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FABRICATION AND EVALUATION OF NEW RESINS

VOLUME I: SYNTHESIS OF PARA-ORDERED AROMATIC POLYMERS

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April 1978

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Air Force Wright Aeronautical Laboratories
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

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F. E. ARNOLD
Project Monitor

FOR THE COMMANDER

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Poly(diphenylbenzobisimidazoles)
Polybenzobisoxazoles
Thermally Stable Polymers

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

Four potential aromatic rodlike polymer systems were screened for potential use in ordered polymer films. High molecular weight polybenzobisthiazoles were prepared from a new monomer, 2,5-diaminodithiohydroquinone dihydrochloride. The isomeric polybenzobisthiazoles from 4,6-diaminodithioresorcinol dihydrochloride were obtained with low molecular weights due to monomer instability. Poly(3,5-diphenylbenzobisimidazoles) were obtained by a two step procedure.

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FOREWORD

This annual report presents the results of the past 10 months from an effort to synthesize para-oriented aromatic polymers for the Air Force Materials Laboratory, Wright-Patterson AFB, under Contract F33615-76-C-5109, Project No. 2419/04, "New Polymers to Provide the Basis for Non-Metallic Materials for Aircraft and Missile Structures." This work was administered under the direction of Dr. F. E. Arnold (AFML/MBP), Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio.

This report, covering work from 1 April 1977 to 30 January 1978, was prepared by James F. Wolfe. The technical assistance of B. Loo, D. W. Penhale, W. Tally, C. Coon, D. V. Son, M. Geigel, and P. Trescony is gratefully acknowledged.

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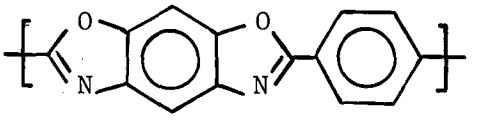
SECTION I

INTRODUCTION

The work described in this report is aimed at the synthesis of new aromatic polymer systems which are composed entirely of linear aromatic ring structures. The main goal of the research is to prepare a polymer with the anisotropic solution properties of the linear polybenzobisoxazole (PBO)[1], but with improved solubility, higher molecular weight, and increased thermooxidative stability.



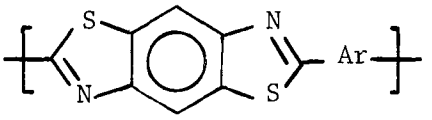
PBO

PBO is soluble to the extent that anisotropic solutions are formed only in strongly corrosive acids, such as methanesulfonic and chlorosulfonic acids. The ideal candidate polymer would be soluble to this extent in common organic solvents, thereby facilitating fabrication.

Although measurement of accurate molecular weights of PBO is difficult due to solution aggregation, the maximum number average molecular weight attained is only on the order of 10,000.[2] In order to develop high strength in the oriented film or fiber this molecular weight may have to be increased.

Although the thermooxidative stability of PBO is excellent, there is room for improvement. In circulating air, PBO loses only 15% of its weight at 316°C after 200 hr, but loses 80% at 371°C after the same time period.

Four polymer systems were investigated in attempts to improve on these properties of PBO. These polymers all possessed the linear 5-6-5 fused ring system of PBO but with various combinations and positions of the hetero atoms. The repeat unit of the polymers also contained only para-aromatic units in order to maintain the linearity of the PBO system. The four polymers are shown in Figure 1. The required monomers for these four systems are shown in Figure 2.



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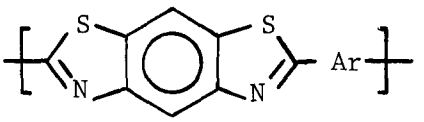

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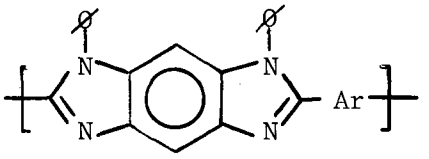

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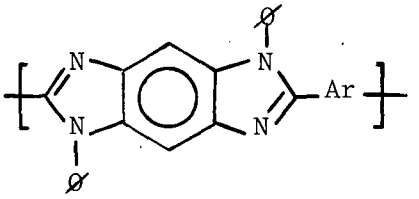

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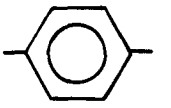
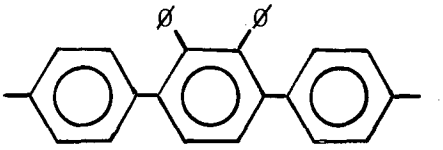
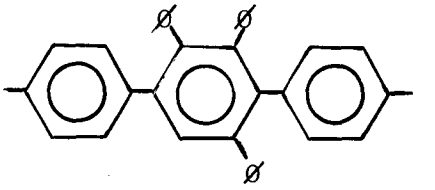
a. Ar= 

b. Ar= 

c. Ar= 

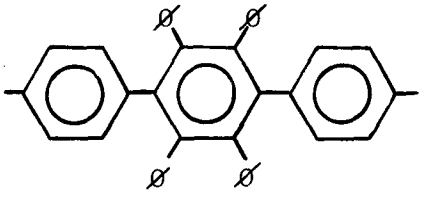
d. Ar= 

Figure 1

Para-ordered Polybenzobisthiazoles, 1 and 2

and Poly(N,N'-diphenylbenzobisimidazoles), 3 and 4

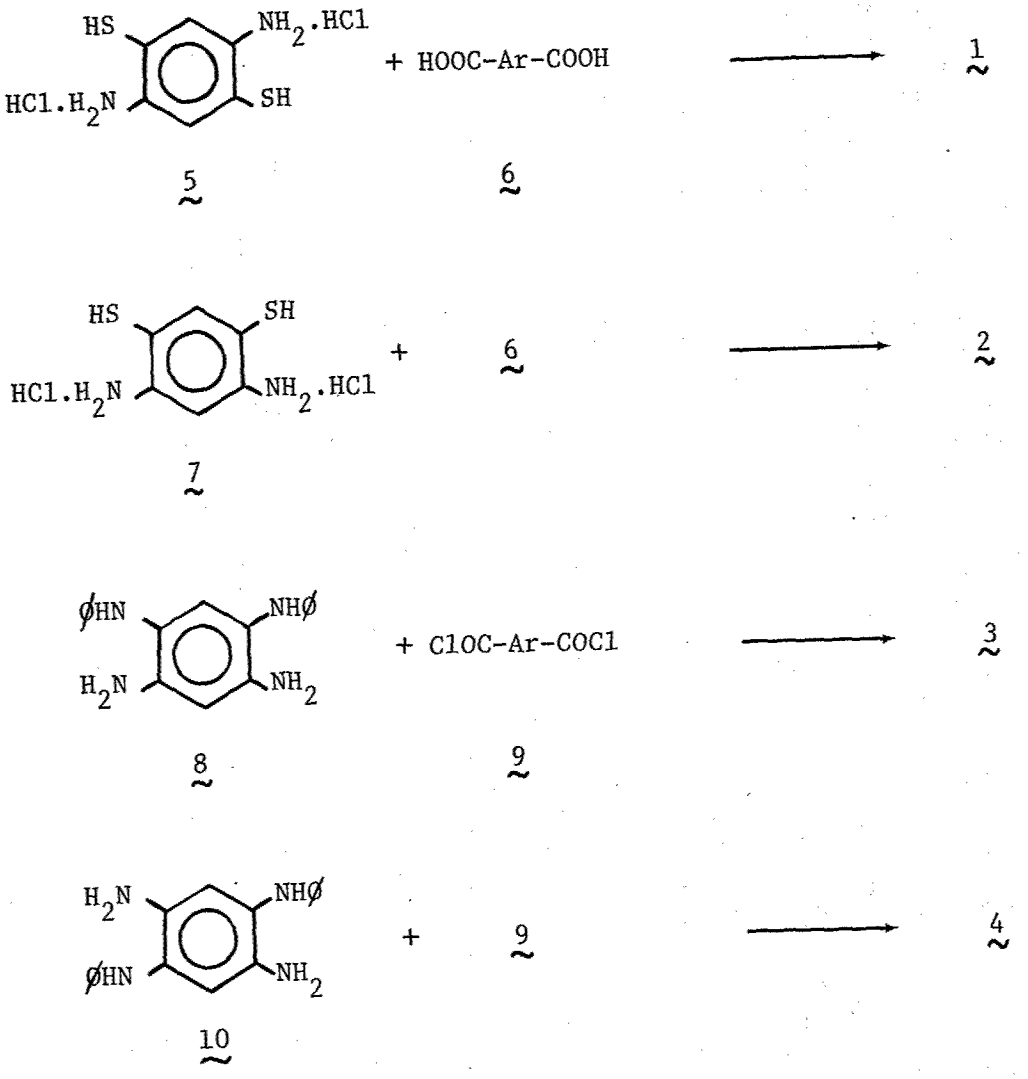


Figure 2

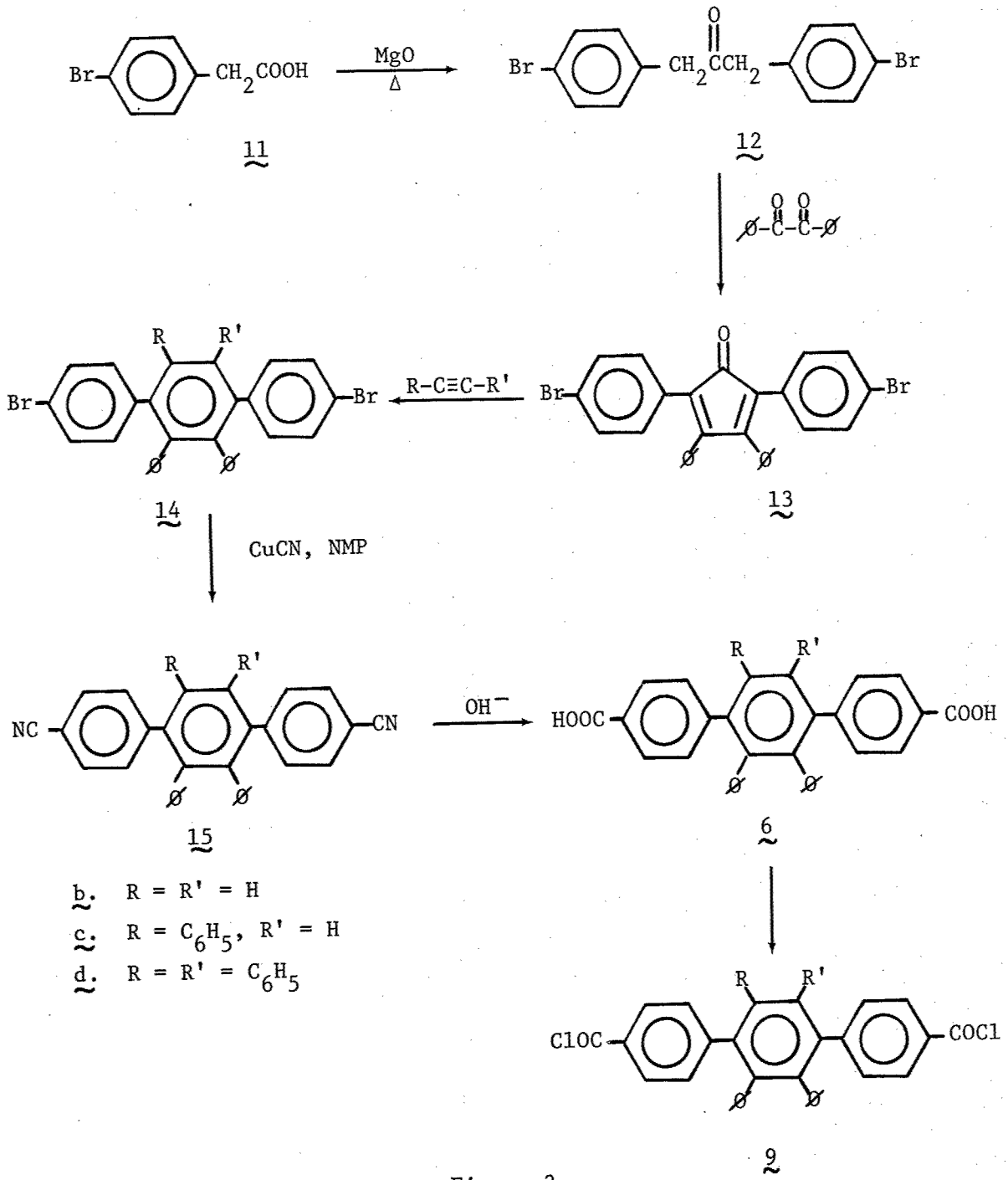
Monomers Required for Polymers 1, 2, 3, and 4

SECTION II

RESULTS AND DISCUSSION

A. Synthesis of Para-Aromatic Diacids (6) and Diacid Dichlorides (9).

Terephthalic acid, (6a) (99+%, Matheson), was purchased and used as received in the preparation of polymers 1a and 2a. Terephthaloyl chloride, (9a) (99+%, Matheson), was used as received for the preparation of polymer 3. An outline of the synthesis of phenylated diacids 6b-d and phenylated diacid dichlorides 9b-d is presented in Figure 3.



b. R = R' = H

c. R = C_6H_5, R' = H

d. R = R' = C_6H_5

Figure 3

Synthesis of Para-Aromatic Diacids 6b-d and Diacid Dichlorides 9b-d

The phenylated diacids 6b-d were prepared by the following procedure. An intimate mixture of p-bromophenylacetic acid (11) and magnesium oxide was heated to 340°C under reduced pressure and 1,3-bis(p-bromophenyl)-2-propanone (12) was collected in 70% yield by distillation. Condensation of 12 with benzil in ethanolic potassium hydroxide gave 2,5-bis(p-bromophenyl)-3,4-diphenyl-cyclopentadienone 13 in 93% yield. The Diels-Alder reactions of 13 with norbornadiene at 110°, phenylacetylene at 139° and diphenylacetylene at 305° gave the 4,4"-dibromophenylated-p-terphenyl compounds 14b, 14c, and 14d, respectively in yields of >90%. These reactions are easily monitored visually by the loss of the dark purple color of 13. The nucleophilic displacement of the bromo groups by cuprous cyanide in dry N-methyl-2-pyrrolidinone (NMP) gave the dicyano intermediates 15b-d in yields of 65-85%. The use of dry NMP raises the yield and reduces the amount of hydrolyzed cyano groups and thus facilitates purification of 15, which in turn raises the purity of 6. Hydrolysis of 15b-d in alkaline ethylene glycol gave the di-potassium salt of monomers 6b-d, which crystallized directly from the hydrolysis mixture. Acidification of the purified salt gave monomers 6b-d in yields of 60-94%.

The diacid monomers 6b-d are white solids that are thermally stable up to their melting points of 425°, 425° and 450°, respectively, as shown by differential scanning calorimetry.

The diacid dichloride monomers 9 were prepared by heating a mixture of 6 and thionyl chloride at the reflux temperature until a clear solution resulted. Removal of the excess thionyl chloride and recrystallization from benzene gave 9b-d as white crystalline solids.

Detailed experimental procedures and analytical results are presented in the Experimental Section.

