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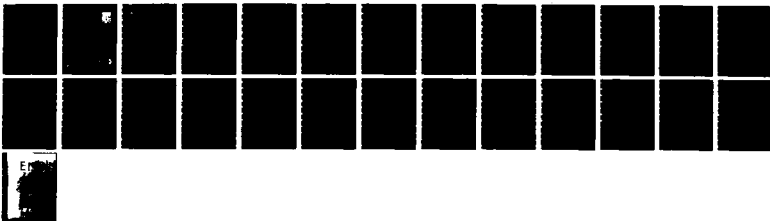
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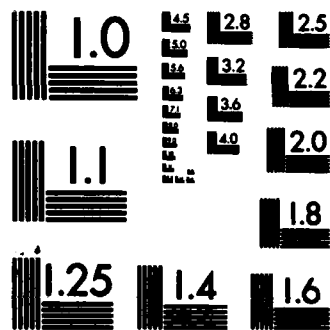
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SYNTHESIS AND PROPERTIES OF PHENYLATED AROMATIC
HETEROCYCLIC IMIDE AND THIAZOLE POLYMERS CONTAINING
PENDANT DIPHENYLEETHER AND DIPHENYLSULFIDE GROUPS

B. A. Reinhardt
F. E. Arnold
Polymer Branch
Nonmetallic Materials Division

October 1983

Final Report for Period January 1982 - August 1982

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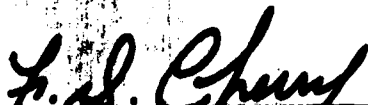


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FOREWORD

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

This report covers research conducted from January 1982 to August 1982.

The authors wish to thank Mr E. J. Soloski for the determination of glass transition temperatures and isothermal aging studies of the polymer, as well as, Dr E. G. Jones for mass spectra TGA analysis.



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SECTION I
INTRODUCTION

The utilization of pendant groups to promote solubility in common organic solvents was first demonstrated (Reference 1) with the aromatic polyphenylenes. Polymers prepared by the oxidation of benzene or dehydrogenation of polycyclohexadiene are crystalline materials and insoluble (References 2, 3). Phenylated polyphenylenes obtained from the Diels-Alder polymerization of bistetracyclones with *m*- or *p*-diethynylbenzene are amorphous materials and are soluble in toluene. The pendant phenyl groups serve to decrease crystallinity and promote solubility.

Aromatic heterocyclic polymer systems which contain pendant phenyl groups also exhibit unusual solubility properties. The polyphenylquinoxalines (Reference 4) exhibit good solubility in chloroform and *sym*-tetrachloroethane, whereas the polyquinoxalines (Reference 5) are soluble only in high boiling aprotic solvents such as hexamethylphosphoramide, dimethylformamide, and *n*-methylpyrrolidone. Other heterocyclic systems which contain pendant phenyl groups and are soluble in low boiling chlorinated hydrocarbon solvents, include the polyquinolines (Reference 6), polyimides (Reference 7), poly-*as*-triazines (Reference 8), and polyimidines (Reference 9).

Longer pendant groups which encompass diphenylether moieties have been incorporated into the quinoxaline and *as*-triazine polymer systems (Reference 10). No increase in solubility was described; however, a substantial decrease in glass transition temperatures was obtained from the diphenylether pendant when compared to the phenyl pendant polymer systems.

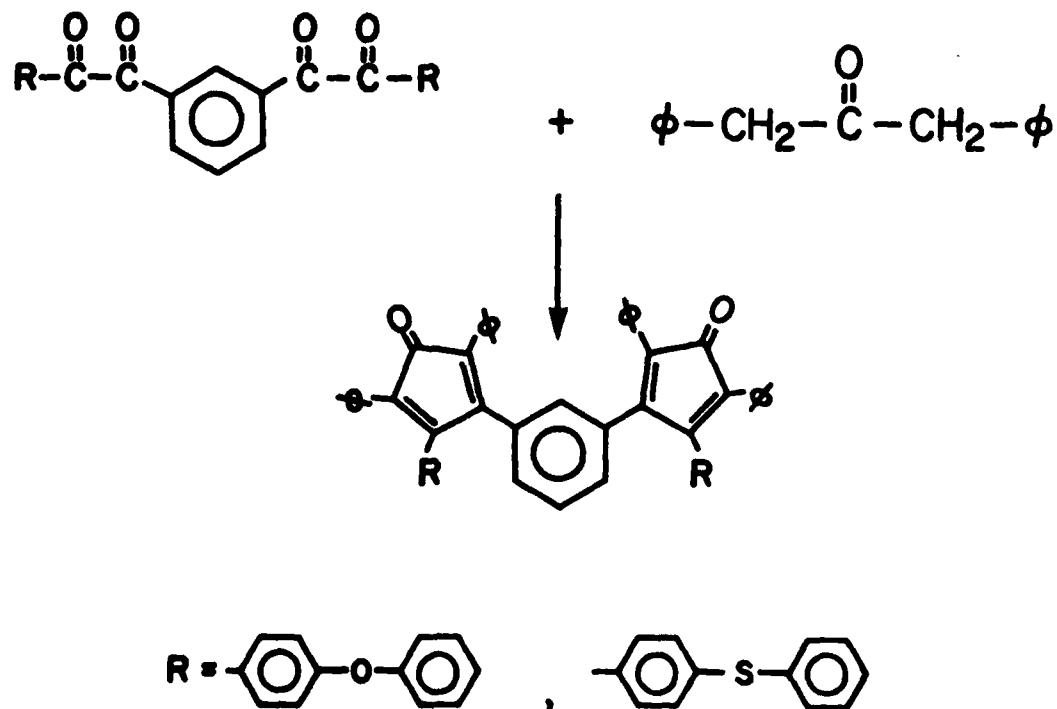
This work is concerned with the synthesis and characterization of several new polymers where diphenylether and diphenylsulfide pendants are in conjunction with pendant phenyl groups along heterocyclic polymer backbones. The objective of the work was to determine how the substituents affected the properties of the polymers.

SECTION II

DISCUSSION AND RESULTS

A series of new polymers were prepared in an effort to determine what effects a pendant diphenylether or diphenylsulfide group in conjunction with pendant phenyl groups would have on the physical properties of two different heterocyclic systems. The thiazole and imide heterocyclic ring structures were selected for this study from their good thermal oxidative stability and poor solubility properties. High molecular weight polybenzothiazoles are only soluble in strong mineral or organic acids and aromatic polyimides exhibit solubility only in high boiling aprotic solvents. The polymers were conveniently prepared by using the Diels-Alder polymerization of substituted biscyclopentadienone monomers with heterocyclic diacetylenes.

