OCH_2CH_2$.** The DEG diester was synthesized as above from diethylene glycol. The product, recrystallized from $CCl_4$/ethanol, was obtained in 87% yield with mp 90–96 °C.

**Triethylene Glycol Diester A-3, R = $(CH_2CH_2O)_2CH_2CH_2$.** The TEG diester was also synthesized by using the same procedure as above from triethylene glycol. Recrystallization from $CCl_4$/ethanol gave the TEG diester in 72% yield with mp 72–74 °C.

The elemental analysis and $^1H$ NMR data of all the above diesters are given in Table I.

**Chlorinolysis and Polymerization.** All polymerizations were carried out by chlorinolysis of the benzyl thioether diesters (premonomers), followed by reaction of the bis(sulfenyl chlorides) that are formed, with the bis((trimethylsilyl)imides). A typical reaction procedure is given below.

**PTPD–TEG Polymer.** Triethylene glycol diester, TEG diester (1.0 g, 1.66 mmol) was dissolved in 10 mL of $CHCl_3$ in a round-bottom flask equipped with a dropping funnel. Sulfuryl chloride (1.12 g, 8.3 mmol) in 7 mL of $CHCl_3$ was added dropwise to the stirred solution of the diester over a period of 1.5 h. An exit bubbler was provided to allow the escape of $SO_2$ generated during chlorinolysis. After the gas evolution had stopped, a very small aliquot of the solution was freed of solvent to be replaced with $CDCl_3$, and its $^1H$ NMR spectrum was recorded. The completion of chlorinolysis was confirmed by the absence of the benzyl protons in the spectrum (Figure 1).

After completion of chlorinolysis, the excess $SO_2Cl_2$ and $CHCl_3$ were removed by evacuation to give a reddish oil. Fresh $CHCl_3$ (20 mL) was then added to the oil to form a red solution of the bis(sulfenyl chloride). Bis(trimethylsilyl)sulfur diimide (0.3418 g, 1.66 mmol) was then added, which turned the solution deep red immediately. The reaction was allowed to go on for 24 h, after which the solution was concentrated by removal of some solvent and was further heated to gentle reflux to allow completion of the reaction. The polymer was precipitated by pouring the reaction mixture into methanol. The fibrous polymer was thoroughly washed and dried under vacuum. The yield obtained was 648 mg (81%). The $^1H$ NMR spectrum of the polymer is shown in Figure 2.

The other polymers were prepared similarly by using the appropriate diesters. In the case of the PDBPD–TEG polymer, the TEG–bis(sulfenyl chloride) obtained after chlorinolysis was polymerized by condensation with equimolar quantity of *N,N′*-bis(trimethylsilyl)phenylenebis(dithiazyl), $Me_3SiNSNSPhSNSNSiMe_3$. The yields of various polymers and their elemental analysis results are given in Table II.

**Doping and Conductivity Measurements.** In the case of soluble polymers, conductivity measurements were made on cast films; pressed pellets of insoluble polymers were used. Doping of pellets and films with bromine was carried out in vapor phase.

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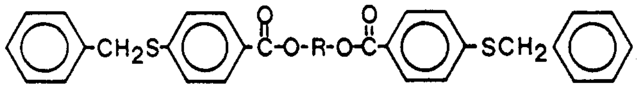
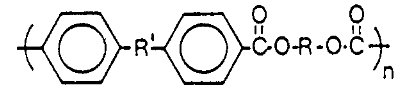
**Table I**
**Elemental Analysis and $^1$H NMR Spectral Data of Premonomer A**



| | R | mp, °C | yield, % | elemental anal.[a] C | H | S | $^1$H NMR ($CDCl_3$, TMS), δ |
|---|---|---|---|---|---|---|---|
| A-1 | $(CH_2)_{10}$, C10 | 96–98 | 82 | 72.91<br>(72.81) | 6.81<br>(6.75) | 10.21<br>(10.23) | 1.32–1.45 (m, 12 H); 1.74 (m, 4 H) 4.20 (s, 4 H); 4.28 (t, 4 H); 7.27–7.35 (m, 12 H); 7.91 (d, 4 H) |
| A-2 | $CH_2CH_2OCH_2CH_2$, DEG | 90–96 | 87 | 68.71<br>(68.79) | 5.51<br>(5.41) | 11.65<br>(11.48) | 3.85 (t, 4 H); 4.20 (s, 4 H) 4.47 (t, 4 H); 7.25–7.36 (m, 12 H); 7.88 (d, 4 H) |
| A-3 | $(CH_2CH_2O)_2CH_2CH_2$, TEG | 72–74 | 72 | 67.9<br>(67.75) | 5.77<br>(5.69) | 10.73<br>(10.64) | 3.70 (s, 4 H); 3.81 (t, 4 H) 4.19 (s, 4 H); 4.66 (t, 4 H); 7.25–7.36 (m, 12 H); 7.91 (d, 4 H) |

