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HETEROAROMATIC POLYMERS . POLYBITHIAZOLES

by

Howard Ho-Wei Un

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
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To My Parents

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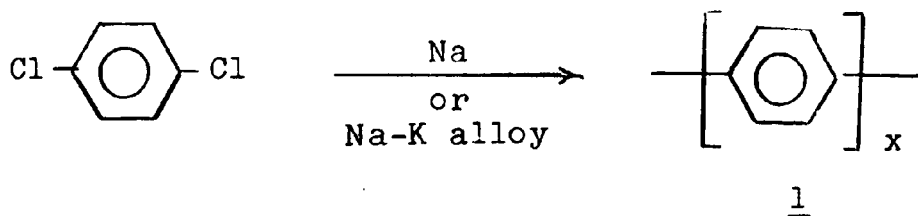
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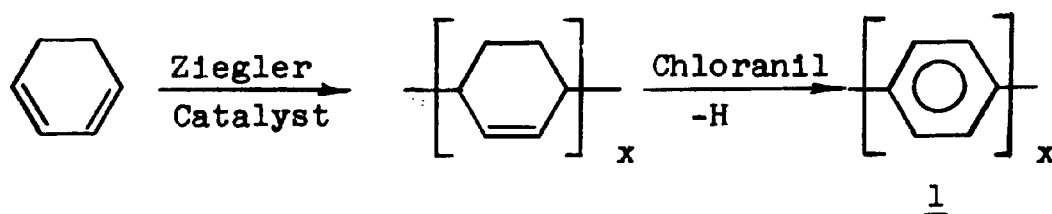
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I. HISTORICAL BACKGROUND

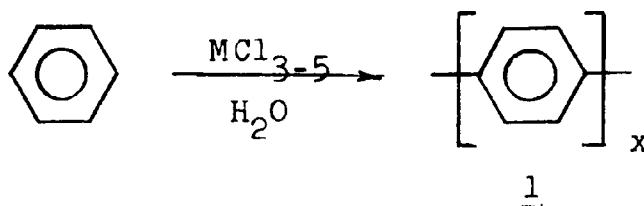
The acute need for high molecular weight material possessing hydrolytic, oxidative and thermal stabilities has more recently stimulated extensive high polymer synthetic efforts. One approach to such species lies in the development of new polymer-forming reactions based on well-known organic reactions. The increase in melting points in the series *p*-terphenyl to *p*-sexiphenyl, anthracene to pentacene, and phenanthrene to fulminene (benzo [c]picene) suggests that high molecular weight material containing these basic units -- poly(*p*-phenylenes), poly(acenes) and poly(phenes) -- would not melt below 900°C, and perhaps possess thermal stability at high temperatures.^{1,2} Several methods have been successfully developed for the synthesis of poly(*p*-phenylene).³ For example, Edwards and Goldfinger^{4,5} prepared poly(*p*-phenylene) (1) by the condensation of *p*-dichlorobenzene in the presence of sodium, or the liquid alloy of sodium and potassium. The polymer was dark brown in color, and possessed a linear structure. It did not melt at 550°C, but lost hydrogen at 500°C.



Marvel and Hartzell⁶ attempted to obtain high molecular weight poly(p-phenylene), starting from poly-1,3-cyclohexadiene. With a Ziegler catalyst, 1,3-cyclohexadiene gave a linear polymerizate, poly-1,3-cyclohexadiene with a molecular weight* of ca. 10,000. Dehydrogenation with chloranil gave a black, incompletely aromatized polymer, which did not melt at 530°C in a nitrogen atmosphere.

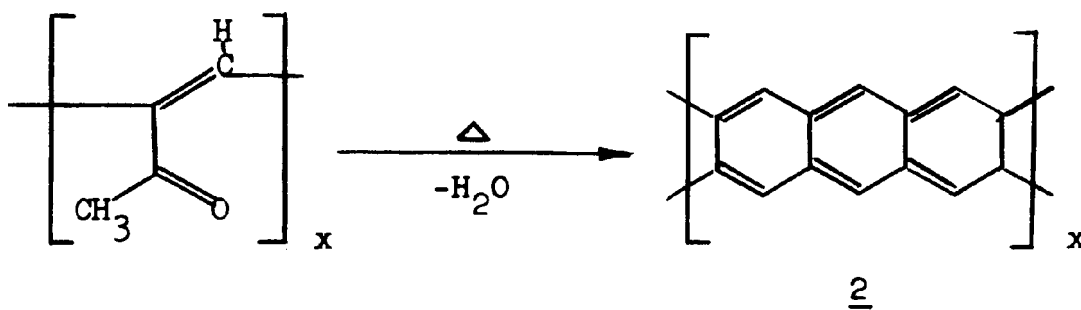


More recently, Kovacic and co-workers⁷⁻¹¹ prepared the same polymer (1) by the low temperature polymerization of benzene with metal halide-water co-catalysts. The properties of the polymers obtained were similar to those of Marvel and Hartzell.⁶



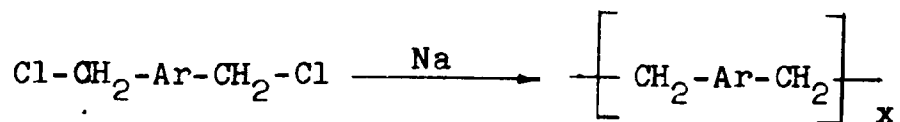
*Unless otherwise stated, molecular weights refer to number average molecular weights.