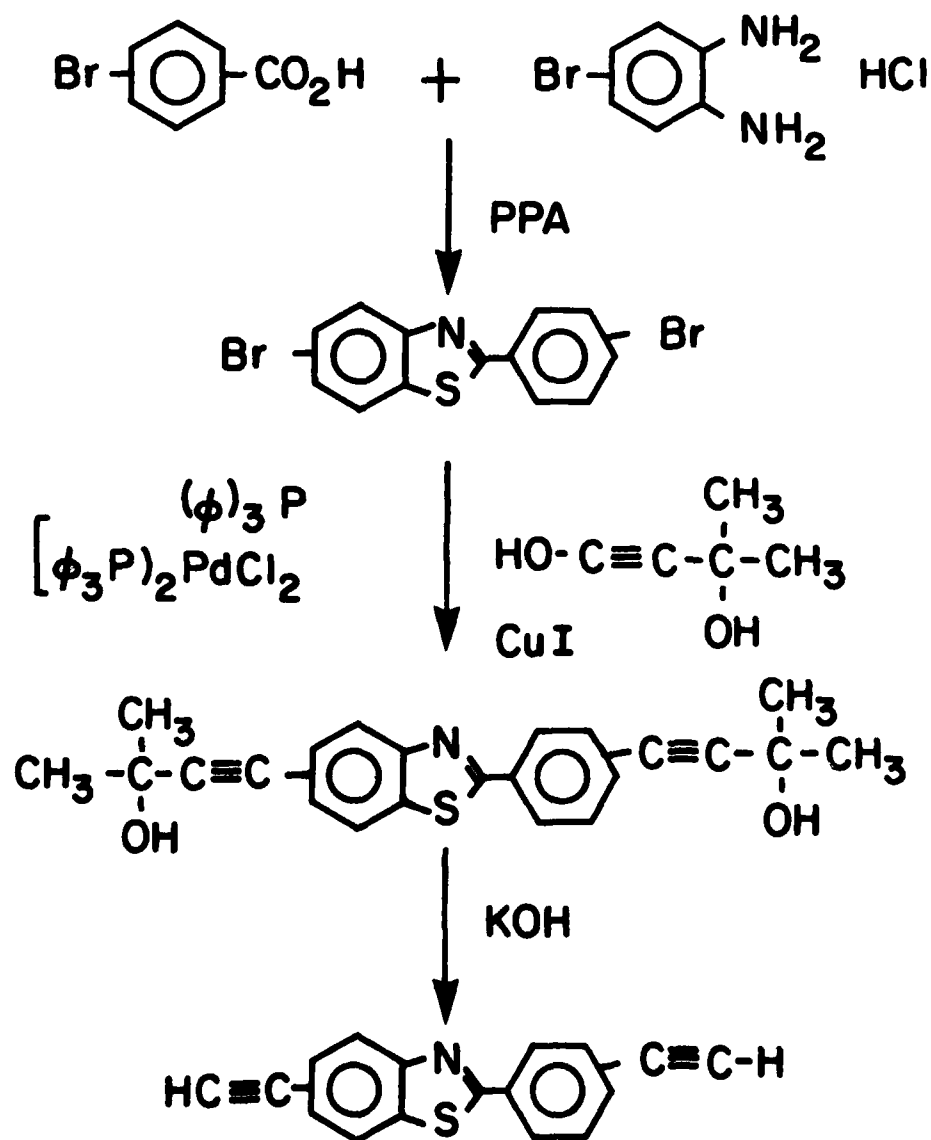
Introduction of the diphenylether and diphenylsulfide pendants was to incorporate such groups into biscyclopentadienone monomers. The synthesis of the monomers was carried out by the base catalyzed condensation of the appropriately substituted bis-tetraketone with 1,3-diphenylacetone. The resulting products were purified to monomer grade purity by column chromatography. This method provided a 2/1 ratio of phenyl to diphenylether pendants.



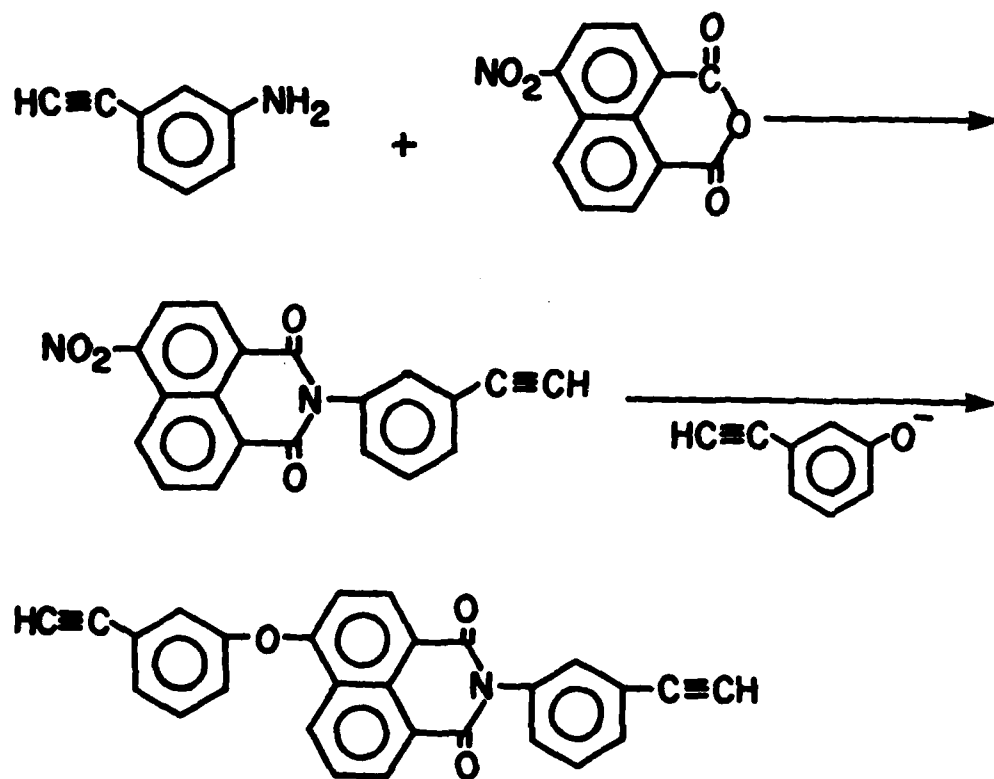
1. SYNTHESIS

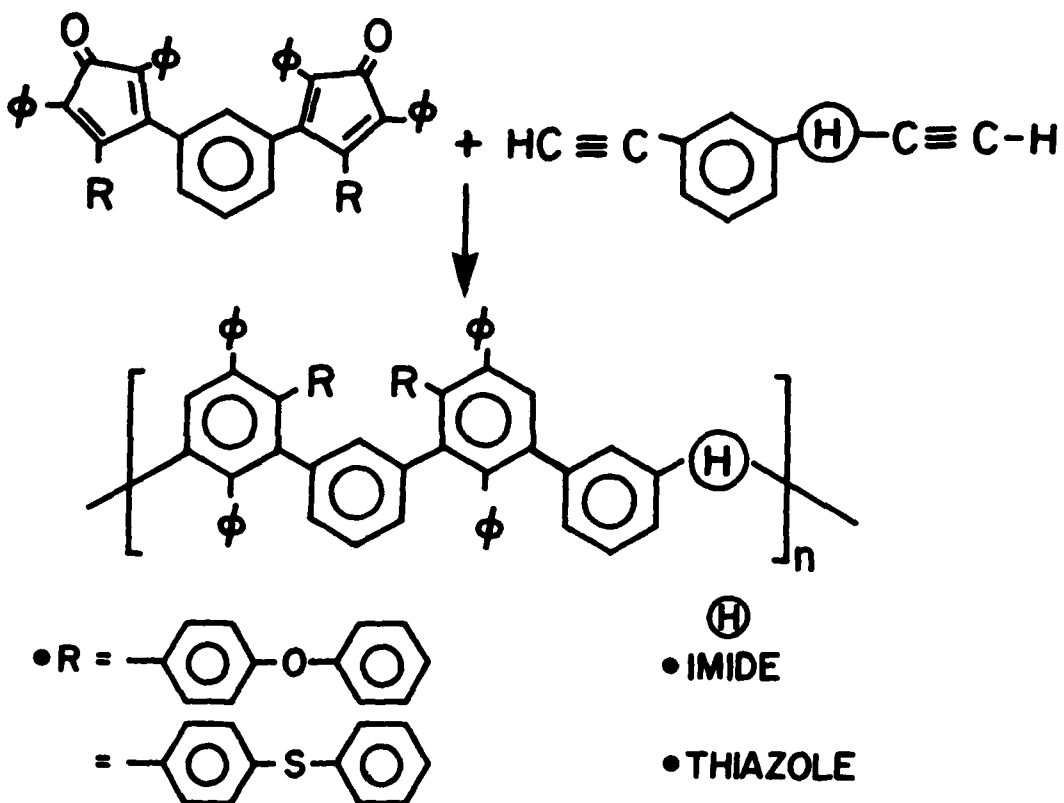
a. Monomers

Two isomeric acetylenic benzothiazole monomers, 2-(ethynylphenyl)-5-ethynylbenzothiazole and 2-(3-ethynylphenyl)-6-ethynylbenzothiazole were prepared (general reaction scheme shown below) according to a previously reported procedure (Reference 13). The synthesis of the benzothiazole heterocyclic structure was carried out by the condensation of *m*-bromobenzoic acid with isomeric bromo-substituted *o*-aminomercaptobenzenes in polyphosphoric acid (PPA). The bis-bromobenzothiazoles were converted to the acetylene systems by the reaction with 2-methyl-3-butyn-2-ol and subsequent displacement of acetone with base. The bromo displacement reaction utilized a catalyst composed of triphenylphosphine, (bis-triphenylphosphine)palladium dichloride and cuprous iodide.