[a] Calculated values given in parentheses.

**Table II**
**Yields and Elemental Analysis of the Polymers**



| polymer | R′ | R | yield, % | elemental anal.[a] C | H | N | S |
|---|---|---|---|---|---|---|---|
| 1, PTPD–$C_{10}$ | S–N=S=N–S | $(CH_2)_{10}$ | 89 | 57.25<br>(57.12) | 5.73<br>(5.59) | 5.27<br>(5.55) | 18.99<br>(19.06) |
| 2, PTPD–DEG | S–N=S=N–S | $CH_2CH_2OCH_2CH_2$ | 85 | 49.77<br>(49.53) | 3.61<br>(3.69) | 6.17<br>(6.41) | 21.58<br>(22.03) |
| 3, PTPD–TEG | S–N=S=N–S | $(CH_2CH_2O)_2CH_2CH_2$ | 81 | 50.15<br>(50.00) | 4.00<br>(4.20) | 5.38<br>(5.83) | 20.13<br>(20.02) |
| 4, PDBPD–TEG | S–N=S=N–S–Ph–S–N=S=N–S | $(CH_2CH_2O)_2CH_2CH_2$ | 98 | 45.81<br>(45.87) | 3.69<br>(3.55) | 8.15<br>(8.23) | 28.20<br>(28.25) |

[a] Calculated values given in parentheses.

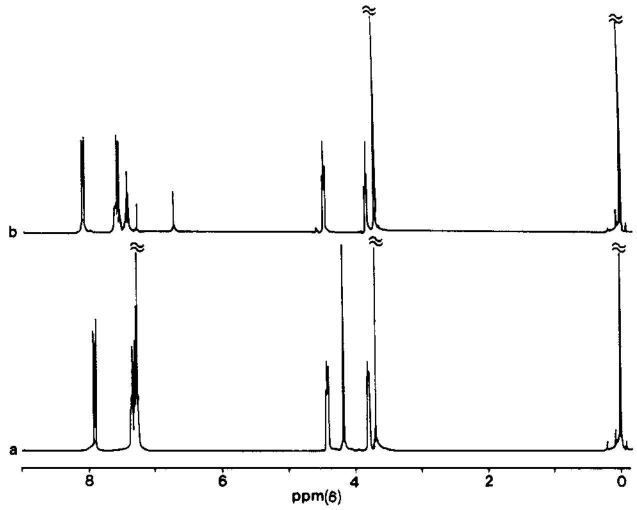


**Figure 1.** $^1$H NMR spectra of TEG diester (A-3) (a) before chlorinolysis and (b) after chlorinolysis.

Bromine was cryogenically distilled over $P_2O_5$ and degassed by freeze–pump–thaw cycles prior to use.

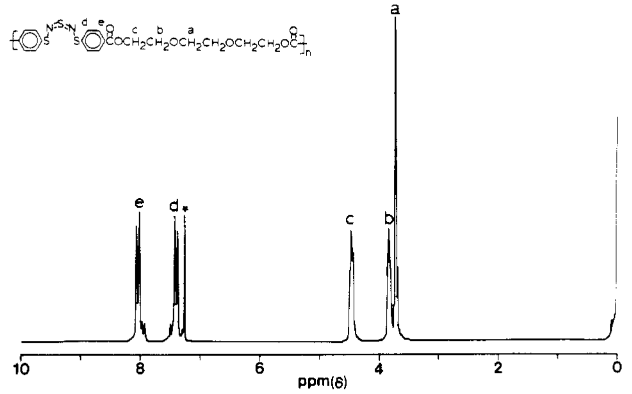
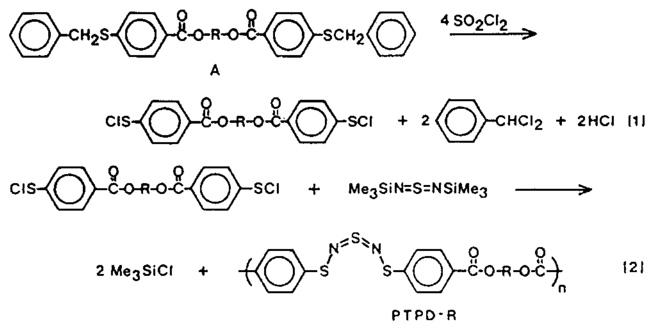