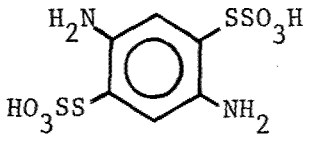
B. Polymers Containing the Benzo[1,2-d:4,5-d']bisthiazole Moiety.

1. Summary of Results

A new monomer, 2,5-diaminodithiohydroquinone dihydrochloride (5), was prepared in excellent yield and purity. The model compound, 2,6-diphenylbenzo[1,2-d:4,5-d']bisthiazole (16a), was prepared in 99% yield by the reaction of 5 with benzoic acid in polyphosphoric acid (PPA). High molecular weight, golden polymers 1a resulted from the reaction of 5 with terephthalic acid in PPA. Polymer 1a was readily soluble in methanesulfonic acid (MSA). Phenylated polymers 1b-d were prepared by the reaction of 5 with diacids 6b-d in PPA/sulfolane mixtures. Polymers 1b-d were either insoluble or difficultly soluble in MSA or MSA/chlorosulfonic acid mixtures.

2. Synthesis of 2,5-Diaminodithiohydroquinone Dihydrochloride (5).

The synthesis of 2,5-diaminodithiohydroquinone dihydrochloride 5 was reported by Osman and Mohamed[3] using zinc and hydrochloric acid to reduce 1,4-diaminobenzene-2,5-dithiosulfonic acid (17),



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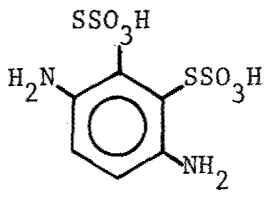
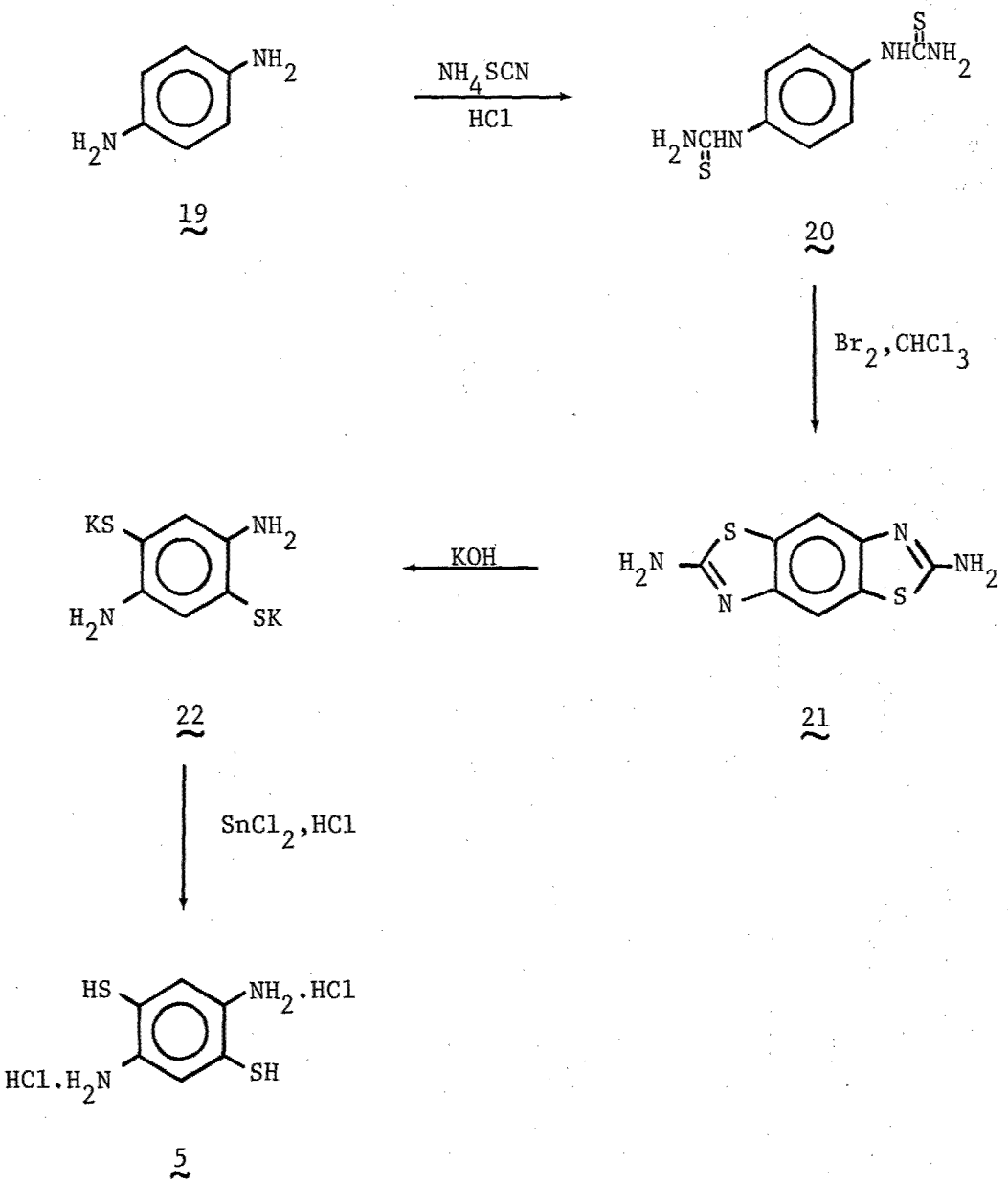


18

which had been prepared by the method of Green and Perkin.[4] However, Landquist[5] and Solar et. al.[6] have shown that the material prepared by Green and Perkin was in fact the 1,4-diamino-2,3-dithiosulfonic acid 18. We therefore present the first synthesis of 5 as shown in Figure 4.

When we treated p-phenylenediamine (19) with ammonium thiocyanate in dilute hydrochloric acid, we obtained the bisthiourea 20 in an 84.7% yield. Compound 20 was cyclized in chloroform by treatment with bromine[5] to give 2,6-diaminobenzo[1,2-d:4,5-d']bisthiazole (21) in a 31.2% yield after two recrystallizations. Hydrolysis of 21 in concentrated aqueous potassium hydroxide under a nitrogen blanket gave the dipotassium salt 22 as long white needles. Compound 22 was then transferred to a nitrogen-filled glove bag, filtered, and stirred with deaerated water containing 10% concentrated hydrochloric acid and 5% stannous chloride. When the bright yellow slurry was heated almost to boiling and an equal volume of concentrated hydrochloric acid was added, the solid dissolved and a white precipitate formed. The mixture was cooled and the precipitate was collected by filtration. The product was washed with ether, and then placed in vials in a drying pistol. The monomer was dried at room temperature overnight under reduced pressure (0.05 torr). The product was isolated in 81% yield. Elemental analysis showed that the monomer had the desired molecular formula. Infrared analysis (see Experimental Section) showed absorptions between 2700 and 3000 and at 2590 cm^{-1} as indication of the aminohydrochloride group and at 2460 cm^{-1} for the mercapto group.

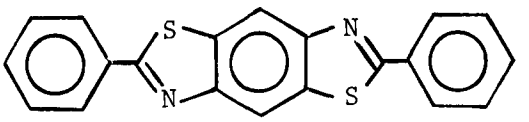


19 20 21 22 5

Figure 4

Synthesis of 2,5-Diaminodithiohydroquinone Dihydrochloride (5)

3. Synthesis of 2,6-Diphenylbenzo[1,2-d:4,5-d']bisthiazole (16a).



16a

The model compound, 2,6-diphenylbenzo[1,2-d:4,5-d']bisthiazole (16a) was obtained in 98.9% yield. This high yield is a good indication of excellent purity of monomer 5. Monomer 5 was heated with 20% excess benzoic acid in PPA to a maximum temperature of 200°. Sulfolane was added to the dehydrochlorinating mixture in an attempt to reduce the amount of foaming; however, mixing of the PPA and sulfolane did not occur readily at room temperature. The model compound was soluble throughout the reaction. Recrystallization from toluene afforded colorless crystals. See the Experimental Section for analytical data.

4. Synthesis of Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4-phenylene}(1a)

Monomer 5 was weighed by taking the vial in which 5 had been dried, weighing it, pouring approximately the desired amount into the nitrogen swept reaction vessel, and reweighing the vial to determine the exact amount of 5 added. Freshly prepared PPA was added to give concentrations of 5 in the range of 2-4%. After dehydrochlorination was complete a stoichiometric amount of terephthalic acid was added as a powder. PPA was then added to bring the volume of the slurry up to the level of highest foaming and to ensure that all terephthalic acid powder was incorporated into the slurry. This addition of PPA gave polymer concentrations of 1.5-3.1%. The

polymerizations were then heated, as described in the Experimental Section to a maximum temperature of 175°C. At termination of the reaction the polymerizations were too viscous to stir. The solutions in PPA were amber, with purple fluorescence. The polymers were precipitated into methanol after dilution with methanesulfonic acid (MSA). Extraction with methanol and then drying in air gave material which was readily soluble in MSA. The green fluorescent solution was then diluted to 0.3% and was filtered through a coarse sintered-glass funnel into a large volume of stirred methanol. The color of the polymer was reddish rust, which gradually turned to gold as the water washes became neutral. The polymers were freeze-dried from benzene to give a fluffy golden material. The infrared spectra of the polymers showed a slight absorption near 1700 cm^{-1} which may be due to carboxyl end groups.

Intrinsic viscosities in MSA at 30°C of 5.1 and 9.5 dL/g were obtained. These values represent a significant increase over the values obtained for PBO, which had intrinsic viscosities in the range of 2-3.7 dL/g, and may be a result of one or more of the following factors.

- Actual higher molecular weight, due to higher conversion in the polycondensation.
- Less aggregation in solution of Polymer 1a than of PBO.
- Greater rodlike character of Polymer 1a, due to symmetry of "para"-benzobisthiazole unit.
- Higher purity of the dihydrochloride monomer.

5. Synthesis of Phenylated Poly[benzo(1,2-d:4,5-d')bisthiazoles] (1b-d).

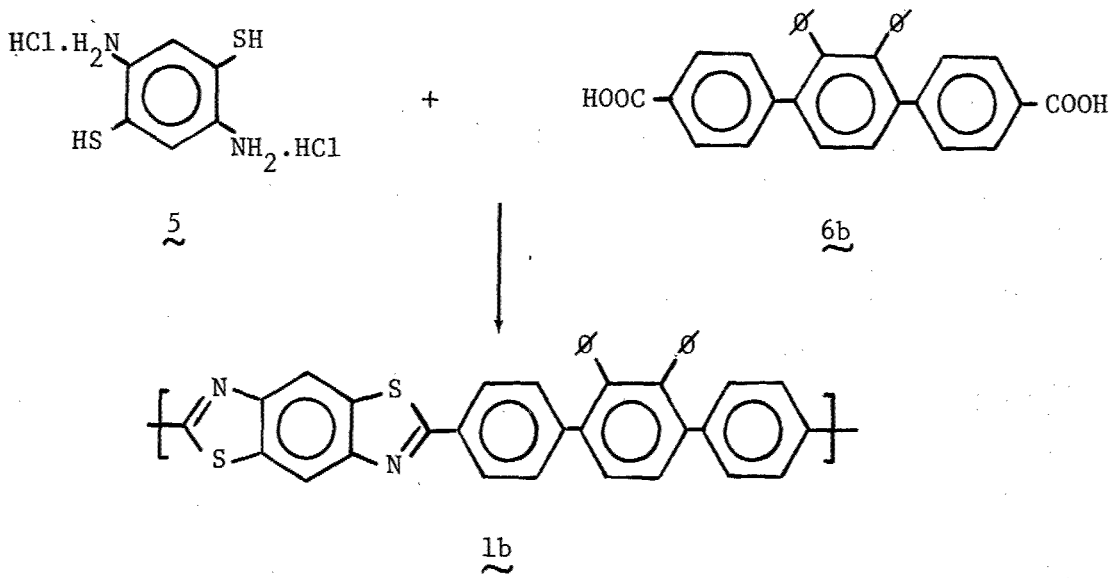
Phenylated polybenzobisthiazoles were prepared to determine the effect of pendant phenylation of the rodlike backbone on solubility and thermal stability. In theory, the increase of aromatic hydrocarbon nature could cause solubility of polymers 1b-d in organic

solvents. When this effect is coupled with the bulkiness of the phenylated p-terphenyl moiety, which should cause a modification of chain packing, one might expect swelling in organic solvents. A small amount of strong acid could then be added to protonate the backbone which would cause dissolution.

An attempt to prepare polymer 1c in PPA without adding sulfolane resulted in recovery of the phenylated diacid monomer 6c. The diacid did not dissolve and hydrogen sulfide was liberated due to the decomposition of monomer 5 as the temperature was slowly raised to 200°C. Successful polymerizations, therefore, require the addition of monomer 6 as a finely divided slurry in sulfolane.

a. Synthesis of Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3'-diphenyl)-p-terphenyl} (1b).

Polymerization of 2,5-diaminodithiohydroquinone dihydrochloride (5) and 4,4"-dicarboxy-2',3'-diphenyl-p-terphenyl (6b) gave a light tan polymer 1b as shown in Figure 5. The final polymer concentration during polymerization (theoretical weight of polymer/weight of polymerization medium) was 1.08%. The PPA/sulfolane ratio (weight PPA/weight sulfolane) was 0.83.



5 6b

1b

Figure 5

Synthesis of the Phenylated Polybenzobisthiazole 1b

The dehydrochlorination proceeded smoothly within 24 hr at a concentration of 5 in PPA of 1.02%. The sulfolane slurry of monomer 6b was added and the temperature was raised to 140°C within 30 min. At this point the mixture was a clear, homogeneous, amber solution; however, two or three small particles of monomer 6b did not dissolve. We did not consider this condition significantly detrimental to the stoichiometric balance. The dark amber polymerization mixture was climbing up the stirring shaft after 16 hr at 160 to 175°C. The mixture was heated for an additional hour at 195°C, then poured into methanol to give a dark brown fibrous material. The polymer was continuously extracted with methanol for 2 days and then dried briefly in an oven and placed in MSA. The bulk of the polymer did not dissolve. The mixture was precipitated and a small portion was worked up and dried thoroughly. The sample was again placed in MSA and filtered. A slight amount of insoluble material remained. The soluble portion was reprecipitated into methanol, washed successively with water, distilled ammonium hydroxide, water, and methanol, then freeze-

dried from benzene. The light golden polymer had an intrinsic viscosity in MSA of 6.5 dL/g at 30°C.

b. Synthesis of Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3',5'-triphenyl)-p-terphenyl} (1c)

Polymerization of monomers 5 and 6c was carried out at a polymer concentration of 0.95% and a PPA/sulfolane ratio of 1.07. A significant amount of monomer 6c never dissolved and insoluble polymer resulted. In a repeat of this polymerization, monomer 6c was ground to a finer powder and redried, and the PPA/sulfolane ratio and the polymer concentration were adjusted to 0.75 and 0.71%, respectively.

The mixture became homogeneous after a short period of time and gave a light tan polymer 1c with an intrinsic viscosity of 4.0 dL/g in MSA. The polymer was readily soluble in MSA, possibly due to the lower molecular weight that was obtained.

c. Synthesis of Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3',5',6'-tetraphenyl)-p-terphenyl} (1d).