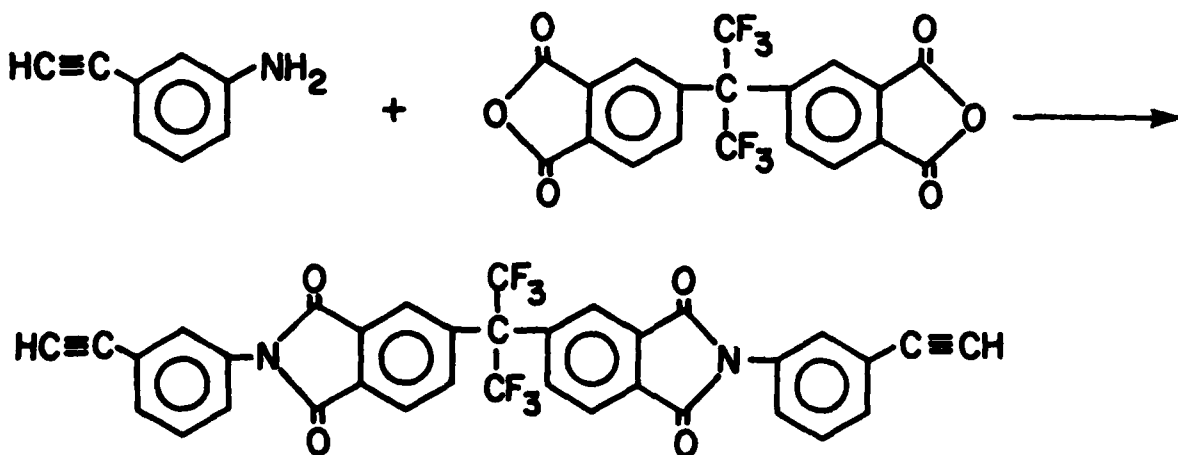


The second class of acetylenic monomers prepared for this study was those containing the imide heterocyclic ring system. Treatment of 4-nitronaphthalic anhydride with 3-aminophenylacetylene in glacial acetic acid gave 4-nitro-N-(3-ethynylphenyl)naphthalimide in 58% yield. As the imide, the nitro group becomes activated for nucleophilic displacement. Subsequent treatment with the sodium salt of 3-ethynylphenol in DMAC gave 4-(3-ethynylphenoxy)-N-(3-ethynylphenyl)naphthalimide in 36% yield after purification. In an analogous fashion, the five-membered 4-(3-ethynylphenoxy)-n-(3-ethynylphenyl)phthalimide was obtained in a 44% yield from 4-nitrophthalic anhydride.





Another diacetylene containing two imide rings was synthesized in an effort to provide a higher imide content along the polymer backbone. The condensation of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride with two moles of 3-aminophenylacetylene provided a 73% yield of 2,2-bis 4-(3-ethynylphenyl-n-phthalimide) hexafluoropropane after purification by column chromatography.



b. Polymers

The Diels-Alder polymerizations of the appropriately substituted bicyclopentadienone monomers with the various diacetylenic monomers were carried out in sealed tubes using 1,2,4-trichlorobenzene as the solvent. All polymerizations were conducted at 220°C for 38 hours followed by heating at 240°C for an additional 24 hours. The resulting polymers (Table 1) upon precipitation into methanol, reprecipitation from chloroform-methanol, freeze drying from benzene and drying at 150°C, gave intrinsic viscosities of 0.28 to 0.61 in DMAC or toluene. The general reaction scheme is shown below. Tough flexible films could be cast from 2% solutions of polymers in chloroform.

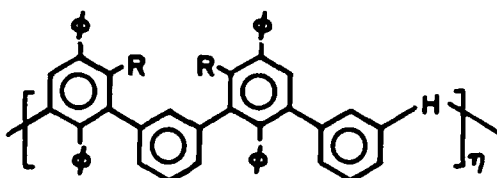
2. PROPERTIES

a. Polymer Solubility

Solubility properties of the new polymers were very interesting and quite different from any other heterocyclic polymer containing pendant phenyl groups. Most interesting, the polymers were found to be soluble in aromatic hydrocarbons such as benzene, toluene, and xylene. Concentrations as high as 10% could be obtained in benzene. This offered a convenient method by which the polymers could be purified for combustive analysis. As part of the purification procedure, the polymers were freeze-dried from benzene which provided a large surface area for combustion. The solubility increase is presumed to result from a modification of chain packing, which allows greater solvent-polymer interaction and increases the distance between adjacent chains. The polymers were also soluble in chloroform, sym-tetrachloroethane and chlorinated aromatic hydrocarbons, as well as, aprotic solvents such as dimethylformamide, dimethylacetamide and n-methylpyrrolidone.

In an effort to obtain a direct comparison of the solubility properties for an analogous phenylated system the bis-imide acetylene monomer was polymerized with 3,3'-(1,3-phenylene)bis[2,4,5-trephenylcyclopentadienone]. The polymer gelled from trichlorobenzene when allowed to cool to room temperature and exhibited only partial solubility in refluxing toluene.

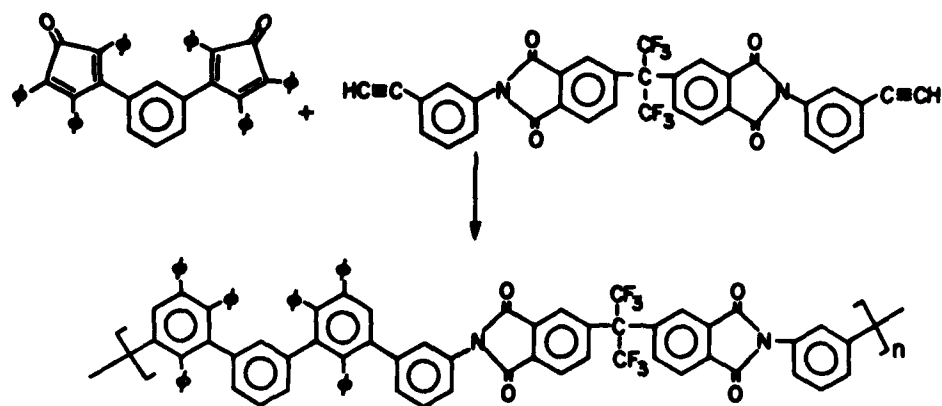
TABLE 1
POLYMER STRUCTURES AND PROPERTIES



H	R	$[\eta]$	T_g^a	ISOTHERMAL AGING % ^b
		0.30	282	50
" "		0.35	255	80
		0.45	269	55
" "		0.28	266	35
		0.61	238	80
" "		0.57	233	89
		0.54	273	44
" "		0.48	264	29
		0.55	240	86

a = GLASS TRANSITION TEMP. AS DETERMINED BY DSC ▲ RATE 10°/ MIN

b = % WEIGHT RETAINED (ISOTHERMAL AGING IN AIR 650F FOR 200 HR)



b. Thermal Mechanical Behavior

The glass transition temperatures (T_g 's) reported (Table 1) were determined by differential scanning calorimetry (DSC) at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen. In all cases, the extrapolated onset of the DSC baseline shift was taken as the T_g . T_g 's for the polymers were in the range of 230 - 280°C which are generally lower than normal for aromatic imide and thiazole polymer backbones having the same degree of flexibility. Lower T_g 's for these polymers is apparently due to both a decrease molecular symmetry and intermolecular associations. Molecular symmetry is decreased since various isomeric structures are formed via the Diels-Alder polymerization. The decrease in intermolecular association (induced dipole-dipole interactions) is due to the lower heterocyclic content per repeat unit. The polyimide containing only pendant phenyl groups exhibited a T_g of 292°C , whereas substitution of two phenyl pendants with diphenylether groups lowers the T_g to 240°C . It is interesting to note that the same equivalent lowering of the T_g has been shown to occur for the as-triazine and quinoxaline polymer systems (Reference 10).

c. Thermal Evaluation

The thermal properties of the polymers were evaluated using isothermal aging and thermogravimetric-mass spectral analysis. Isothermal aging studies were carried out with an automatic multisample apparatus, which

allowed weight loss to be obtained in the aging environment. Freeze-dried samples were examined in circulating air at 343°C (650°F). The weight retention data after 200 hours exposure time is summarized in Table 1. Of the two heterocyclic systems studied, the more stable seems to be the five-membered polyimides. The instability of the six-membered imide polymers is likely associated with the exposed peri proton which has been shown in our laboratory to be susceptible to oxidative degradation.