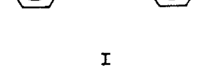
**Figure 2.** $^1$H NMR spectrum of PTPD–TEG polymer in $CDCl_3$. The peak marked with an asterisk is due to chloroform.

**Scheme I**

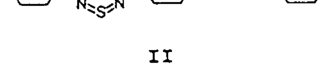


## Results and Discussion

The X-ray crystal structure[12] of *p,p′*-dichloro(phenylthio)phenyldithiazyl indicates that it has an elongated and rather planar structure (I, R = Cl). It is reasonable to assume the longer PDBPD unit also will tend to have a similar conformation around the thiazyl bonds (II). These phenylthiazyl compounds have been shown to form semiconducting complexes upon oxidation with bromine.[9] High polymers with the above kinds of repeat units were found to be insoluble.[5] In view of obtaining soluble conducting polymers, these moieties have been connected via flexible

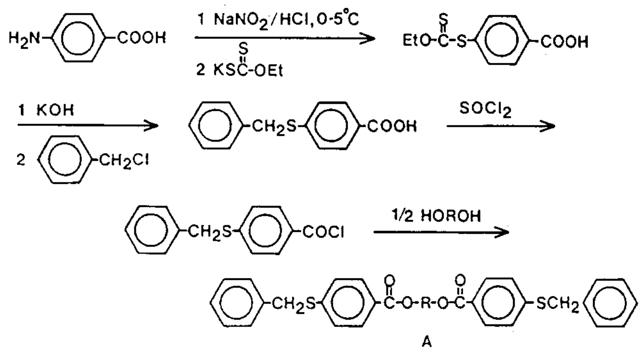


I



II

**Scheme II**



spacers. The synthetic scheme we used is shown in Scheme I. Although it has been observed that in the presence of electron-donating R groups (in structures I and II), these phenylthiazyl segments form stronger charge-transfer complexes upon doping with bromine,[9] a weakly electron withdrawing ester group was used as the functionality connecting the phenylthiazyl segments and the spacers for two reasons that originate from a purely synthetic standpoint.

First, sulfuryl chloride in addition to being a potent chlorinolysis agent also chlorinates the aromatic ring in the presence of electron-donating groups on it. Second, it is also known that aromatic sulfenyl chlorides with electron-donating groups promote a side reaction during the condensation reaction (eq 2), leading to the formation of a salt,[6] which would preclude the formation of a uniform high polymer. This side reaction, however, does not occur in the presence of electron-withdrawing ester groups.

The alternative, polycondensation of phenylthiazyl compounds having reactive functionality at the para positions with appropriately functionalized spacers, is ruled out due to the formidable synthetic constraint of preparing the former. One is also concerned about the possibility of cleavage of the thiazyl unit during the polycondensation reaction. Therefore, the reaction of the sulfenyl chloride with the (trimethylsilyl)imide (eq 2), being a rather mild reaction with $Me_3SiCl$ as the only byproduct, was considered the most viable route.

The synthesis of the benzyl-protected premonomer A was achieved fairly easily from *p*-aminobenzoic acid (Scheme II).

The elemental analysis and $^1H$ NMR data of the premonomers A are given in Table I.