The synthesis of the tetraphenylated polymer 1d was carried out with very finely divided monomer 6d by adding a sulfolane slurry of 6d to a dehydrochlorinated mixture of PPA and monomer 5. The PPA/sulfolane ratio was 0.77 and the theoretical polymer concentration was 0.77%. The sulfolane slurry of monomer 6d was stirred for 3 hr with a magnetic stirrer before addition to the reaction to provide a very finely divided mixture. Homogeneity was achieved within 6 hr of reaction. The heating schedule is presented in the Experimental Section. The polymer was precipitated into methanol to give a fibrous purple material which became tan after washing with water. The polymer appeared to be high molecular weight but was insoluble in MSA or MSA/chlorosulfonic acid mixtures.

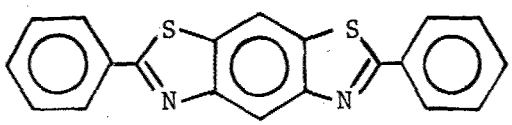
C. Polymers Containing the Benzo [1,2-d:5,4-d'] bisthiazole Moiety.

1. Summary of Results

Marvel reported[8] the synthesis of 4,6-diaminodithioresorcinol dihydrochloride (7) and the polymerization of 7 with tetrachloro aromatic compounds to obtain a highly fused ring system containing the thiazine ring. Relative viscosities were in the range of 0.2 to 1.5 dL/g which are very low for a structure that is so rigid. Thermal stabilities were also surprisingly low. He stated that 7 was unstable, even as the dihydrochloride, and therefore the purity of the monomer was in question.

The success in the preparation of the positional isomer 5 prompted us to try an alternate route to that of Marvel's. We report our results in which we prepared analytically pure 2,6-diaminobenzo-[1,2-d:5,4-d'] bisthiazole (23) and our attempts to obtain pure monomer 7 by hydrolysis of 23.

The model compound, 2,6-diphenylbenzo[1,2-d:5,4-d'] bisthiazole (16b) was prepared in only 79% yield using monomer 7 prepared by Marvel's method. Polymer 2a was prepared by the reaction of 7 with terephthalic acid, but the molecular weight was very low.



16b

2. Synthesis of 4,6-Diaminodithioresorcinol Dihydrochloride (7)

The three different routes that were attempted in order to obtain monomer 7 as a pure, stable compound are outlined in Figure 6.

Method a.

The procedure reported by Marvel[8] involves the reduction of 4,6-diamino-1,3-dithiocyanobenzene (24) with sodium sulfide. This route affords the free amine 7 which is extremely air sensitive. We conducted the reduction of 24 in a nitrogen-filled glove bag and converted the free amine to the hydrochloride immediately. Monomer 7 crystallized as fine, colorless needles from aqueous stannous chloride/hydrochloric acid. The monomer turned pale yellow after drying at room temperature under reduced pressure.

Monomer 7 prepared in this manner gave the model compound with benzoic acid in only 79% yield. One polymerization of 7 with terephthalic acid was carried out in PPA. Dehydrochlorination was unusually rapid (2.5 hr) which may indicate that additional recrystallizations may be necessary to form a completely hydrochlorinated monomer.

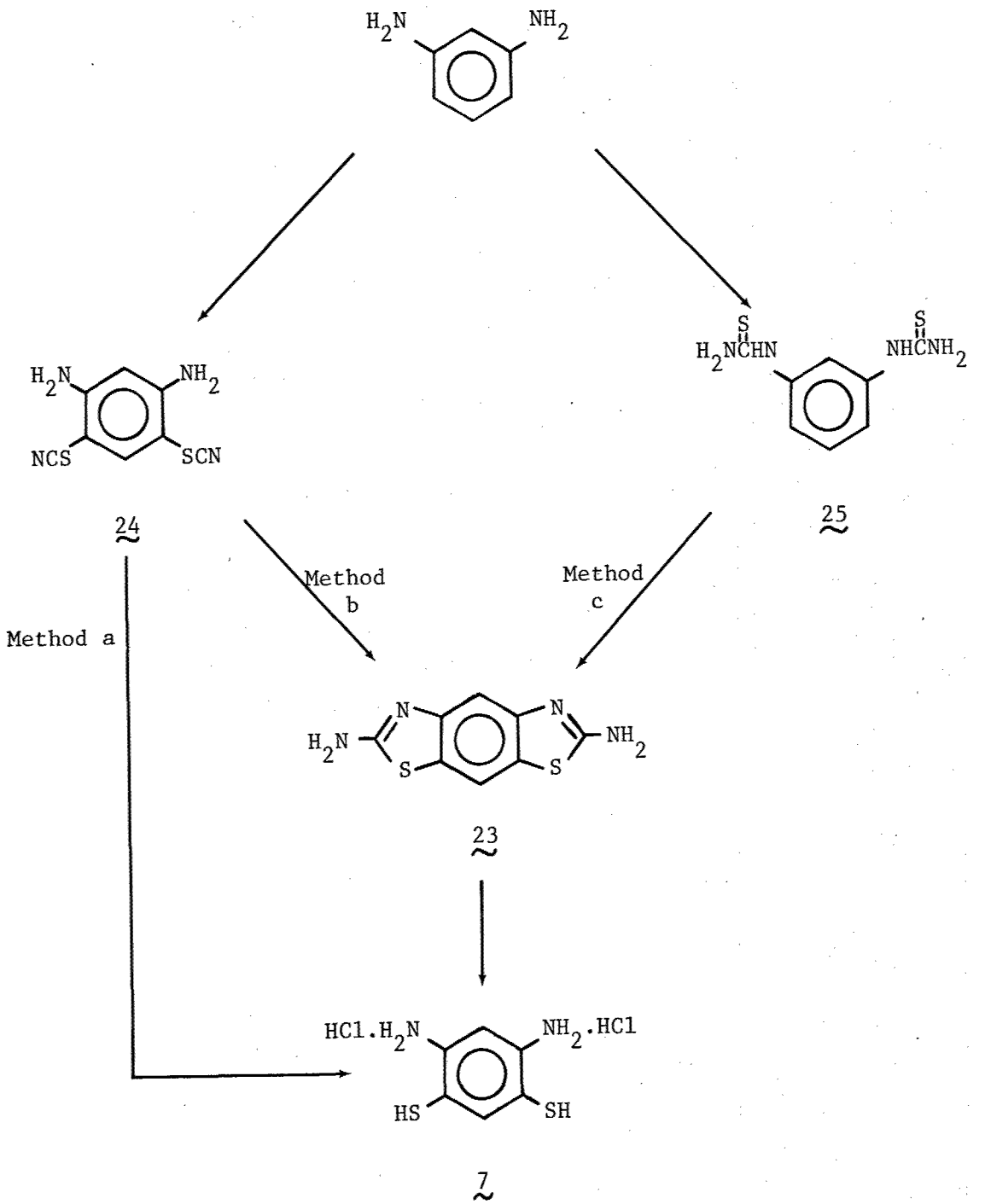


Figure 6

Synthesis of 4,6-Diaminodithioresorcinol Dihydrochloride (7)

Method b.

The cyclization of the dithiocyano compound 24 has been reported.[9] We obtained the diaminobenzobisthiazole 23 in a purified yield of 20%. Recrystallization was carried out in ethanol; the compound was dissolved in dilute hydrochloric acid, treated with charcoal and then recrystallized again.

Hydrolysis of 23 was carried out in a manner identical to the hydrolysis of the benzo[1,2-d:4,5-d']bisthiazole isomer 21. However, the potassium salt of the monomer did not crystallize and therefore could not be separated from the excess potassium hydroxide. When the stannous chloride/HCl solution was cooled, a precipitate formed (weighing 250% of theoretical), which contained only 8% carbon (29.4% theoretical), as determined by elemental analysis. Experiments will be conducted in the future in an attempt to isolate the potassium salt of 7 from the hydrolysis mixture. The concurrent precipitation of potassium chloride with 7 should thus be prevented.

Method c.

The formation of intermediate 23 had also been reported[5] by the cyclization of the m-phenylenebisthiourea 25. We obtained 23 in only 25-30% yield, and the bisthiourea is formed in only 50% yield and is difficult to purify. This method appears to afford a slight benefit over Method b.

D. Polymers Containing the 3,5-Diphenylbenzo[1,2-d:5,4-d']bisimidazole Moiety.

1. Summary of Results

Korshak et. al. have reported[10] the two step synthesis of the rodlike polymer, poly{[3,5-diphenylbenzo(1,2-d:5,4-d')bisimidazole-2,6-diyl]-1,4-phenylene} (3a) as shown in Figure 7. The polymer was prepared by the low temperature reaction of N^1,N^5-diphenyl-1,2,4,5-tetraaminobenzene (8) with terephthaloyl chloride (9a) to afford the intermediate poly(o-anilinoamide) 26. Polymer 26 which had a reported

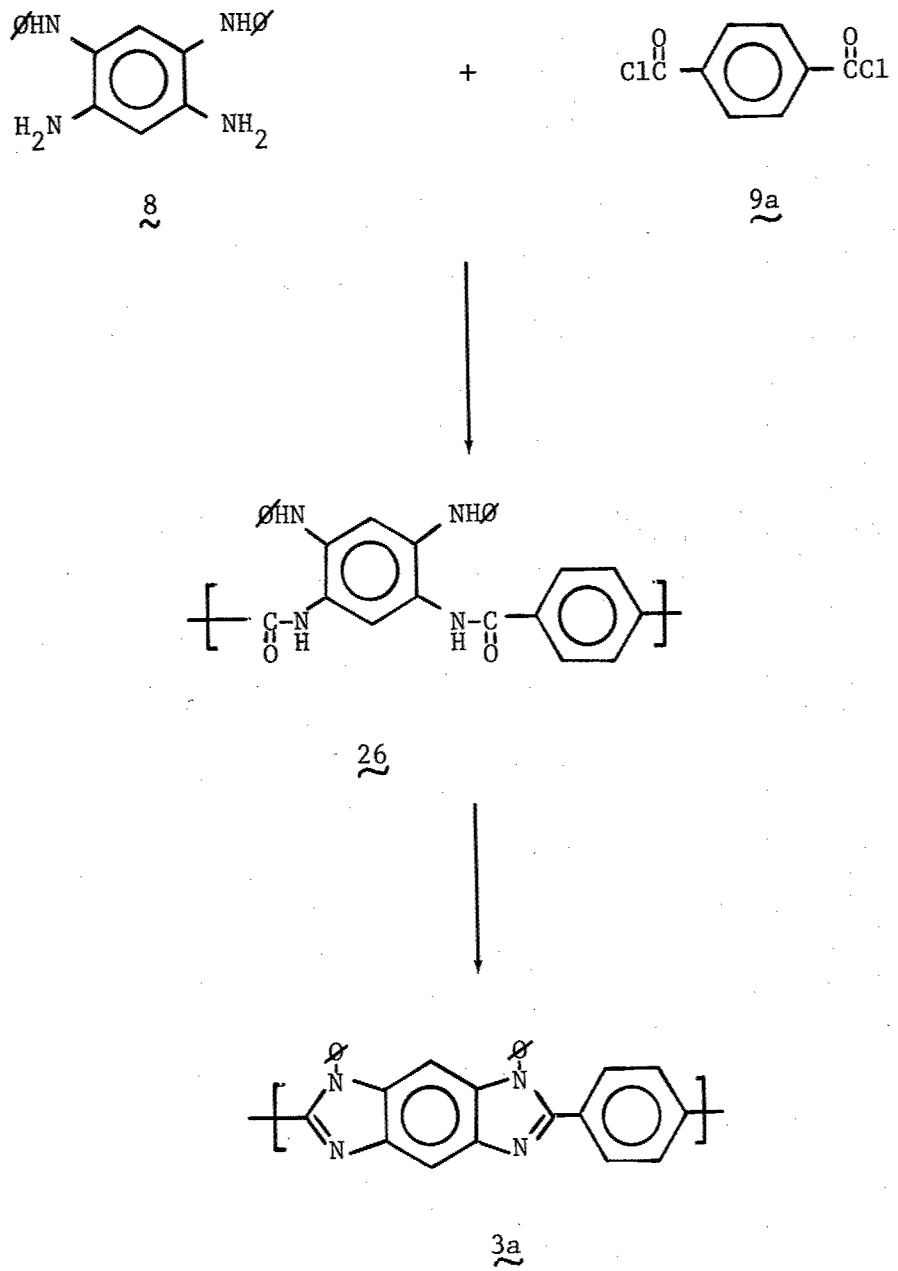


Figure 7

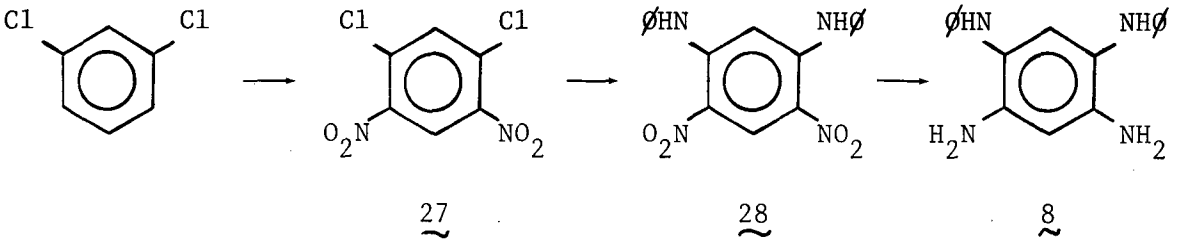
Synthesis of Poly{[3,5-diphenylbenzo(1,2-d:5,4-d')-bisimidazole-2,6-diyl]-1,4-phenylene} (3a)

reduced viscosity (0.5% in dimethylformamide) of 0.4 was cyclized either in the melt at 300-310°C or in PPA at 170°. The resulting polymer was reported to have a reduced viscosity (0.5% in tetrachloroethane/phenol (3/1)) of 9.9 dL/g.

We prepared the monomer 8 by the published procedure[10] and polymerized it with commercially obtained, monomer grade terephthaloyl chloride in carefully dried dimethylacetamide (DMAC). We obtained polymer 26 with an intrinsic viscosity of 0.33 dL/g in DMAC. Cyclization of 26 in PPA at 130° gave polymer with an intrinsic viscosity of 1.1 in MSA and without the reported solubility in tetrachloroethane/phenol. Initial polymerizations were carried out with the phenylated diacid dichloride monomers, but low molecular weight materials were obtained.

2. Synthesis of N^1,N^5-Diphenyl-1,2,4,5-tetraaminobenzene (8)

The synthesis of N^1,N^5-diphenyl-1,2,4,5-tetraaminobenzene was carried out according to the literature procedure[11] as shown in Figure 8. The dinitration of m-dichlorobenzene in nitric acid/sulfuric acid afforded the dinitro compound 27 in 64% yield.



27 28 8

Figure 8

Synthesis of N^1,N^5-Diphenyl-1,2,4,5-Tetraaminobenzene (8)

Nucleophilic displacement of the chloro groups by aniline was carried out above 200° to afford the dinitro-dianilino compound 28. Catalytic hydrogenation of the nitro groups gave the monomer as light tan crystals in 69% yield. The monomer was recrystallized under nitrogen from charcoal and toluene and dried immediately prior to each use to give colorless needles.