Thermogravimetric-mass spectral analysis conducted under vacuum on a phenylphenoxy pendant benzothiazole polyphenylene showed that degradation commences at 500°C and continues to the highest temperature studied, 850°C. There are basically two regions of volatile product evolution, 600° and 750°C. The major volatile products released at 600°C include, benzene, phenol, biphenyl, and phenylether with the highest molecular weight product identified as triphenyl. The higher temperature cracking processes (750°C) release methane, carbon monoxide, and hydrogen.

SECTION III
EXPERIMENTAL

1. MONOMERS

4-(3-Ethynylphenoxy)-N-(3-Ethynylphenyl)phthalimide. The monomer was prepared in two steps from 4-nitrophthalic anhydride as previously described (Reference 11), mp 159-160°C.

4-(3-Ethynylphenoxy)-N-(3-Ethynylphenyl)Naphthalimide. The monomer was prepared in two steps from 4-nitronaphthalic anhydride as previously described (Reference 11), mp 200-202°C.

2,2-Bis[4-(3-Ethynylphenyl)-n-phthalimide]hexafluoropropane. The bisimide was prepared from the reaction of 2,2-bis(3',4'-dicarboxyphenyl)-hexafluoropropane dianhydride with two moles of 3-aminophenylacetylene in glacial acetic acid. Purification by chromatographing on silica gel provided the material with a mp of 185-186°C, reported in Reference 12, mp 180-186°C.

2-(3-Ethynylphenyl)-5-Ethynylbenzothiazole mp 150-151°C.

2-(3-Ethynylphenyl)-6-Ethynylbenzothiazole mp 186-187°C. The above benzothiazole monomers were prepared by the condensation of m-bromobenzoic acid with isomeric bromo-substituted o-aminomercaptobenzenes.

3,3'-(1,3-phenylene)Bis[2,5-diphenyl-4-p-phenyloxyphenyl-cyclopentadienone]

A stirred suspension of 10g (19 mmole) of m-bis(p'-phenoxyphenyl-glyoxylyl)benzene and 8.4g (40 mmole) of 1,3-diphenyl acetone in 250ml of 95% ethanol was heated to reflux. To the mixture was added 20ml of a potassium hydroxide solution (0.6g KOH in 20ml H₂O) in two portions over a period of five minutes. The reaction mixture immediately turned purple with the first addition of base. Heating was continued for 40 minutes during which time a purple solid began to precipitate. The reaction mixture was then cooled in ice, filtered, and air-dried.

The crude product was purified by chromatography on a dry silica gel column using a (9/1) toluene/ether mixture as the eluant to give 15.2g (82.7%) of purified product mp 205-206°C. (IR Spectrum Figure 1).

Analysis Calcd for $C_{64}H_{42}O_4$: C,87.85;H,4.84

Found: C,87.50;H,5.10

3,3'-(1,3-phenylene)bis 2,5-diphenyl-4-p-phenylthiophenyl-cyclopentadienone

A solution of 10g (17.9 mmole) of *m*-bis(*p*'-thiophenoxyphenylglyoxylyl)-benzene and 10.5g (50 mmole) of 1,3-diphenyl acetone in 225ml of 95% ethanol was heated to reflux. To the reaction mixture at reflux was added a solution of 0.6g (5 mmole) of potassium hydroxide in 25ml of water. Upon addition of base the solution turned brown in color. Reflux was continued for a total of 30 minutes at which time the reaction mixture was allowed to cool to room temperature, filtered, and air-dried to give 16g (98.8%) of crude product. The material was purified by column chromatography on dry silica gel using toluene as the eluant mp 202-203°C. (IR Spectrum Figure 2).

Analysis Calcd for $C_{64}H_{42}S_2O_2$: C,84.73;H,4.66

Found: C,84.25;H,4.58

2. POLYMERS

The following are representative of the procedures used in the preparation of polymers:

Poly[(1,3-dioxo-2,5-isoindolinediyl)oxy[4',6''-bis(*p*-phenoxyphenyl)-2',2''',5'5'''-tetraphenyl-*m*-quinquephenyl-3,3'''-ylene]].

In a 25ml polymerization tube were placed 0.8399g (0.96 mmole) of 3,3'-(1,3-phenylene)bis[2,5'-diphenyl-4-p-phenyloxyphenyl cyclopentadienone], 0.3448g (0.96 mmole) of 4-(3-ethynylphenoxy)-*N*-(3-ethynylphenyl)-phthalimide and 7ml of 1,2,4-trichlorobenzene. The contents of the tube were degassed by several freeze-thaw cycles at liquid nitrogen

temperatures and then sealed in vacuo. Approximately 50ml of 1,2,4-trichlorobenzene was added to a Parr pressure reactor, the polymerization tube was placed inside, and the reactor heated at 220°C for 18 hours. The temperature was then increased to 240°C and heating continued for an additional 24 hours. After the reaction had cooled to room temperature, the tube was opened, the contents diluted with 30ml of chloroform and precipitated into 1ℓ of rapidly stirring methanol. The fluffy white polymer was filtered, reprecipitated from chloroform into absolute methanol, and freeze-dried from benzene. After drying at 120°C (0.4 mm Hg) overnight, the polymer had an intrinsic viscosity at 30°C of 0.61 in DMAC. (IR Spectrum Figure 3).

Analysis Calcd for (C₈₆H₅₅NO₅): C,87.36; H,4.69; N,1.18

Found: C,87.16; H,4.49; N,1.31

Poly[2,5-benzothiazole-diyl[6,6"-bis(p-phenoxyphenyl)-2,2",5,5"-tetraphenyl-m-quaterphenyl-3,3"'-ylene]].

A mixture of 3.368g (3.85 mmole) of 3,3'-(1,3-phenylene)bis-(2,5-diphenyl-4-p-phenoxyphenyl cyclopentadienone) and 1.0g (3.85 mmole) of 2-(3-ethynylphenyl)-5-ethynylbenzothiazole (mp 169°C) was placed in a 20ml polymerization tube with 7ml of 1,2,4-trichlorobenzene. The contents of the tube were degassed by several freeze-thaw cycles at liquid nitrogen temperature, then sealed in vacuo. The sealed polymerization tube was placed in a Parr Bomb pressure reactor and heated to 225°C for 42 hours. The tube was cooled to room temperature. After opening, 8ml of chloroform was added to the viscous solution in the tube. The contents were poured into methanol to precipitate out the polymer, which was recovered by filtration, yielding 4.0g (96%). The polymer exhibited an intrinsic viscosity of 0.30 as determined in N,N-dimethylacetamide at 30°C. (IR Spectrum Figure 4).

Analysis Calcd for (C₇₉H₅₁NSO₂): C,87.99; H,4.77

Found: C,87.70; H,4.58

Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)oxy[2',2'',-5',5''-tetraphenyl-4',6''-bis[p-(phenylthio)phenyl]-m-quinquephenyl-3,3''-ylene]].

A solution of 0.493g (0.54 mmole) of 3,3'-(1,3-phenylene)bis[2,5-diphenyl-4-p-phenylthiophenyl cyclopentadienone] and 0.224g (0.54 mmole) of 5-(3-ethynylphenoxy)-N-(3-ethynylphenyl)naphthalimide in 7ml of 1,2,4-trichlorobenzene was degassed under vacuum by several freeze-thaw cycles and sealed in a tube. The tube containing the reaction mixture was heated at 220°C for 18 hours and the temperature then raised to 240°C for 24 additional hours. The tube was cooled to room temperature, frozen in liquid nitrogen, and opened. When the contents had warmed to room temperature, the solution was diluted with 30ml of chloroform, and precipitated into 1ℓ of methanol. The off-white polymer was reprecipitated from chloroform to give a quantitative yield of polymer with an intrinsic viscosity in DPMAC of 0.48. (IR Spectrum Figure 5).