Polymerization was carried out by in situ chlorinolysis of the benzyl protecting group in premonomer A, followed by its reaction with the bis((trimethylsilyl)imide). The chlorinolysis reaction (eq 1) required 2 mol of sulfuryl chloride per cleavage, leading to the formation of benzal chloride rather than the expected benzyl chloride.[13,14] The chlorinolysis of the benzyl sulfide occurs via a two-step process.[15,16] The first is the chlorination of the benzyl methylene followed by cleavage of the carbon–sulfur bond. The two-step process predominates in the absence of a strongly electron withdrawing group on the aromatic ring. The chlorinolysis reaction was conveniently followed by $^1H$ NMR (Figure 1). The complete disappearance of the benzyl methylene protons ($\delta$ 4.19) as a result of chlorinolysis was taken as an indication of completion of the reaction. The singlet at 6.72 ppm and multiplet in the aromatic region (7.3–7.4 ppm) is due to the presence of benzal chloride. A test reaction indicated that benzal chloride is inert under the polymerization conditions. The excess of sulfuryl chloride was removed by evacuation prior to condensation with the bis((trimethylsilyl)imide).

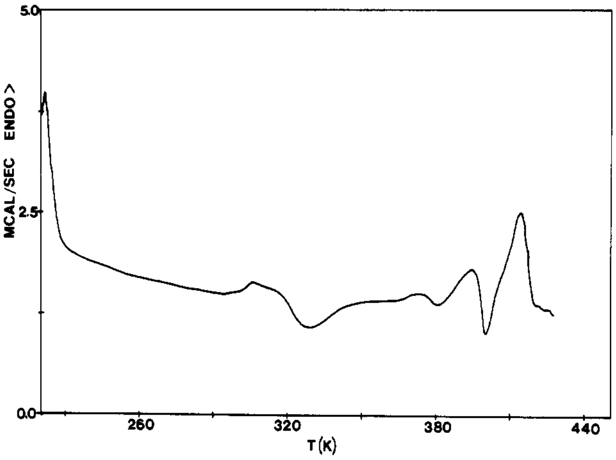


**Figure 3.** DSC thermogram of PTPD–TEG polymer that was first heated to melt, quenched to −40 °C, and further heated at a rate of 20 °C/min.

**Table III**
**Conductivities of Doped and Undoped Polymers**

| | $\sigma RT$, $(\Omega\ cm)^{-1}$ | | |
|---|---|---|---|
| polymer | undoped | $Br_2$ doped | doped and pumped[a] |
| PTPD–$C_{10}$ | $3.6 \times 10^{-12}$ | $6.3 \times 10^{-5}$ | $1.4 \times 10^{-8}$ |
| PTPD–DEG | $1.6 \times 10^{-11}$ | $5.8 \times 10^{-5}$ | $4.7 \times 10^{-10}$ |
| PTPD–TEG | $1.6 \times 10^{-11}$ | $3.9 \times 10^{-5}$ | $7.0 \times 10^{-8}$ |
| PDBPD–TEG | $3.8 \times 10^{-12}$ | $2.0 \times 10^{-3}$ | $6.8 \times 10^{-7}$ |

[a] The samples were subjected to a vacuum of $10^{-4}$ Torr for a period of 17–24 h, until the conductivity remained constant.

All the polymers, excluding PTPD–TEG, precipitated out during polymerization and were insoluble in common organic solvents. The PTPD–TEG polymer was soluble in chloroform, and films could be cast. The yields and elemental analysis of the various polymers are given in Table II. The molecular weight of the PTPD–TEG polymer was found to be 3890 by vapor pressure osmometry ($\overline{DP} \sim 8$); its $^1H$ NMR is given in Figure 2, along with the assignment of various peaks. The small peaks that appear in the aromatic region may be due to the end groups.

The differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data of the polymers indicated that all except the PTPD–TEG polymer had a melting point in the range of 160–175 °C, followed by decomposition. The TGA exhibited a stepwise decomposition as in the case of the model compounds, indicating decomposition of the thiazyl segment and loss of sulfur–nitrogen fragments. PTPD–TEG polymer on the other hand had a lower melting transition at around 151 °C followed by decomposition at 163–165 °C. Quenching the polymer melt to −40 °C prior to its decomposition followed by reheating gave the DSC thermogram shown in Figure 3. Repeating this experiment gave reproducible thermograms provided the polymer was not allowed to remain in the molten state for more than a few minutes, suggesting slow decomposition even at these temperatures.