3. Synthesis of Poly{[3,5-diphenylbenzo(1,2-d:5,4-d')bisimidazole-2,6-diyl]-1,4-phenylene} (3a).

The polymerization of N^1,N^5-diphenyl-1,2,4,5-tetraaminobenzene (8) with terephthaloyl chloride was carried out in dry DMAC at 0-5°C. The diacid dichloride was added as a powder to the DMAC solution under a stream of dry nitrogen. Hydrogen chloride acceptors such as lithium hydride were added without noticeable increase in molecular weight as shown by comparison of GPC curves. Polymer 26 was soluble in DMAC, but not in DMF, and had an intrinsic viscosity in DMAC of 0.33 dL/g. Cyclodehydration of 26 at 120 to 130°C was carried out in freshly prepared PPA. The prepolymer was not completely soluble in the PPA but the highly swollen golden polymer 3a was obtained by precipitating the PPA mixture into methanol. The polymer was not completely soluble in the solvents reported (tetrachloroethane/phenol 3/1, and formic acid). The infrared spectrum of polymer 3a showed no amide carbonyl absorption. The intrinsic viscosity of polymer 3a in MSA was 1.1 dL/g.

4. Synthesis of Poly{[3,5-diphenylbenzo(1,2-d:5,4-d')bisimidazole-2,6-diyl]-1,4"-(2',3',5'-triphenyl)-p-terphenyl} (3c).

The reaction of the triphenylated diacid dichloride monomer 9c with the tetraamine 8 in DMAC at 0-5°C afforded a low molecular weight polymer 3c. GPC of this polyamide and of the non-phenylated polyamide from terephthaloyl chloride, when compared with polystyrene, gave peak molecular weights of 12,000 and 60,000, respectively.

An attempted polymerization of the monomer 8 with 4,4"-dicyano-2',-3',5'-triphenyl-p-terphenyl 15c in PPA/sulfolane afforded a dark product that showed strong cyano absorption in the infrared. Therefore, this possible one-step synthesis of poly(N-phenylbenzobisimidazoles) was ruled out.

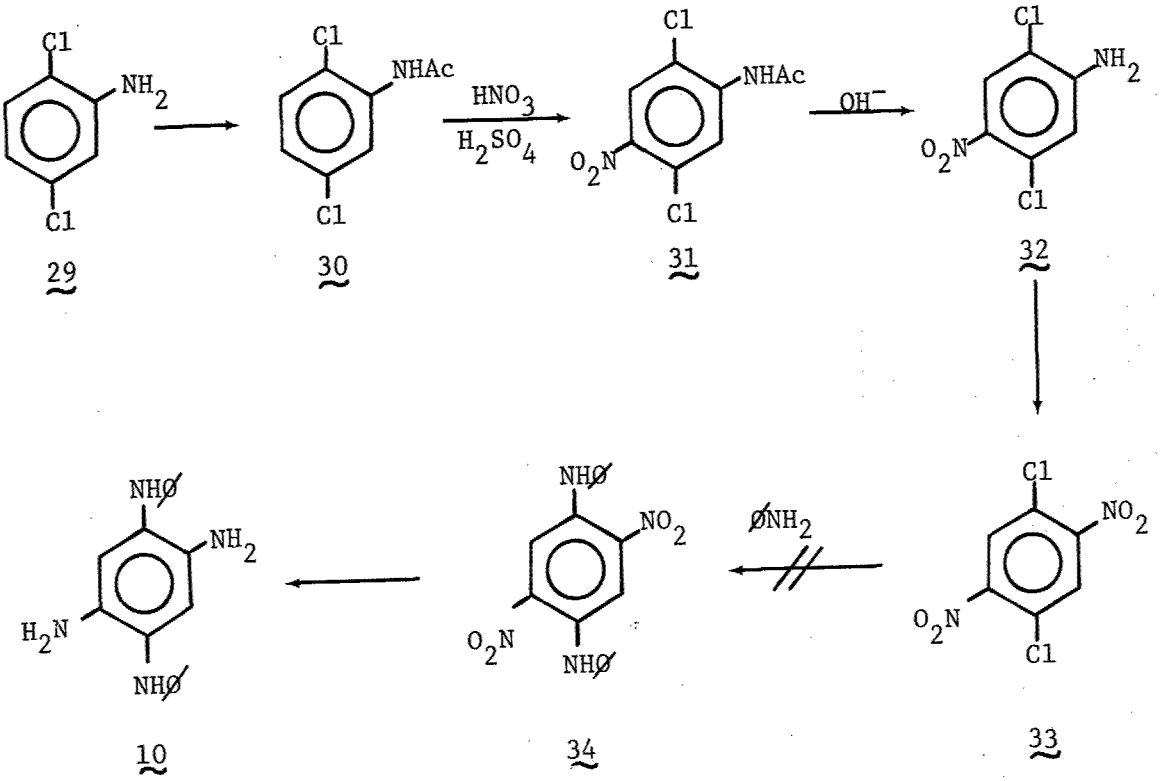
The reaction between the diacid monomer 6c and the monomer 8 in PPA/sulfolane (1/1) produced a low molecular weight polymer. The dark product shows no carboxyl absorption in the infrared but was partly soluble in benzene. Slight decomposition of the tetraamine may have occurred before the diacid became completely soluble (150°C) in the PPA/sulfolane. Optimization of this reaction should be studied.

E. Attempted Synthesis of N^1,N^4-Diphenyl-1,2,4,5-tetraaminobenzene (10)

The synthesis of monomer 10 is not reported in the chemical literature. By analogy with the synthesis of the isomeric monomer 8, shown in Figure 8, we proposed the scheme shown in Figure 9.

Commercially available 2,5-dichloroaniline (29) was acetylated to give compound 30, with subsequent nitration in good yield to afford 2,5-dichloro-4-nitroacetanilide (31). The acetyl group was hydrolyzed to give the nitroamine 32 and the amino group was then oxidized with trifluoroacetic acid/90% hydrogen peroxide to give the dichlorodinitro compound 33.

When we heated 33 to 200°C with aniline, we obtained a complex mixture of products. One of the nitro groups in 33 is activated by the other p-nitro group toward nucleophilic displacement, and thus the product mixture indicated the single displacement of one nitro or one chloro group and the double displacement of one chloro and one nitro group. It was hoped that the dibromo analog would be so much more reactive that double displacement of the bromo groups would occur at a temperature that would preclude nitro displacement.



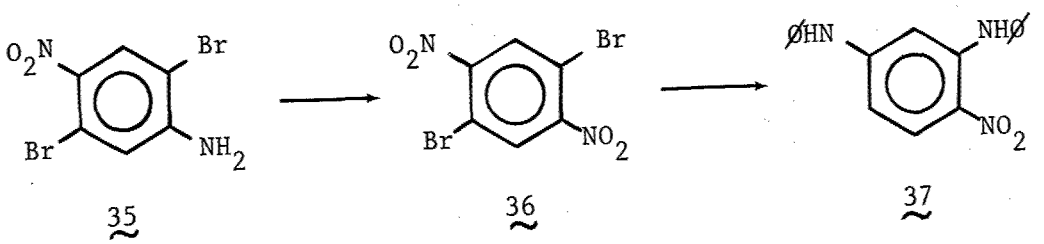


Figure 9

Attempted Synthesis of N^1,N^4-Dipheny1-1,2,4,5-Tetraaminobenzene (10)

The same scheme was repeated using 2,5-dibromoaniline as the starting material. The oxidation of 2,5-dibromo-4-nitroaniline (35) to the corresponding dinitro compound 36 proceeded in 82-83% yield by the action of 90% hydrogen peroxide in glacial acetic acid. The proton nmr of 36 showed a single aromatic peak as expected. When 36 was treated with aniline at 170°C for 2 hr, a black tarry material was formed. After extraction with methanol and chromatography on silica gel, the major product was a red crystalline solid, mp 174-175°C. The infrared spectrum was very similar to the m-dianilino-m-dinitro precursor 28 to the isomeric monomer 8. However, the proton nmr showed two distinct N-H peaks of equal intensity and two large peaks for two different monosubstituted-phenyl groups. Three other peaks in the aromatic region were indicative of trisubstituted aromatic ring. The elemental analysis agreed very closely with 2,4-dianilinonitrobenzene 37. The ir and pmr are also consistent with this assignment. Product 37 would arise from initial nitro displacement by aniline and then displacement of the bromo group ortho to the remaining nitro group. The remaining bromo group is then reduced. Alternative routes to monomer 10 should be considered.

F. Synthesis of a Phenylated Benzobisoxazole Model Compound--2,6-Bis-(2',3',5',6'-tetraphenyl-p-terphenyl)benzo(1,2-d:5,4-d')bisoxazole (38).

The synthesis of model compound 38 was performed as outlined in Figure 10. The Diels-Alder reaction of 4-carboxydiphenylacetylene (39) and tetraphenylcyclopentadienone (40) in refluxing benzophenone gave the acid 41 in good yield. The reaction of 2 moles of 41 with 4,6-diaminoresorcinol dihydrochloride 42 in PPA/sulfolane gave 38 in excellent yield. The product crystallized from the reaction mixture at 200°C and was filtered directly. An additional quantity of 38 was obtained by precipitation of the PPA/sulfolane mixture. Compound 38 was delivered to AFML for x-ray diffraction studies.

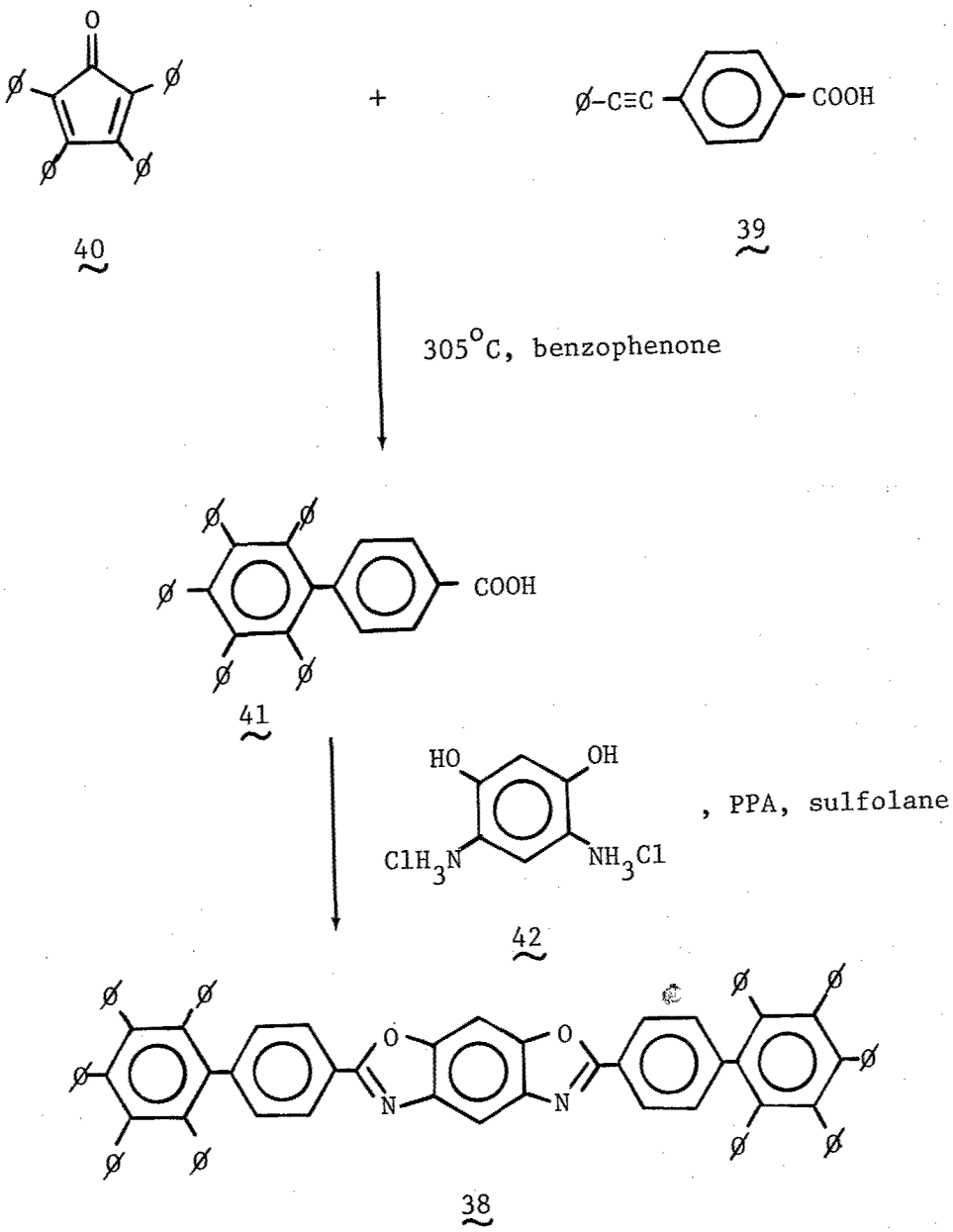


Figure 10

Synthesis of Phenylated Benzobisoxazole Model Compound 38

SECTION III

EXPERIMENTAL SECTION

A. Synthesis of Aromatic Diacids and Diacid Dichlorides

1. 1,3-Bis(p-bromophenyl)-2-propanone (12)

An intimate mixture of p-bromophenylacetic acid (11) (323 g, 1.50 mole) and 94% magnesium oxide (66.5 g, 1.65 mole) was heated at 250°C under reduced pressure to remove the water of condensation. Raising the temperature to 340°C at 1 to 3 torr caused distillation of 12 (225 g, 81.6%). Recrystallization from ethanol gave 192 g (70%) of 12 as colorless platelets; mp 120 to 122°C (lit[12] mp 121 to 122°C).

2. 2,5-Bis(p-bromophenyl)-3,4-diphenylcyclopentadienone (13)

This intermediate was prepared by the condensation of benzil with 12, as described in reference 12.

3. 4,4"-Dibromo-2,'3'-diphenyl-p-terphenyl (14b)

A mixture of 13 (190 g, 0.35 mole), bicyclo[2.2.1]hepta-2,5-diene (370 g, 4.0 mole), and toluene (1 liter) was heated under reflux until the color faded to pink (3 hr). The solution was cooled in an icewater bath and the resultant pink crystals collected, washed with methanol, and air dried. Yield: 150 g (80%); mp 275 to 278°C.

Anal. Calc'd for $C_{30}H_{20}Br_2$: C, 66.68%; H, 3.73%. Found: C, 65.95%; H, 3.95%.

4. 4,4"-Dibromo-2,'3,'5'-triphenyl-p-terphenyl (14c)

A mixture of 13 (120 g, 0.22 mole), phenylacetylene (56 g, 0.55 mole), and o-dichlorobenzene (925 ml) was heated under reflux for 2 hr. The yellow solution was poured into methanol (3 liters) to give 127 g (93%) of 14c; mp 273-275°C.

Anal. Calc'd for $C_{36}H_{24}Br_2$: C, 70.15%; H, 3.92%; Br, 25.93%. Found: C, 70.67%; H, 4.08%; Br, 25.52%.