Analysis Calcd for (C₉₀H₅₇NO₃S₂): C,85.48; N,4.54

Found: C,84.89; N,4.23

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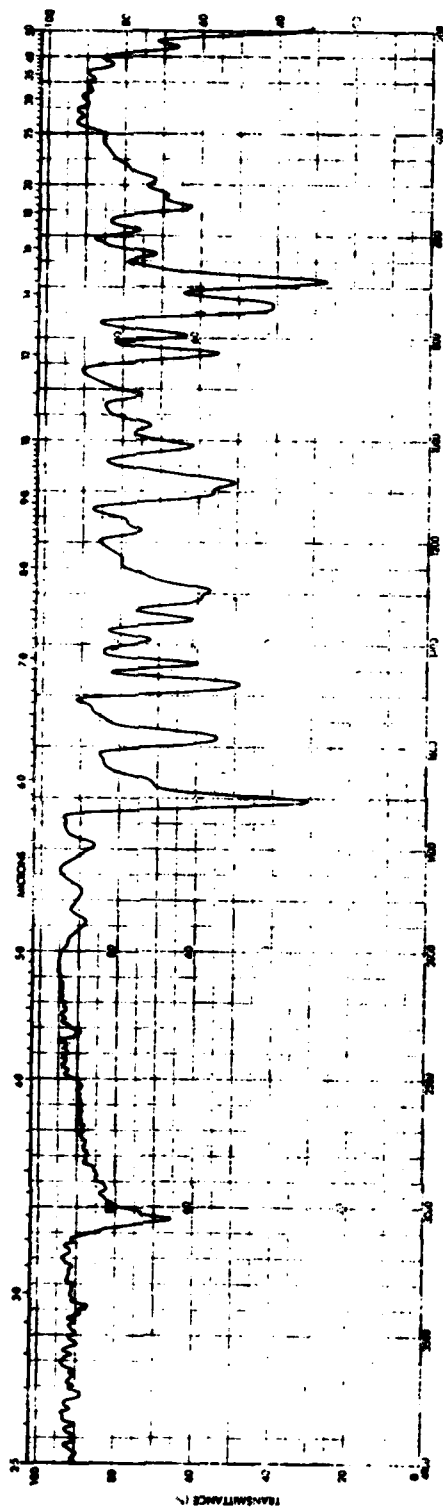


Figure 1. Infrared Spectrum of 3,3'-(1,3-Phenylene)bis[2,5-diphenyl-4-p-phenyloxyphenyl cyclopentadienone]

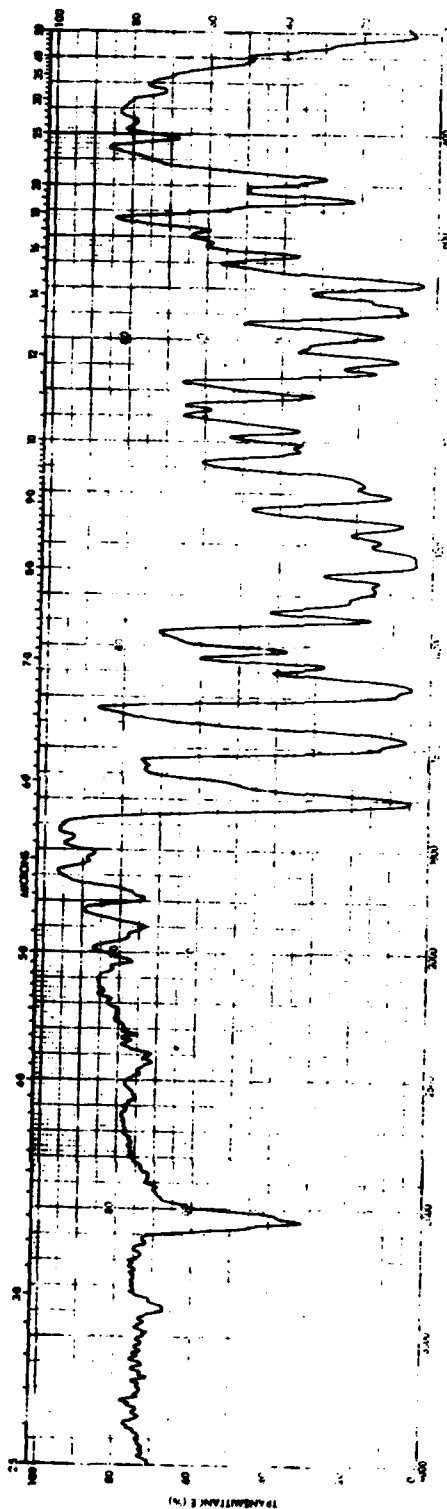


Figure 2. Infrared Spectrum of 3,3'-(1,3-Phenylene)bis[2,5-diphenyl-4-p-phenylthiophenyl cyclopentadienone]

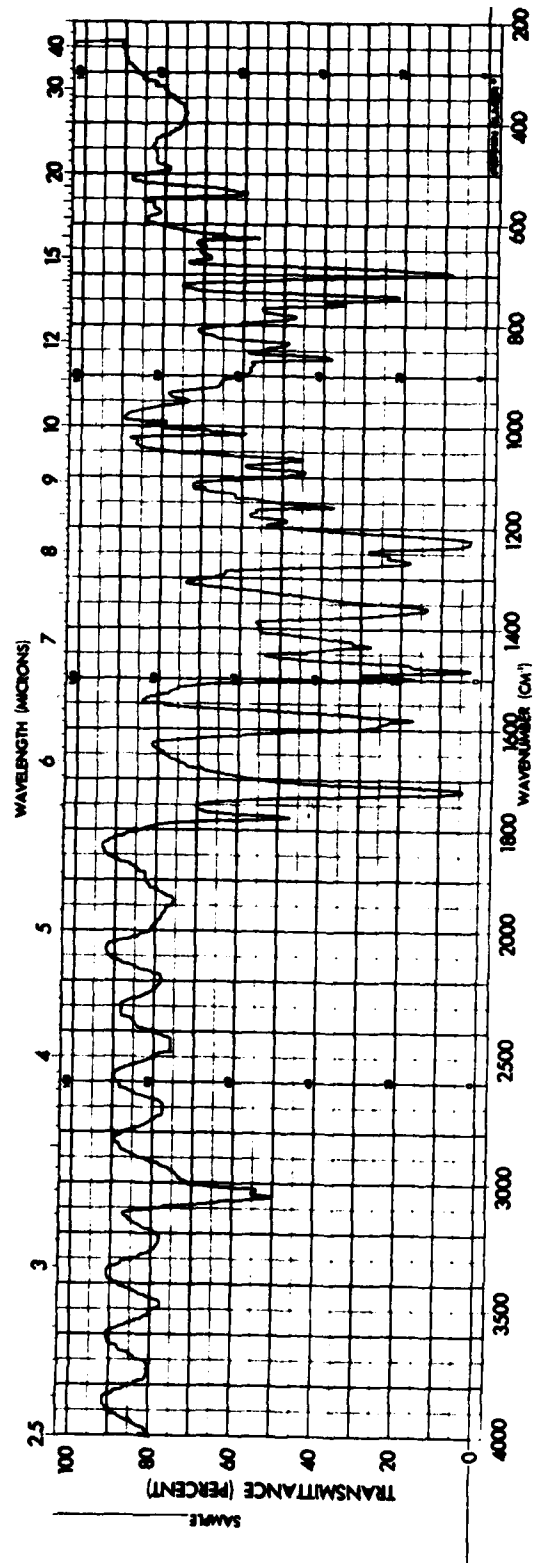


Figure 3. Infrared Spectrum of Poly[(1,3-dioxo-2,5-isoindolinediyl)-
[oxy 4',6''-bis[(p-phenoxyphenyl)-2',2''',5',5''',-tetraphenyl-
m-quinquephenyl-3,3''-ylene]]