All the polymers were insulators in the pristine form with conductivities ranging from $10^{-11}$ to $10^{-12}$ $(\Omega\ cm)^{-1}$. However, on doping with $Br_2$ vapor, their conductivities increased by several orders of magnitude, attaining values in the range $10^{-3}$–$10^{-5}$ $(\Omega\ cm)^{-1}$ (Table III). On subjection of the maximum doped samples to a dynamic vacuum ($10^{-4}$ Torr), their conductivities dropped by 3–4 orders of magnitude. All the polymers changed from a brick red color to black on doping. Visual observation of the cross section of the pellet after doping indicated that the doping was fairly uniform in spite of the weakly electron withdrawing effect of the ester group. The reversibility of doping indicated the existence of bromine that was weakly complexed with the thiazyl segment. The PDBPD–TEG polymer having a longer thiazyl segment exhibited a higher doped conductivity, both before and after pumping, as was the case with the model counterparts.[9]

The pristine polymers do not exhibit an electron paramagnetic resonance signal, but on oxidation with $Br_2$ they exhibit a signal with $g$ values ranging from 2.0069 to 2.011. These values compare fairly well with those of the model compounds, indicating that the same kind of radical cation postulated for the model systems[9] are formed in the case of the polymers.

The maximum doped conductivities of the polymers compare fairly well with those of the model systems. However, the doping is significantly more reversible in the case of the polymers. This suggests that the charge transfer in the case of the polymers may be weaker. It is also interesting that in spite of the significant dilution of the conducting segments with insulating spacers in the case of the polymers, their maximum doped conductivity is comparable to that of the model counterparts. This suggests that there is sufficient constructive interaction between the planar phenylthiazyl segments in the polymers to allow charge transport.

## Conclusion

Polymers that incorporate (phenylthio)phenyldithiazayl and phenylenedithiobis(phenyldithiazyl) segments along with flexible spacers have been synthesized. Although the PTPD–TEG polymer with a flexible triethylene glycol spacer was soluble and fusible, the PDBPD–TEG polymer was insoluble. This may be due to the stronger interaction between the longer thiazyl segments in the latter. The conducting properties of the model systems and polymers are similar, ranging from $10^{-3}$ to $10^{-5}$ $(\Omega\ \mathrm{cm})^{-1}$ upon doping with bromine.

**Registry No.** **1** (copolymer), 114719-89-0; **1** (SRU), 114719-85-6; **2** (copolymer), 114719-91-4; **2** (SRU), 114719-86-7; **3** (copolymer), 114719-93-6; **3** (SRU), 114719-87-8; **4** (copolymer), 114719-96-9; **4** (SRU), 114718-86-4; $C_{10}$, 114719-88-9; DEG, 114719-90-3; TEG, 114719-92-5; *p*-(benzylthio)benzoyl chloride, 114719-94-7; *p*-(benzylthio)benzoic acid, 22855-95-4; 1,10-decanediol, 112-47-0; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6; bromine, 7726-95-6.

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# [2.2]Paracyclophane End-Capped Polyquinoline Prepolymers: Synthesis, Processing, and Thermal Properties

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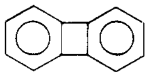
ABSTRACT: Flexible polyquinolines (DP = 11, 22) containing [2.2]paracyclophane end caps were prepared, using 4-acetyl[2.2]paracyclophane as the capping agent. Thermal analysis of the oligomers showed the [2.2]paracyclophane ring-opening exothermic maximum to be near 350 °C. The oligomers were melt-pressed at 350 °C under a 5000-lb load for various times, giving high-quality films which exhibited good Young's moduli. Film quality and moduli were higher for the DP = 22 oligomer. TGA analysis showed the films to be stable to about 550 °C in both air and argon. Oxidative aging at 320 °C for 100 h gave moderate weight losses, relative to various quinoline oligomers end capped with biphenylene.

## Introduction

In previous efforts to prepare readily processible polyquinoline prepolymers which, upon curing, would give highly cross-linked, thermally stable polymer networks, biphenylene (1) has been studied as an end-capping agent. Biphenylene end-capped oligomers provided cured films (and composites) possessing thermal stability that was not as good as might have been expected on the basis of a consideration of the types of structures generated by the thermolysis of biphenylene in an aromatic medium.[1,2] Attempts were made to increase the cross-linking densities obtainable from oligomers of a conveniently processible size by incorporation of reactive internal acetylene functionality,[3] which could react with the biphenylene units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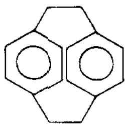
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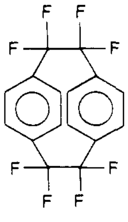

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