5. 4,4"-Dibromo-2,'3,'5,'6'-tetraphenyl-p-terphenyl (14d)

A mixture of 13 (14.2 g, 20.5 mmole), diphenylacetylene (10.7 g, 60.0 mmole), and benzophenone (50 g) was heated to a vigorous reflux with a flame. After 10 min the color faded and heating was continued for an additional 10 min. Diphenyl ether (10 ml) was added to prevent the benzophenone from crystallizing. The reaction mixture was allowed to cool to room temperature and the resultant crystals were collected by filtration and washed with benzene. Yield of 14d: 16 g (86%).

14d was also prepared in 83% yield by heating the above reactants under reflux in o-dichlorobenzene for 3 days.

6. Phenylated Dicyano-p-terphenyl Intermediates 15b-d

The following procedure was used to prepare compounds 15b-d:

To a mixture of 14c (100 g, 0.16 mole) and cuprous cyanide (33 g, 0.37 mole) was added dry N-methyl-2-pyrrolidinone (800 ml) under a stream of dry nitrogen. After heating under reflux for 20 hr, the dark brown mixture was poured while hot into 2 liters of warm water containing 667 g of sodium cyanide. The resulting gray precipitate was washed twice with 10% aqueous sodium cyanide. The solid was air-dried at 100°C and then continuously extracted with benzene to give 61 g (74%) of 4,4"-dicyano-2,'3,'5'-triphenyl-p-terphenyl (15c); mp 305-307°C; ir (KBr) 2200 (C=N), 1670 cm^{-1} (weak, carboxyl C=0).

Anal. Calc'd for $C_{32}H_{20}N_2$ (15b): C, 88.86%; H, 4.66%; N, 6.48%. Found: C, 89.11%; H, 4.75%; N, 6.43%.

Calc'd for $C_{38}H_{24}N_2$ (15c): C, 89.72%; H, 4.75%. Found: C, 89.32%; H, 4.81%.

Calc'd for $C_{44}H_{28}N_2$ (15d): C, 90.38%; H, 4.83%; N, 4.79%. Found: C, 90.39%; H, 4.83%; N, 4.58%.

7. 4,4"-Dicarboxy-2,'3'-diphenyl-p-terphenyl (6b)

A mixture of 15b (4.6 g, 11 mmole), potassium hydroxide (20 g), and ethylene glycol (190 ml) was heated under reflux for 16 hr. The light orange solution was cooled slightly and 150 ml of water was added.

After cooling, the resultant precipitate was collected by filtration, dissolved in hot water, and clarified with activated charcoal, and the solution filtered while hot. The diacid was further purified by dissolving in N,N-dimethylacetamide, treating with charcoal, and precipitating with dilute hydrochloric acid. The white powder (4.70 g, 94%) was washed thoroughly with water and dried at 100°/0.1 torr; mp (DSC) 425°C; ms (70 eV) m/e 470 $(M)^+$, 453 $(M+H-H_2O)^+$, 427 $(M+H-CO_2)^+$; ir (KBr) 1690 cm^{-1} (C=O) (see Figure 11).

Anal. Calc'd for $C_{32}H_{22}O_4$: C, 81.68%; H, 4.72%. Found: C, 81.68%; H, 4.44%.

8. 4,4"-Dicarboxy-2,'3,'5'-triphenyl-p-terphenyl (6c)

A mixture of 15c (50 g, 98 mmole), potassium hydroxide (153 g), and ethylene glycol (1.3 liters) was heated under reflux for 20 hr. The diacid was isolated as described for 15b to give 39 g (72%) of 15c; mp; (DSC) 425°; ms (70 eV) m/e 546 $(M)^+$, 529 $(M+H-H_2O)^+$, 503 $(M+H-CO_2)^+$; ir (KBr) 1690 cm^{-1} (C=O) (See Figure 12).

Anal. Calc'd for $C_{38}H_{26}O_4$: C, 83.50%; H, 4.89%. Found: C, 83.41% H, 4.65%.

9. 4,4"-Dicarboxy-2,'3,'5,'6'-tetraphenyl-p-terphenyl (6d)

A mixture of 15d (46 g, 70 mmole), potassium hydroxide (98 g), and ethylene glycol (600 ml) was heated under reflux for 20 hr. The diacid was isolated as described for 15b to give 26 g (60%) of 15d; mp: sublimes without melting at 450°C as shown by DSC; ms (70 eV) m/e 622 (M^+); ir (KBr) 1690 cm^{-1} (C=O) (See Figure 13).

Anal. Calc'd for $C_{44}H_{30}O_4$: C, 84.87%; H, 4.86%. Found: C, 84.64%; H, 5.00%.

10. 4,4"-Bis(chloroformyl)-2',3',5'-triphenyl-p-terphenyl (9c)

A mixture of 10.00 g (18.29 mmole) of 4,4"-dicarboxy-2',3',5'-triphenyl-p-terphenyl (6c) and 100 ml of freshly distilled thionyl chloride was heated under reflux overnight to give a clear orange solution. The excess thionyl chloride was removed under reduced pressure

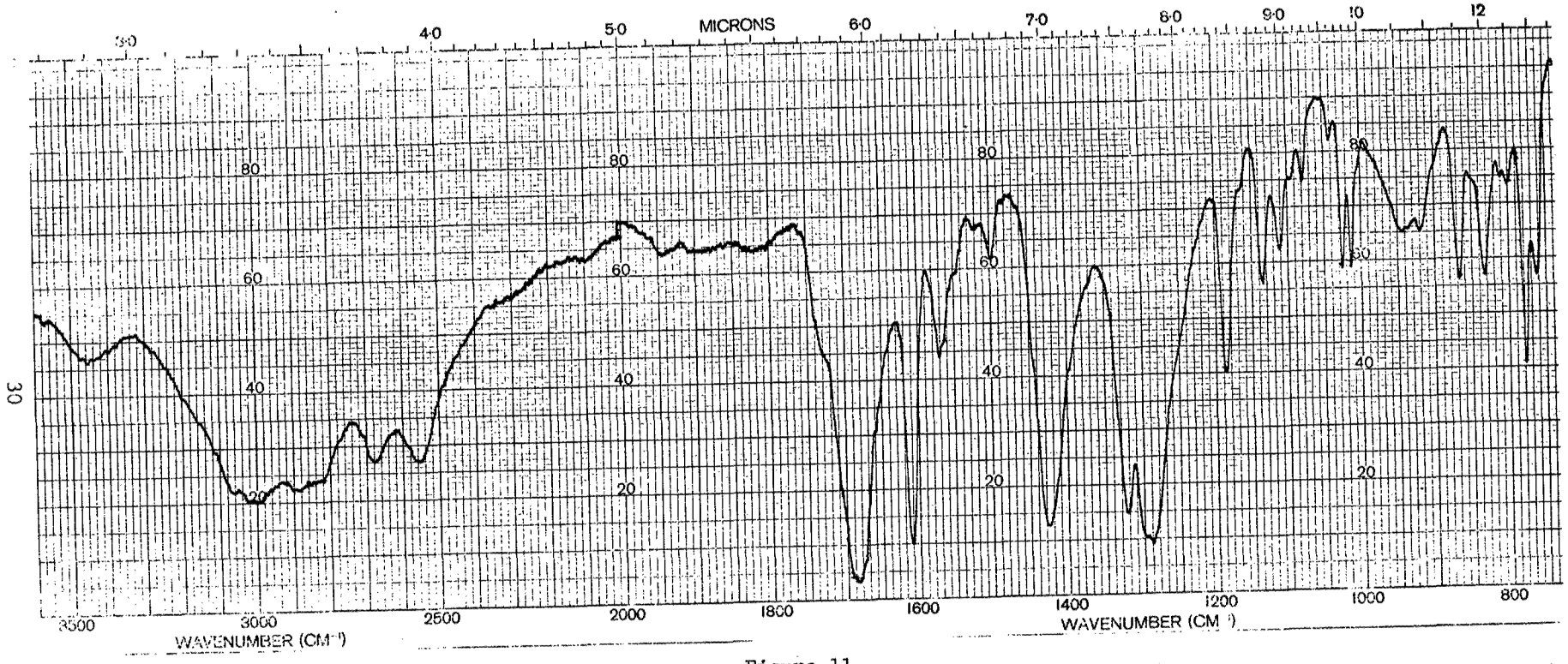


Figure 11

Infrared Spectrum of Monomer 6b

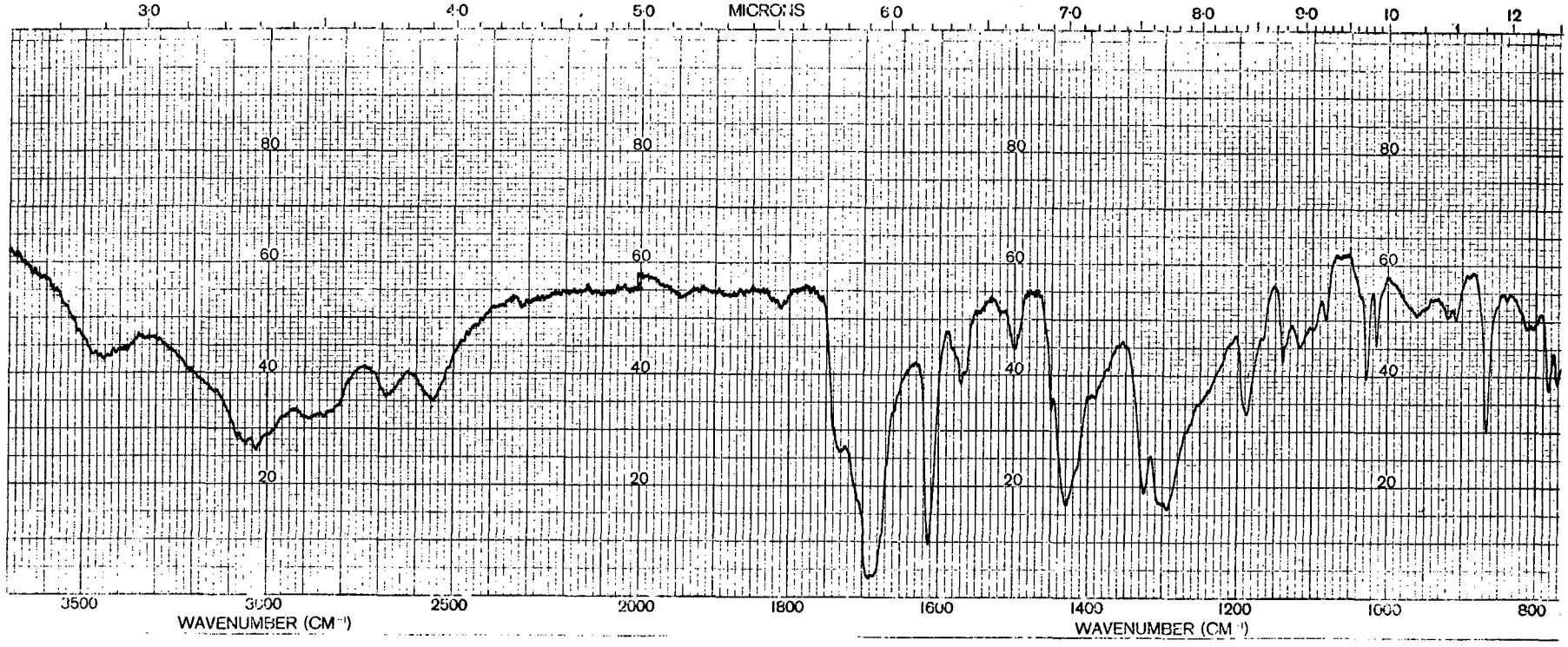


Figure 12

Infrared Spectrum of Monomer 6c

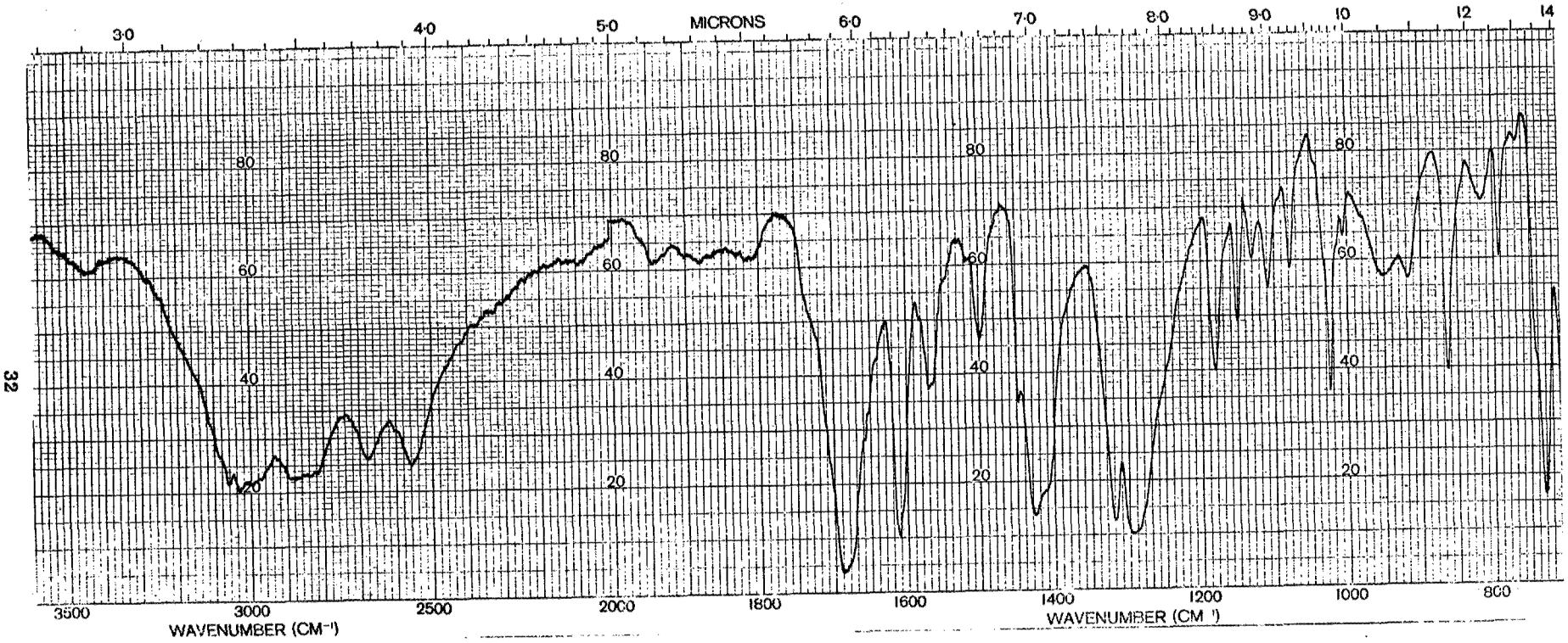


Figure 13

Infrared Spectrum of Monomer 6d

and benzene was added in portions and distilled to remove the last traces of thionyl chloride. The product was then dissolved in benzene, freeze-dried, and recrystallized from benzene to afford 8.0 g (75%) as colorless needles; mp 225 to 228°C; ir (KBr) 1775 and 1745 (strong, C=O), with no peak at 1680 cm^{-1} (COOH) (See Figure 14).