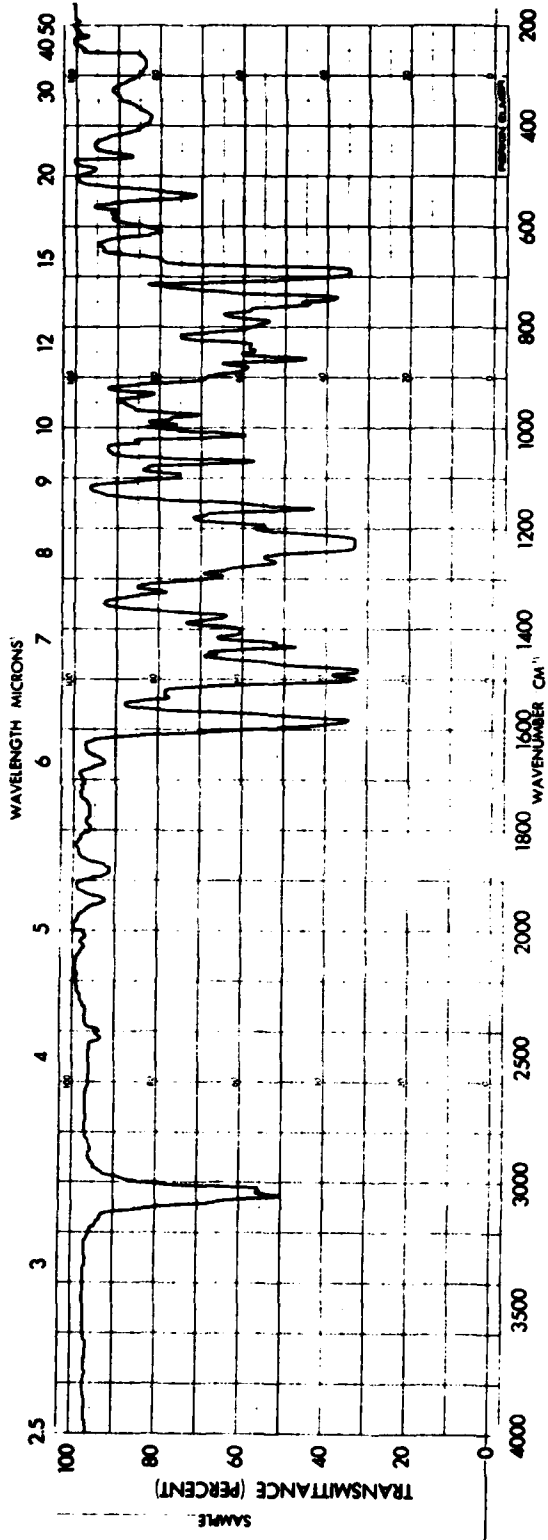


Figure 4. Infrared Spectrum of Poly[2,5-benzothiazoliediy] [6,6'-bis-(p-phenoxyphenyl)-2,2',5,5'-tetraphenyl-m-quaterphenyl-3,3'-ylene]

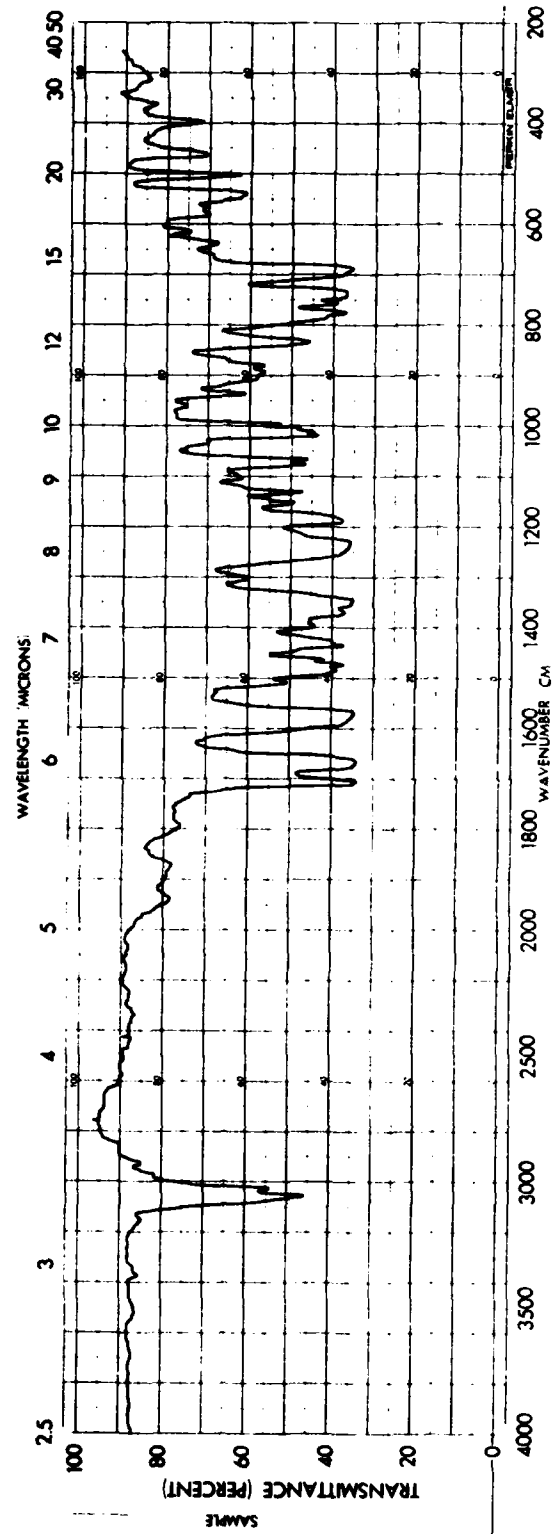


Figure 5. Infrared Spectrum of Poly[(1,3-dioxo-1H-benz[de]isoquinoline-2,6(3H)-diyl)oxy[2',2'',5',5''-tetraphenyl-4',6''-bis[p-(phenylthio)phenyl]-m-quinquephenyl-3,3''-ylene]]

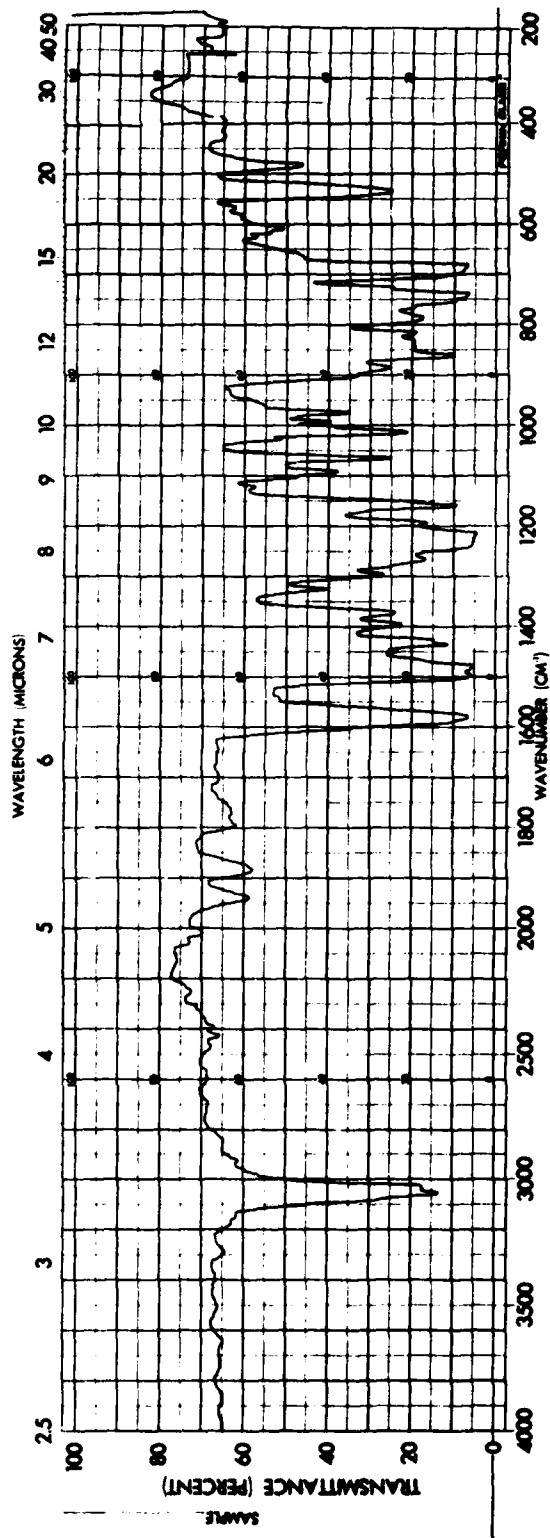


Figure 6. Infrared Spectrum of Poly[2,6-benzothiazole]diyl[6,6"-bis-(p-phenoxyphenyl)-2,2",5,5"-tetraphenyl-m-quatraphenyl-3,3"-ylene]