Anal. Calc'd for $C_{38}H_{24}Cl_2O_2$: C, 78.22%, H, 4.15%. Found: C, 78.24%; H, 3.94%.

The above procedure was also performed with the di- and tetra-phenylated diacids with similar results.

B. Synthesis of 2,5-Diaminodithiohydroquinone Dihydrochloride (5).

1. p-Phenylenebisthiourea (20)

A solution of 54 g (0.50 mol) p-phenylenediamine (19), 1 liter 1.5N HCl and 152 g (2.0 mol) ammonium thiocyanate was heated at the reflux temperature for 1 hr. When the mixture was cooled to room temperature, a precipitate formed. The precipitate was removed by filtration and the water distilled from the filtrate. The resulting yellow solid was washed with water to give 97 g (85%) of 20. This material can be used in the subsequent reaction without further purification. An analytical sample was obtained by recrystallizing 6 g from 6 liters of water; ir (KBr) 3330, 3260, and 3170 (NH and NH_2), 1070 cm^{-1} (C=S).

Anal. Calc'd for $C_8H_{10}N_4S_2$: C, 42.46%; H, 4.45%; N, 24.76%. Found: C, 42.76%; H, 4.39%; N, 24.80%.

2. 2,6-Diaminobenzo[1,2-d:4,5-d']bisthiazole (21)

To 100 g (0.44 mole) of p-phenylenebisthiourea suspended in 1 liter of chloroform we added 147 g (0.92 mol) of bromine in 200 ml of chloroform. The mixture was stirred for 4 hr, then refluxed for an additional 16 hr. After cooling, the precipitate was collected by filtration, washed with chloroform, then stirred with 500 ml 20% aqueous sodium bisulfite at 90°C for 1 hr. The solid was collected by filtration, washed with water, dissolved in 3N aqueous hydrochloric acid, and filtered. Basification of the filtrate gave a white precipitate, which was recrystallized twice

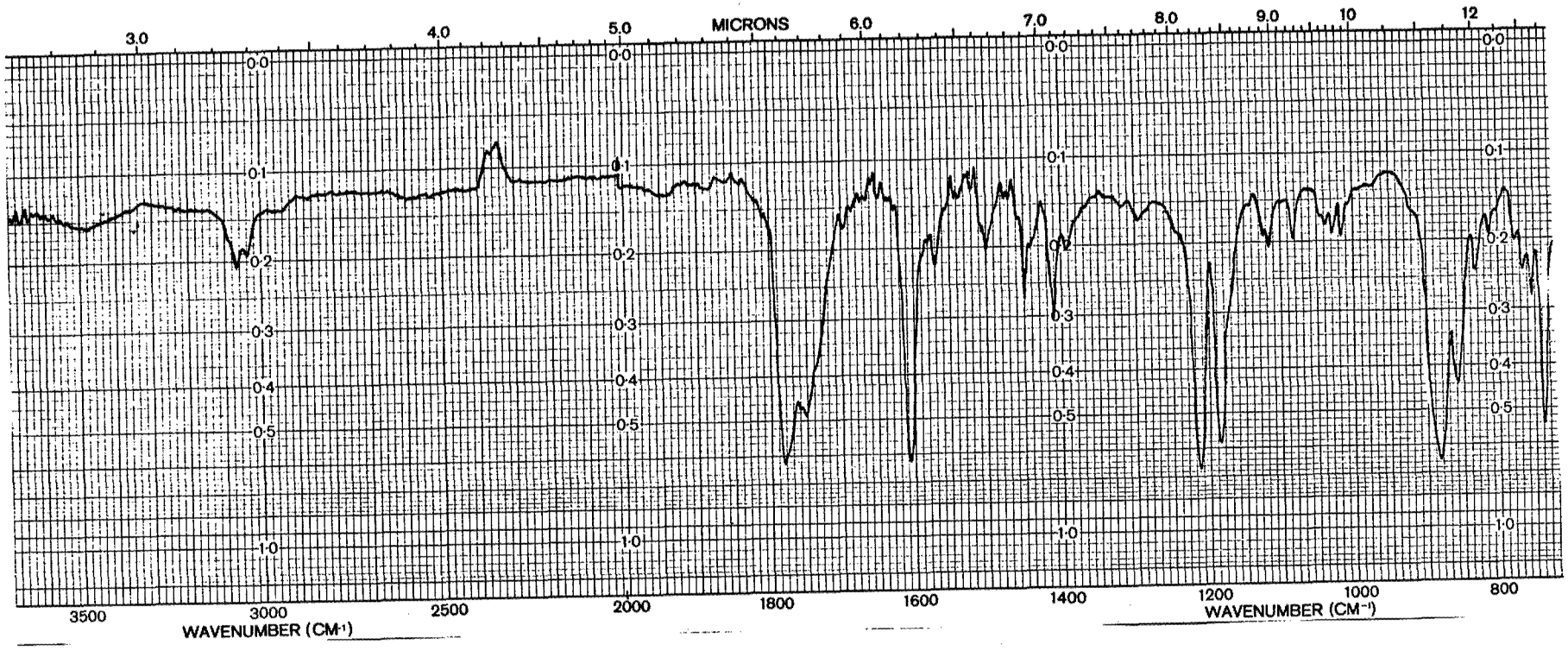


Figure 14

Infrared Spectrum of Monomer 9c

from glacial acetic acid to give 30.6 g (31.2%) of 21; ir (KBr) 3400, 3280 (NH_2), 1640 cm^{-1} (C=N).

Anal. Calc'd for $C_8H_6N_4S_2$: C, 43.13%; H, 2.71%. Found: C, 42.95%; H, 2.45%.

3. 2,5-Diaminodithiohydroquinone Dihydrochloride (5)

A solution of 14.5 g (0.065 mol) of 21 and 80 g potassium hydroxide in 55 ml water was heated at the reflux temperature for 4 hr under a nitrogen blanket. The clear yellow solution was allowed to stand overnight under nitrogen. The reaction flask containing the resultant long white needles was transferred to a nitrogen-filled glove bag and the dipotassium salt 22 was collected by filtration. The salt 22 was then stirred with 250 ml water, which had been deaerated, containing 25 ml concentrated hydrochloric acid and 12 g stannous chloride. The bright yellow slurry was heated to near boiling and 250 ml concentrated hydrochloric acid was added. The white product was collected by filtration after cooling, washed with ether, then placed in vials in a drying pistol. The closed pistol was then removed from the glove bag and evacuated, and the monomer was dried overnight at room temperature under reduced pressure (0.05 torr). The yield was 13 g (81%) of a white powder; ir (KBr) 300-2700 (broad) and 2580 (NH_3Cl), 2460 cm^{-1} (SH). (See Figure 15).

Anal. Calc'd for $C_6H_{10}N_2S_2Cl_2$: C, 29.39%; H, 4.11%; N, 11.43%. Found: C, 29.17%; H, 4.08%; N, 11.60%.

C. Synthesis of 2,6-Diphenylbenzo [1,2-d:4,5-d'] bisthiazole (16a)

Polyphosphoric acid (PPA) was prepared immediately before each use by the following method. Phosphorus pentoxide (330 g) was added slowly to 85% phosphoric acid (217 g) while the mixture was stirred under nitrogen and cooled with an ice-water bath. The viscous slurry was then heated with stirring under nitrogen at 150°C for 6 hr to give water-white homogeneous PPA.

2,5-Diaminodithiohydroquinone dihydrochloride (5) (3.35 g, 13.7 mmole) was stirred at room temperature with 56 g of PPA and 20 g of sulfolane until the dehydrochlorination was complete (24 hr). The mixture was then

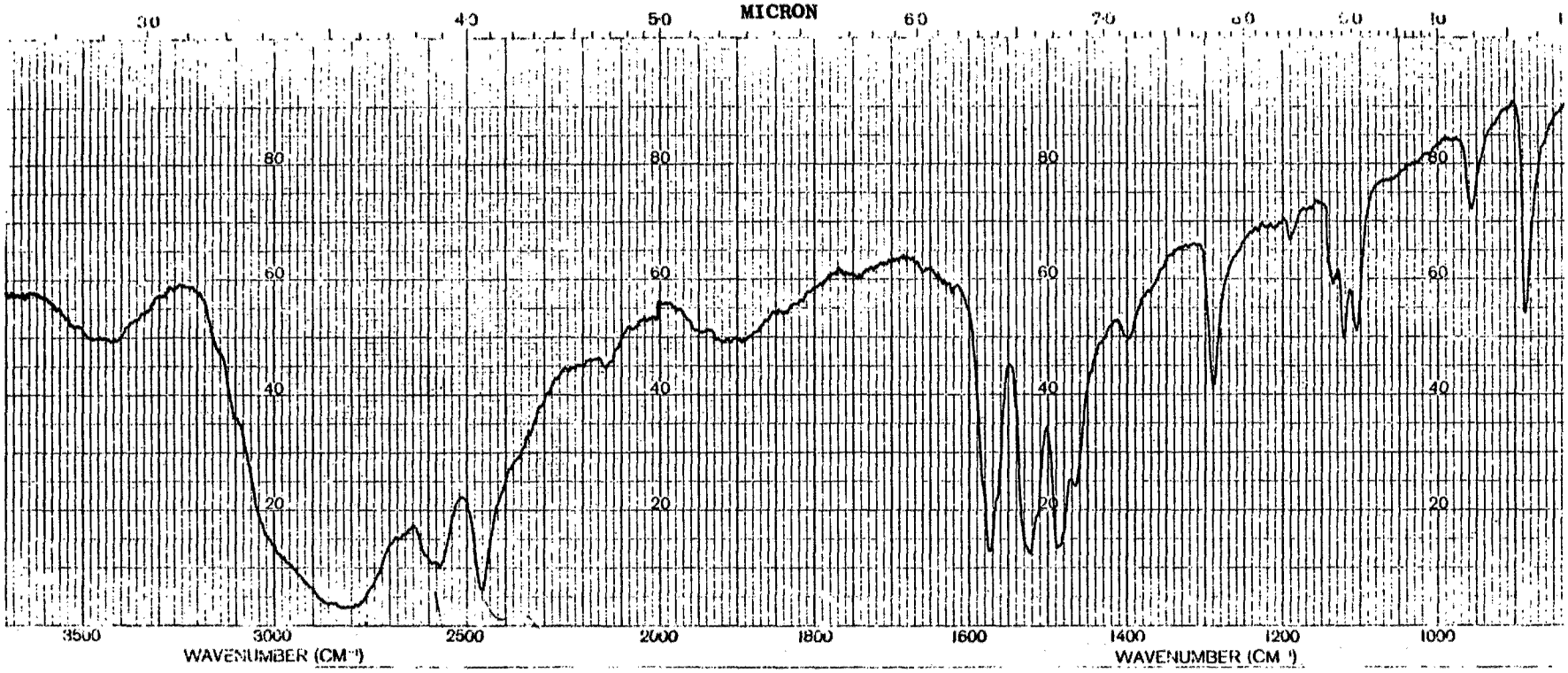


Figure 15

Infrared Spectrum of Monomer 5

heated to 90°C and 4.00 g (32.7 mmol) of benzoic acid was added. The mixture was then heated with an oil bath at the indicated temperature for the indicated time with the aid of a Love temperature controller:

Temperature, °C	Time, hr
90	5
145	13
170	4
200	1

The dark solution was poured into methanol to give a white precipitate. The model compound was washed with water and dilute ammonium hydroxide, air dried, and recrystallized from toluene as white platelets. The yield was 4.66 g (98.9%); ir (KBr), see Figure 16; mass spectrum (70 eV) m/e 344 $(M)^+$, 241 $(-C_6H_5CN)$ (See Figure 17).

Anal. Calc'd for $C_{20}H_{12}N_2S_2$: C, 69.74%; H, 3.51%; N, 8.13%. Found: C, 70.55%; H, 3.37%; N, 8.34%.

D. Synthesis of Polymers Containing the benzo[1,2-d:4,5-d']bisthiazole Moiety.

1. Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4-phenylene} (1a)

Method A

To a 100 ml round-bottom flask fitted with a mechanical stirrer and a nitrogen inlet/outlet was added 2.2358 g (9.1186 mmole) of 5 under a slow stream of dry nitrogen. The monomer was covered with 55 g of freshly prepared PPA and stirred at room temperature to give a bubbly, viscous, white mixture. Any heating caused uncontrollable foaming. After 24 hr, the mixture was heated to 70°C for 5 hr and then to 90°C for 12 hr. The resultant PPA solution was clear, with a slight tan color. Terephthalic acid (6a) (1.5149 g, 9.1188 mmole) was added as a powder . After stirring to incorporate all the powder into the slurry, 9.5 g of PPA was added, and the mixture became orange-yellow. The temperature was raised to 130°-135°C for 30 min and then to 155°C for 3 hr. All of the terephthalic acid had not dissolved, so 12.4 g of PPA was added. The temperature was maintained at 155°C for an additional 1.5 hr, then raised to 165°C for 1.5 hr. When

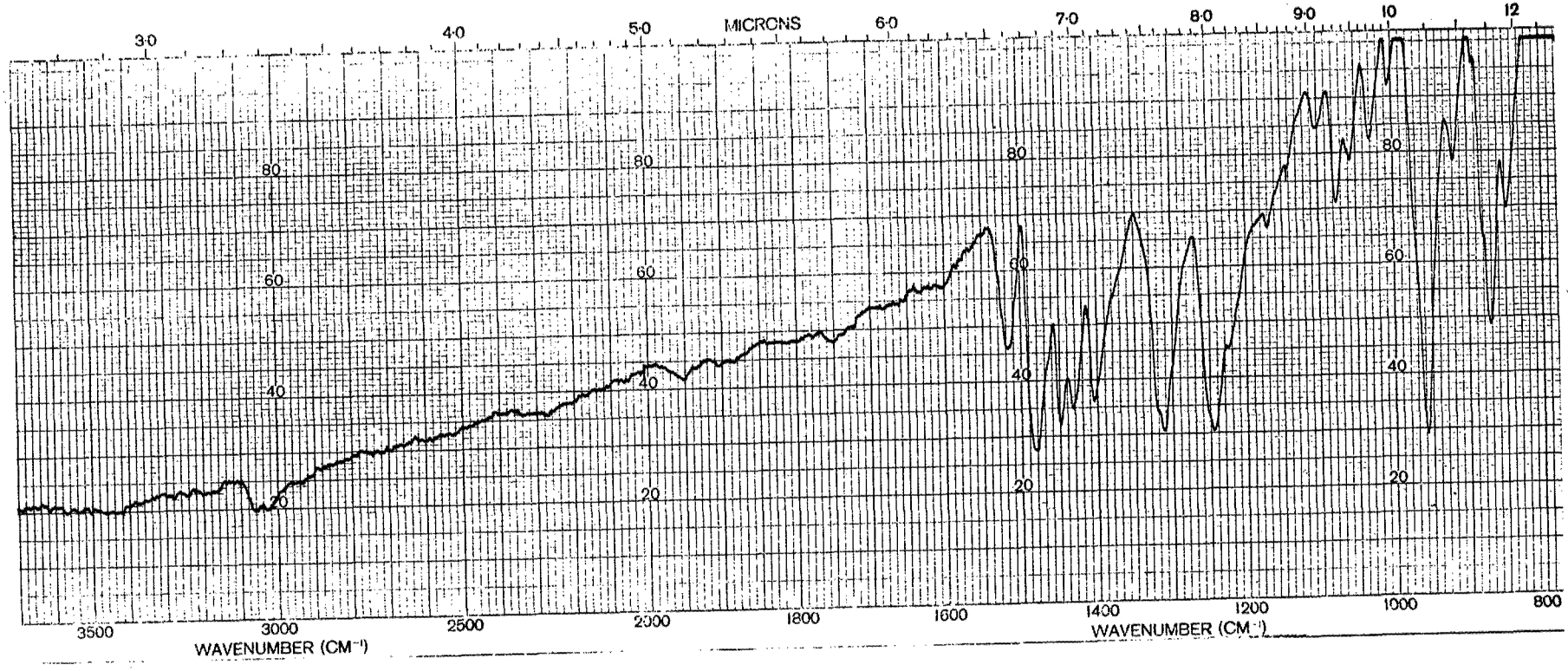


Figure 16

Infrared Spectrum of Model Compound 16a

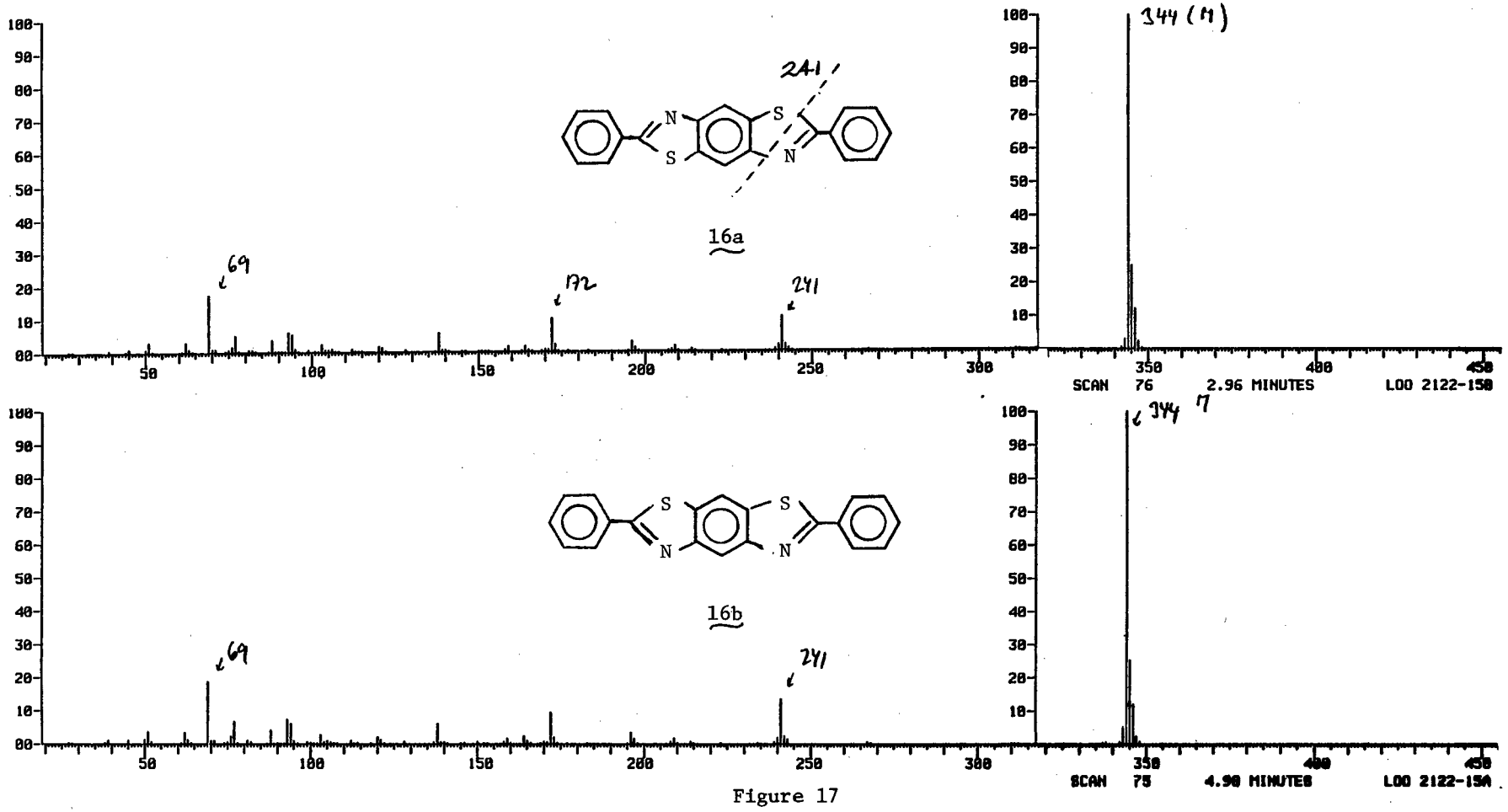


Figure 17

Mass Spectra of Model Compounds 16a and 16b

the temperature was raised to 175°C, the mixture turned darker and more viscous, and all of the acid monomer dissolved. The reaction mixture became so viscous it could not be stirred and thus was scooped out of the flask into methanol. The polymer was washed with methanol, partially dried in air, and dissolved in 1L of methanesulfonic acid. The solution was filtered into 4L of methanol, collected by filtration, and washed successively with methanol, aqueous ammonium hydroxide, water, methanol again, methanol/benzene mixtures, and finally benzene. Freeze drying from benzene and drying at 100°C/0.5 torr for 12 hr gave 2.4 g (99%) of a golden polymer. $[\eta]$= 5.07 dL/g in methanesulfonic acid (MSA) at 30°C.

Method B

To a 500 ml resin kettle equipped with a mechanical stirrer and nitrogen inlet/out was added 6.3848 g (26.040 mmole) of 5 under a slow stream of dry nitrogen. The monomer was covered with 325 g of freshly prepared PPA. After the mixture was stirred at room temperature for 24 hr, dehydrochlorination had ceased, and the solution became clear. Heating to 70°C and then 90°C caused dehydrochlorination to resume until, after 4 hr, it was complete. Terephthalic acid (4.3260 g, 26.040 mmole) was added, and then 135 g of PPA. With the aid of a Love temperature controller, the temperature of the surrounding oil bath was raised to the values and maintained for the times indicated below:

Temperature, °C	Time
90	30 min
110	40 min
135	15 min
140	1.5 hr
150	7.0 hr
175	9.0 hr

Because of high viscosity, stirring stopped sometime within the last time interval. The PPA-polymer mixture was mixed with MSA scooped into methanol, and worked up as described in Method A. $[\eta]$ = 9.52 dL/g in MSA at 30°C; ir (KBr) See Figure 18.

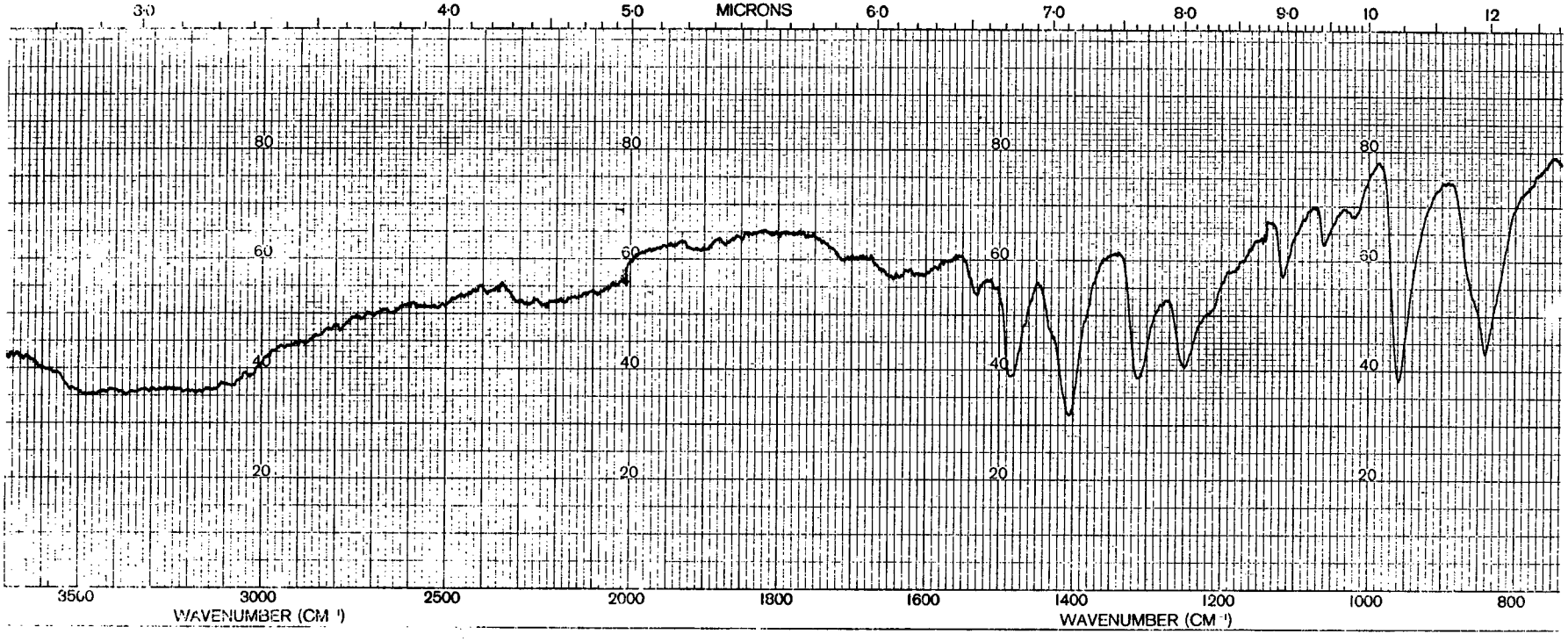


Figure 18

Infrared Spectrum of Polymer 1a

2. Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3'-diphenyl)-p-terphenyl} (1b)

Dehydrochlorination was carried out as described for polymer 1a using 2.14804 g (8.7606 mmole) of monomer 5 in 210 g of PPA. A heated slurry of the diphenylated diacid monomer 6b in 154 g of sulfolane was added to the polymerization flask which had been heated to 125°C. The polymerization was then heated as follows:

Temperature, °C	Time, hr
125	1
140	0.5
160	5
175	11
195	1.5

The polymer was worked up as usual to give a tan polymer with an intrinsic viscosity in MSA of 6.5 dL/g.

3. Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3',5'-triphenyl)-p-terphenyl} (1c)

A mixture of 1.52095 g (62.031 mmole) of monomer 5 and 240 g of PPA was dehydrochlorinated as described previously for polymer 1b. Addition of 3.83731 g of monomer 6c in 317 g of sulfolane and then heating over a period of 3.5 hr to 160°C gave an amber solution. After an additional 3 hr at 160°C the solution was heated at 175°C for 9 hr and then poured into methanol. After the standard workup a light tan polymer was obtained. $[\eta]$ = 4.0 dL/g in MSA at 30°C.

4. Poly{[benzo(1,2-d:4,5-d')bisthiazole-2,6-diyl]-1,4"-(2',3',5',6'-tetraphenyl)-p-terphenyl} (1d)

Monomer 5 (1.56976 g, 64.022 mmole), 262 g of PPA, monomer 6d (3.98679 g, 64.022 mmole) and 341 g of sulfolane were allowed to react as described for polymers 1b and 1c to give a tan polymer. The polymer swelled in MSA but did not dissolve.

E. Synthesis of 4,6-Diaminodithioresorcinol Dihydrochloride (7)

1. Method A

The synthesis of 7 was carried out according to the published procedure[8] with the following modifications. The reduction of 4,6-diamino-1,3-dithiocyanobenzene (24) was conducted as reported[8] in a nitrogen-filled glove bag. The free amine of monomer 7 (1.2 g) was added to 40 ml of water containing 10 ml of concentrated hydrochloric acid and 0.55 g of stannous chloride at room temperature to give an orange slurry. While heating the slurry to 80°C, we added 80 ml of concentrated hydrochloric acid, and obtained a clear water-white solution. The dihydrochloride salt 7 crystallized as colorless needles when cooled in dry ice. Upon drying under reduced pressure, the monomer turned slightly yellow.

2. Method B

To 385 ml of 20% hydrochloric acid solution was added 12.8 g (57.5 mmole) of 4,6-diamino-1,3-dithiocyanobenzene (24). The mixture was heated at the reflux temperature for 1.5 hr, cooled, and filtered. The filtrate was basified with ammonium hydroxide to give 8.5 g (66%) of the diaminobenzobisthiazole 23. Hydrolysis was carried out as described in Method C.

3. Method C

a. m-Phenylenebisthiourea

A mixture of 81 g (0.75 mole) of m-phenylenediamine, 1.5 liters of 1.5 N hydrochloric acid, and 228 g (3.0 mole) of ammonium thiocyanate was heated under reflux for 1 hr. The solution was then cooled and the precipitate that formed was removed by filtration. The filtrate was concentrated by distillation and 121 g (71.7%) of a yellow-brown solid separated. This product was used in the next step without further purification; ir (KBr), very similar to spectrum of isomeric compound 20.

Anal. Calc'd for $C_8H_{10}N_4S_2$: C, 42.46%; H, 4.45%; N, 24.76%. Found: C, 42.66%; H, 4.5%; N, 24.42%.

b. 2,6-Diaminobenzo[1,2-d:5,4-d']bisthiazole (23)

Bromine (180 g) in 200 ml of chloroform was added dropwise to a suspension of m-phenylenebisthiourea (100 g, 0.44 mole) in 1 liter of chloroform and then the mixture was heated under reflux for 20 hr. The reaction mixture was then cooled and the precipitate collected by filtration. The solid was heated to 90°C for 1 hr with 750 ml of 20% sodium bisulfite and filtered. The residue was then heated to boiling in dilute hydrochloric acid and the resulting solution was filtered. The filtrate was basified with ammonium hydroxide to give 60.5 g of crude 23. Recrystallization from ethanol afforded 20 g (20%) of 23 as a white powder.

c. Hydrolysis of 2,6-Diaminobenzo [1,2-d:5,4-d']bisthiazole (23)

A mixture of 6.6 g (30 mmole) of 23, 32 g of potassium hydroxide and 28 ml of water was heated under reflux for 6 hr under a blanket of nitrogen. The clear yellow solution was allowed to cool to room temperature and stand overnight under nitrogen. Upon cooling in an ice bath a very slight amount of precipitate formed. The flask was closed under nitrogen and taken into a nitrogen-filled glove bag, filtered and the filtrate added to a solution of stannous chloride in dilute hydrochloric acid. The orange slurry was heated to 80° and 50 ml of concentrated hydrochloric acid was added. The material dissolved to give a clear, colorless solution. After cooling in an ice bath, filtration under nitrogen and drying in vacuo the product weighed 18.3 g (250%) and showed only 8% carbon content (Calc'd 29.4% C) which indicates the concurrent precipitation of potassium chloride with monomer 7.