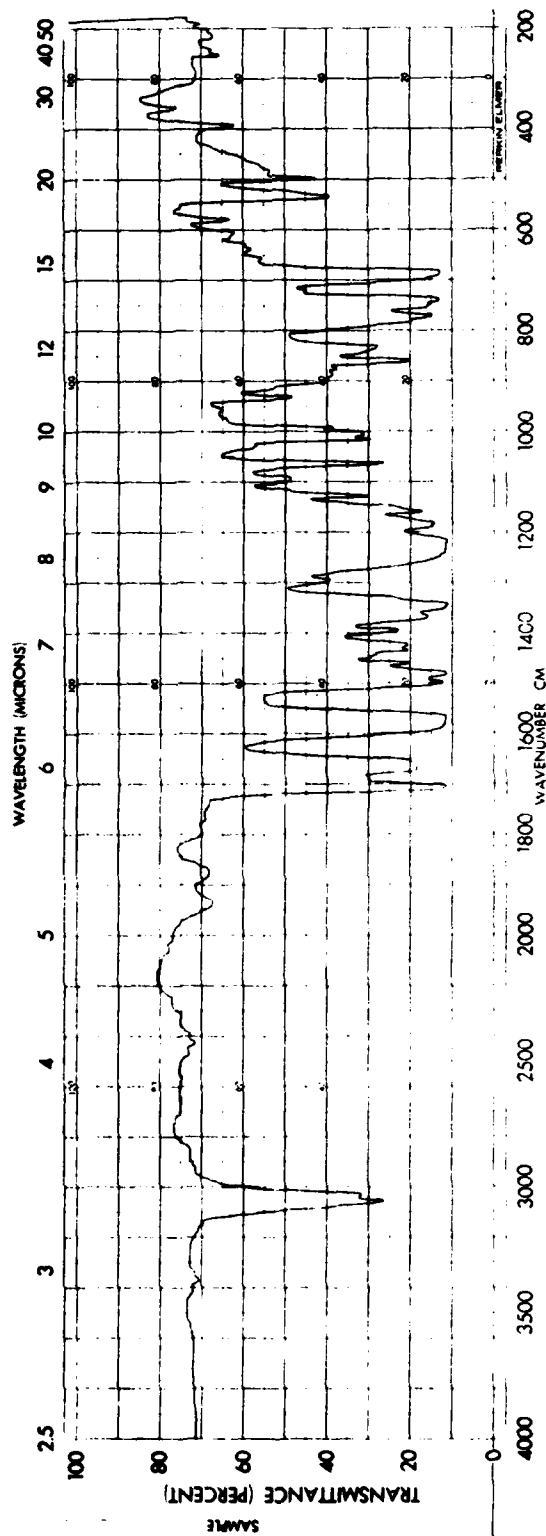


Figure 7. Infrared Spectrum of Poly[(1,3-dioxo-2,5-isoindolinediyl)-(trifluoro-1-(trifluoromethyl)ethylidene)(1,3-dioxo-5,2-isoindolinediyl)[2',2'',5',5''-tetraphenyl-4',6''-bis-[p-(phenylthio)phenyl]-3,3'''-ylene]]

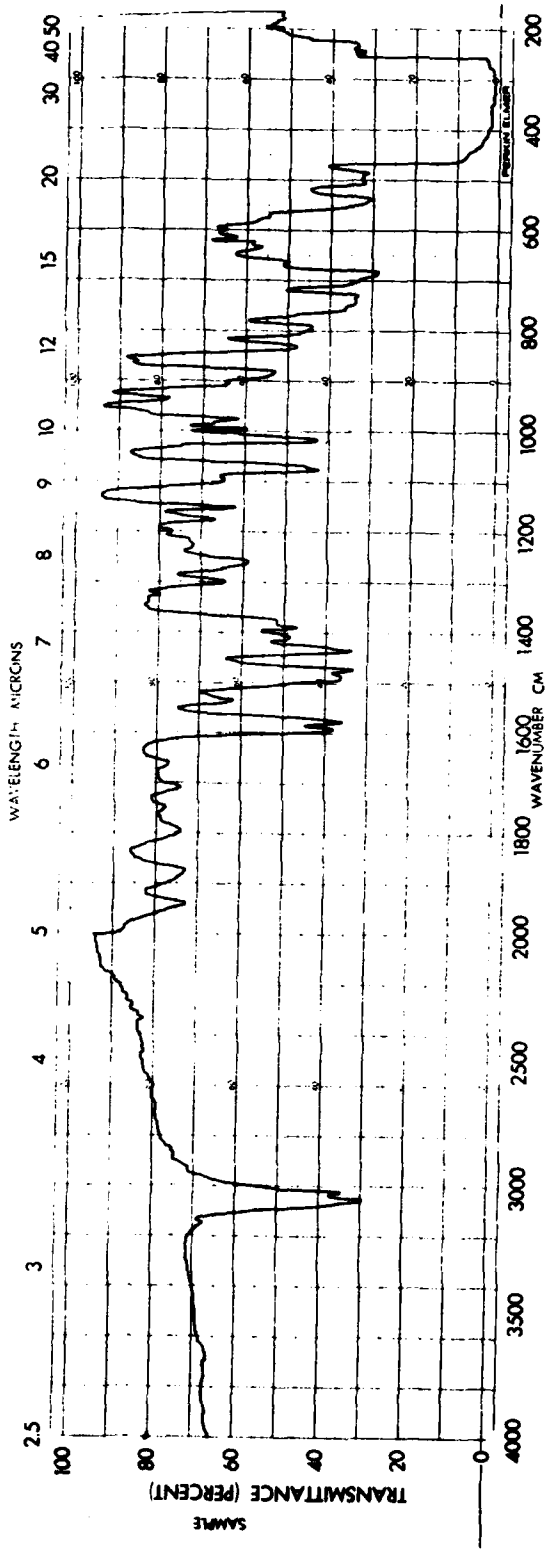


Figure 8. Infrared Spectrum of Poly[2,5-benzothiazole-diyl[6,6"-bis-(p-phenylthiophenyl)-2,2",5,5"-tetraphenyl-m-quatraphenyl-3,3"-ylene]]