F. Synthesis of 2,6-Diphenylbenzo[1,2-d:5,4-d']bisthiazole (16b)

To a flask containing 11 g of freshly prepared PPA we added 0.54 g (2.2 mmole) of 4,6-diaminodithioresorcinol dihydrochloride[8] and 0.56 g (5% excess) of benzoic acid. The mixture was heated slowly to 100°C to effect dehydrochlorination and then treated as described for compound 16a. The model compound 16b was recrystallized from toluene to give 0.60 g (79%) of yellow crystals; ir (KBr) (see Figure 19); mass spectrum (70 eV) m/e 344 $(M)^+$, 241 $(-C_6H_5CN)$ (see Figure 17).

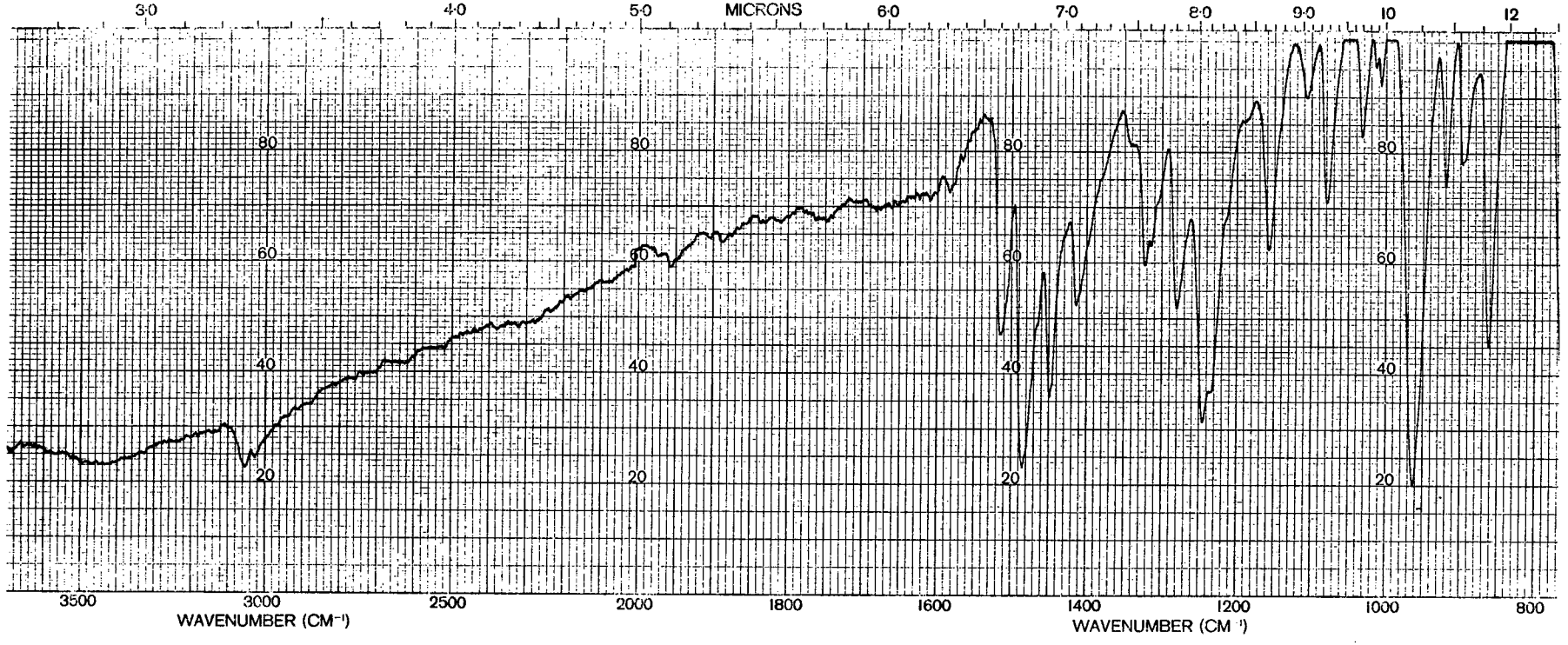


Figure 19

Infrared Spectrum of Model Compound 16b

Anal. Calc'd for $C_{20}H_{12}N_2S_2$: C, 69.74%; H, 3.51%; N, 8.13%. Found: C, 70.84%; H, 3.36%; N, 8.17%.

G. Attempted Synthesis of Poly{[benzo(1,2-d:5,4-d')bisthiazole-2,6-diyl]-1,4-phenylene} (2a)

The polymerization of 4,6-diaminodithioresorcinol (7) and terephthalic acid (6a) was attempted according to the method reported for polymer 1a. The resulting polymer was gold in color and showed a large absorbance at 1690 cm^{-1} for carboxyl termination, indicative of low molecular weight.

H. Synthesis of N^1,N^5-Diphenyl-1,2,4,5-tetraaminobenzene (8)

1. 1,3-Dichloro-4,6-dinitrobenzene (27)

To 2.5 g of concentrated sulfuric acid, we added 750 g 90% nitric acid, with cooling. While stirring, we added 50 g (3.4 mole) of m-dichlorobenzene over a 1 hr period while maintaining the temperature between 10 and 30°C. We then heated the reaction mixture to 85°C for 1 hr to ensure complete nitration, then poured it cautiously onto crushed ice. The precipitate was collected by filtration and recrystallized from methanol yielding 511 g (64%) of light yellow 27; mp 103-104°C.

2. 1,3-Dianilino-4,6-dinitrobenzene (28)

A mixture of 334 g (1.4 mole) of 1,3-dichloro-4,6-dinitrobenzene and 470 g (5.1 mole) of aniline was slowly heated. Within 5 min an exothermic reaction occurred and the temperature reached 230°C with blackening of the mixture. The reaction mixture was held at 180°C for 1 hr, then cooled. The solid product was removed from the flask by dissolving it in hot N,N-dimethylformamide (DMF) and then pouring it into an equal volume of methanol. The product crystallized on cooling. Two additional recrystallizations from 1:1 DMF/methanol yielded 235 g (48%) of gold crystals of 28; mp 192 to 195°C.

3. N^1,N^5-Diphenyl-1,2,4,5-tetraaminobenzene (8)

A mixture of 7 g (0.02 mole) of 1,3-dianilino-4,6-dinitrobenzene, 200 ml of glacial acetic acid and 0.5 g of 1% Pt-C catalyst was shaken in

a Parr autoclave at 30 psi of hydrogen at 30°C. Theoretical hydrogen uptake was complete in 20 min. The catalyst was then removed by filtration and the filtrate brought to pH 10 by slowly pouring it into a sodium hydroxide solution (150 g in 500 ml water). The product was then collected by filtration and washed with water until neutral, then with 200 ml of methanol. The product was recrystallized under nitrogen from toluene (250 ml) with the use of charcoal, then washed with 100 ml of methanol, yielding 4 g (69%) of 8; mp 201 to 205°C.

Anal. Calc'd for $C_{18}H_{18}N_4$: C, 74.46%; H, 6.24%; N, 19.29%. Found: C, 74.54%; H, 6.44%; N, 19.43%.

I. Synthesis of Poly(4,6-dianilino-1,3-phenylene terephthalamide) (26)

A solution of tetraamine 8 (4.35585 g, 15.000 mmole) in 30 ml of dry, freshly distilled DMAC was cooled to 0.5°C with an ice-water bath under a slow stream of dry nitrogen. Terephthaloyl chloride (9a) (3.04556 g, 15.000 mmole) was added as a powder in portions over a 30 min period. The cooling bath was then removed and the reaction was stirred at room temperature for 17 hr. The dark brown reaction mixture was poured into 450 ml of water, washed with water, acetone and extracted with ethanol. The rust colored polymer was dissolved in DMAC and inversely precipitated with water. The polymer was washed as before and dried in vacuo overnight at 100°C. Yield: 6.13 g (97.2%); ir (KBr) See Figure 20. $[\eta]$ = 0.33 dL/g in DMAC at 30°C.

Anal. Calc'd for $C_{26}H_{20}N_4O_2$: C, 74.26%; H, 4.78%; N, 13.32%. Found: C, 72.75%; H, 4.4%; N, 11.34%.

Lithium hydride was added to the reaction mixture in a separate run after 2 hr, 3.5 hr, 20 hr and 22 hr. Each addition caused bubbling due to hydrogen formation. There was no noticeable molecular weight difference as shown by GPC.

The same procedure was carried out with stoichiometric quantities of monomers 8 and the phenylated diacid dichloride 9c. The polymer was mostly soluble in acetone and had a very low molecular weight as shown by GPC. Hydrogen chloride acceptors raised the molecular weight of this material only slightly.

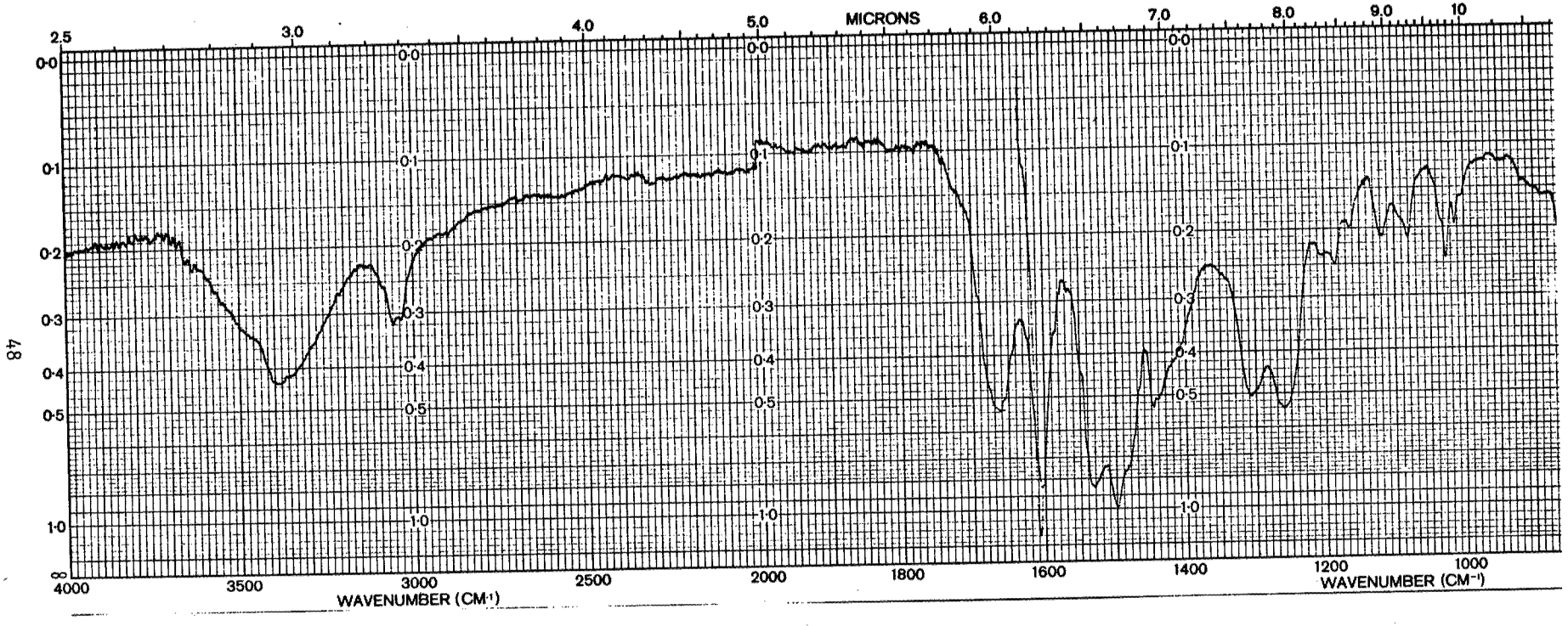


Figure 20

Infrared Spectrum of Polymer 26

J. Synthesis of Phenylated Benzobisoxazole Model Compound 38

1. Pentaphenylphenylbenzoic acid (41)

A mixture of tetraphenylcyclopentadienone (5.0 g, 13 mmole), p-phenyl-ethynylbenzoic acid (5.5 g, 25 mmole), and benzophenone (25 g), was heated under reflux for 30 min. Diphenyl ether (7 ml) was added and the mixture was allowed to cool. The resultant precipitate was collected by filtration and washed with benzene to give 7.4 g (98%) of 41; mp > 350°C, ir (KBr) 1710 (C=O), 730 and 698 cm^{-1} (5 adjacent aromatic H).

2. 2,6-Bis(2',3',5',6'-tetraphenyl-p-terphenyl)benzo[1,2-d:5,4-d']bisoxazole (38)

A mixture of 4,6-diaminoresorcinol dihydrochloride (42) (0.72 g, 3.4 mmole) and freshly prepared PPA (79 g) was heated under a slow stream of nitrogen at 80°C for 16 hr and then at 110°C until dehydrochlorination had ceased (8 hr). A mixture of acid 41 (4.30 g, 7.48 mmole) and sulfolane (175 g) was heated to 140°C and added to the PPA/ 42 mixture. This mixture was heated at 130°C for 16 hr, at 155°C for 5 hr, at 185°C for 2 hr, and finally, at 200 to 205°C for 1.5 hr. The mixture became homogeneous at 200°C, and then fine needles crystallized from solution. The mixture was cooled to 160°C and the precipitate collected by filtration. The fine tan powder was washed with water and dried at 100°C to give 1.8 g of 38. An additional 1.8 g was obtained by adding water to the filtrate. Yield: 3.6 g (87%). An analytical sample was obtained by recrystallization from dichloromethane. ir (KBr) 730 and 698 cm^{-1} (5 adjacent H).

Anal. Calc'd for $C_{92}H_{60}N_2O_2$: C, 90.16%; H, 4.93%; N, 2.28%. Found: C, 90.14%; H, 4.90%; N, 1.99%.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

A new class of high molecular weight, linear polymers, poly(benzo-[1,2-d:4,5-d']bisthiazoles) (1a-d) has been prepared by the polycondensation of a new monomer with diacids in polyphosphoric acid (PPA). The polymers are presently under thorough evaluation under separate contracts, but preliminary data suggest that improvements over PBO have been made in molecular weight and thermooxidative stability.

The solubility of the phenylated polybenzobisthiazoles, even in strong acids, is not as good as the non-phenylated polymer. This property may be a result of polymerization in a mixed solvent medium, which is necessary for monomer solubility. This condition may cause aggregation as high molecular weight is attained and hence a less soluble polymer.

Additional research is required to develop a method for isolation of monomer 7, 4,6-diaminodithioresorcinol, as a stable, pure compound. Purity of 7 appears to be the one factor preventing the formation of high molecular weight poly(benzo[1,2-d:5,4-d']bisthiazoles) 2a-d.

The linear polymer, poly{[3,5-diphenylbenzo(1,2-d:5,4-d')bisimidazole-2,6-diyl]-1,4-phenylene}, (3a), was prepared according to the two-step procedure in the literature.[10] The intrinsic viscosity that we obtained was much lower than the reported value. The polymer also did not possess the reported solubility in tetrachloroethane/phenol. Optimization of polymerization conditions should be possible since monomer purity can be achieved and there are a number of solvents and conditions to be evaluated.

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