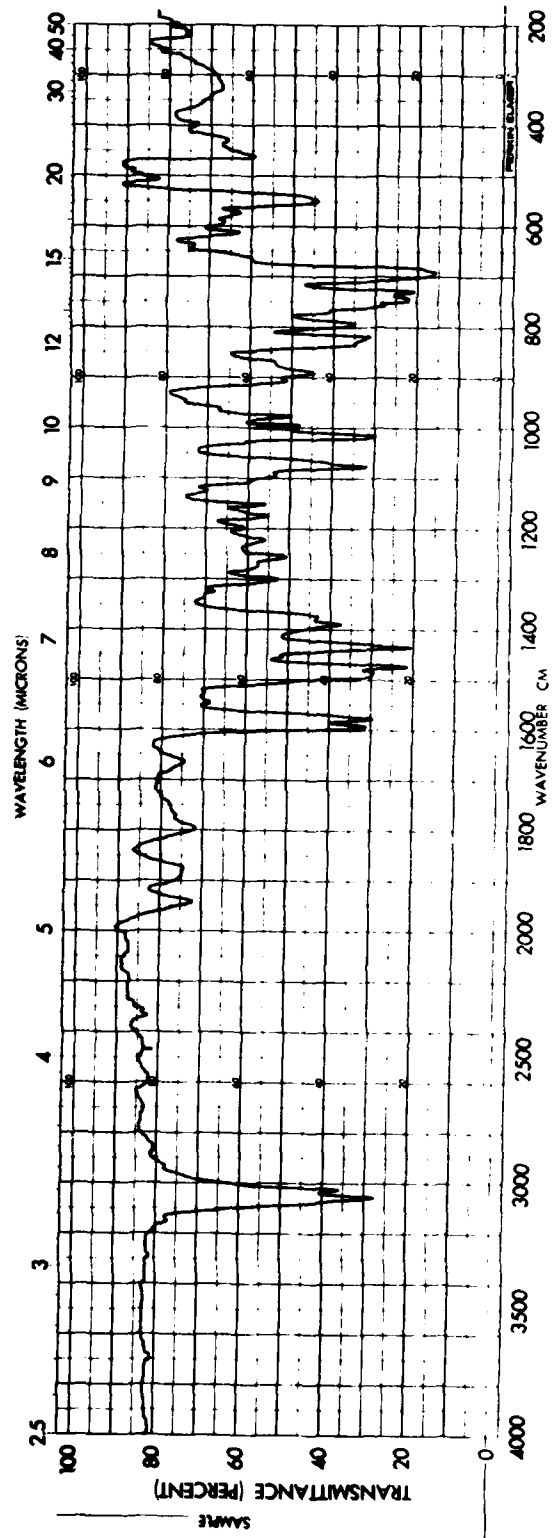


Figure 9. Infrared Spectrum of Poly[2,6-benzothiazole-diyl[6,6"-bis-(p-phenylthiophenyl)-2,2",5,5"-tetraphenyl-m-quatraphenyl-3,3"-ylene]]

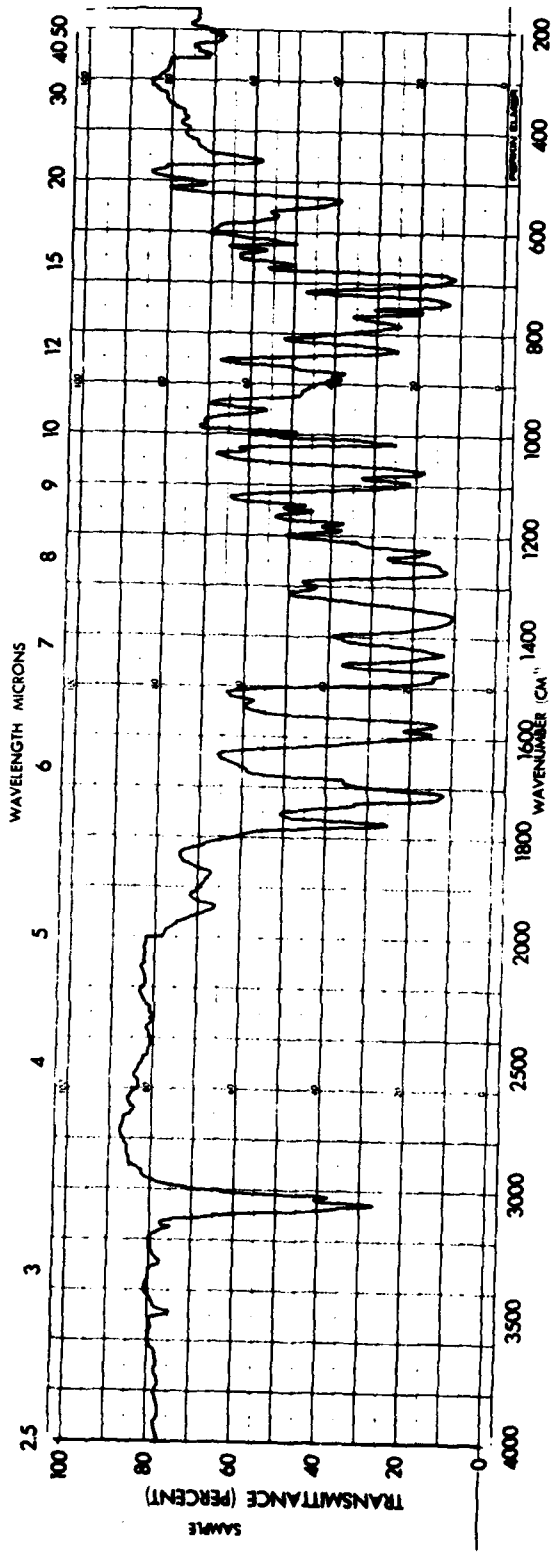


Figure 10. Infrared Spectrum of Poly[1,3-dioxo-2,5-isoindolinediyl]-oxy[4,6''-bis(p-phenylthiophenyl)-2',2'',5',5'',-tetraphenyl-m-quinquephenyl-3,3''-ylene]

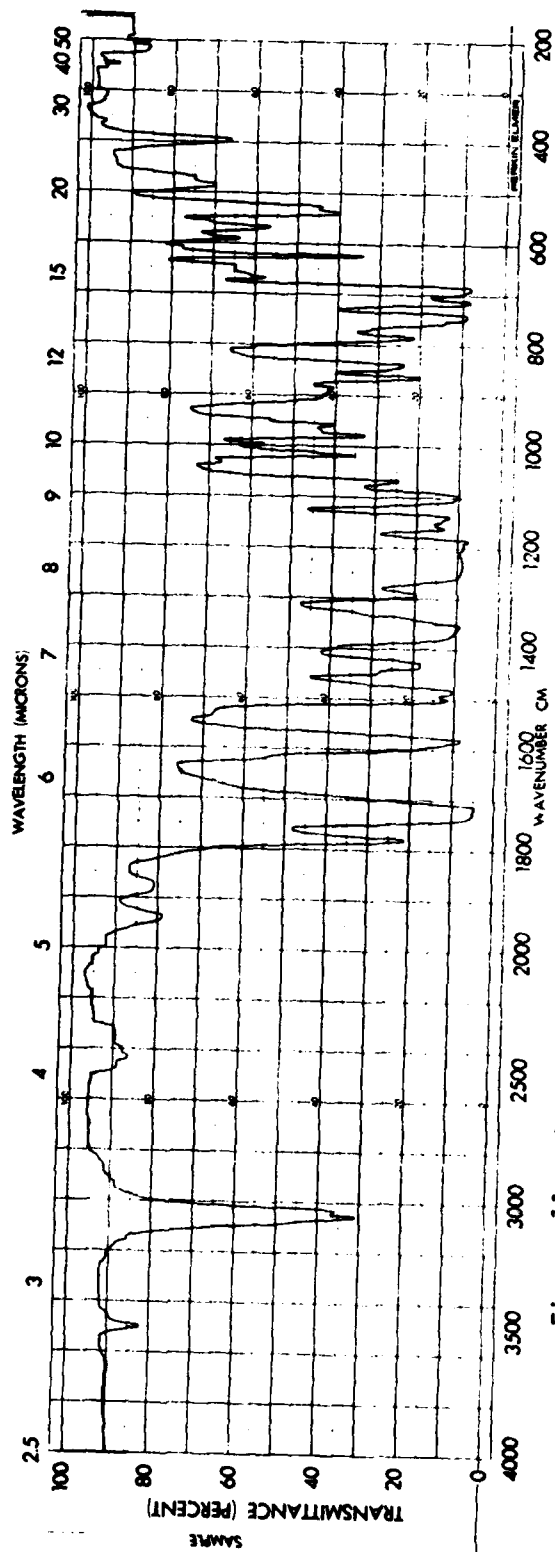


Figure 11. Infrared Spectrum of Poly[(1,3-dioxo-2,5-isoindolinediyl)-[trifluoro-1-(trifluoromethyl)ethylidene](1,3-dioxo-5,2-isoindolinediyl)[2',2'',5',5'',-tetraphenyl-4',6''-bis-[p-phenoxyphenyl]-m-quinquephenyl-3,3''-ylene]]

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