A polymer of the poly(acene) series has been reported by Nesmeyanov and co-workers.^{12,13} A polymer was obtained when 1-chlorobut-1-ene-3-one was allowed to stand (presumably in air) for 20-30 days. Upon heating in vacuo at 300-400°C, cyclopolymerization occurred with the loss of water to form polymer 2. This polymer was claimed to have high thermal stability as well as interesting magnetic and electrical properties.



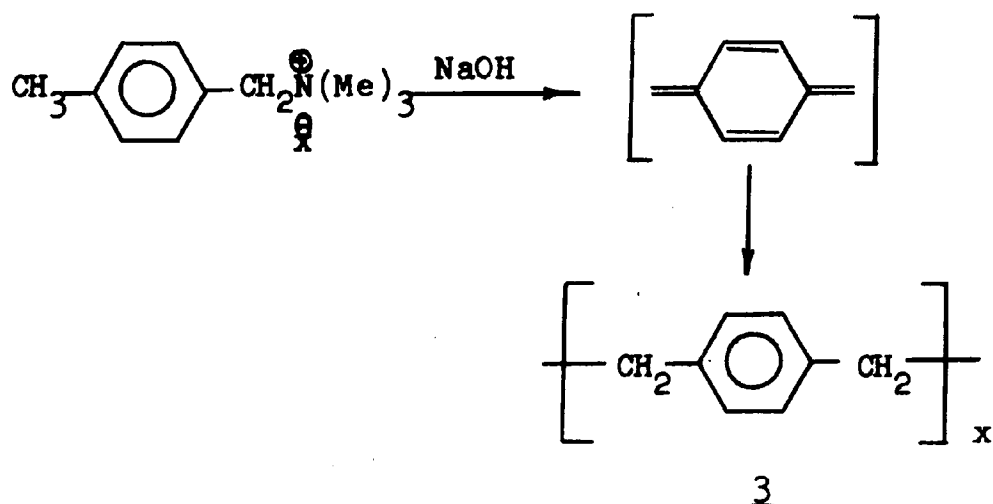
Poly(p-phenylenes) and polymers constructed entirely of benzene rings, in spite of their outstanding thermal stability, find little application due to their infusibility and insolubility in common organic solvents; films cast from poly(p-phenylenes) are very brittle.¹⁴ In recent years, methods have been developed to modify the structures of poly(p-phenylenes). One approach is the synthesis of polymers with flexible links such as methylene, ethereal oxygen, thio-ether, etc., in the main chain in addition to benzene rings. Polymers of this type have been regarded as poly(p-phenylenes) with alternate in-chain modifiers or inserts,¹⁴ and are expected to possess both satisfactory

thermal stability in addition to tractability. **Polyxylylenes**, with $-\text{CH}_2-\text{CH}_2-$ as "modifiers" of poly(p-phenylenes), have attracted the attention of polymer chemists for some time, but not until recently have good synthetic procedures become available for their preparation. Vansheidt and co-workers^{15,16} utilized the Wurtz reaction for the synthesis of poly(p-xylylene). Bischloromethyl derivatives of aromatic hydrocarbons in dioxane at 25°C, on reaction with sodium, afforded polycondensation products as white powders with varying degrees of crystallinity and melting ranges. The polymers (3) are soluble in a variety of organic solvents.

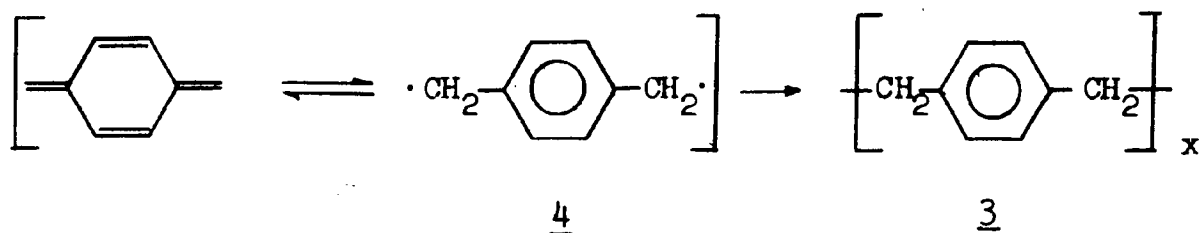


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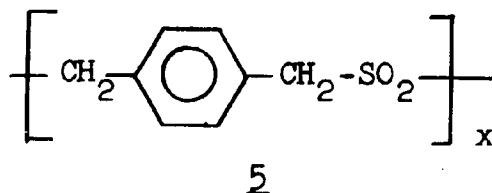
Young¹⁷ demonstrated that polymer 3 can be prepared in good yield by the modified Hofmann degradation of p-methylbenzyltrimethylammonium halides using sodium hydroxide as the base.



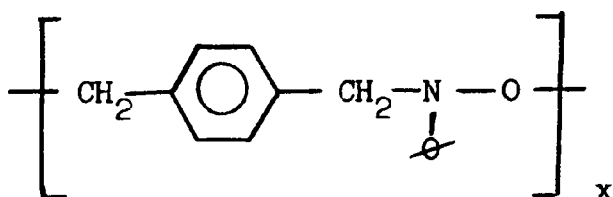
Auspos et.al.,¹⁸ Schaefgen,¹⁹ and Errede²⁰ prepared poly-(p-xylylene) by the fast flow pyrolysis method of Szwarc.^{21,22} Pyrolysis of p-xylene at 1000°C in vacuo gives the p-xylylene pseudo radical 4, which is introduced into a solvent at -78°C, where polymerization takes place forming products with molecular weights of 200,000 or more.



The reactive intermediate, 4, can react with a variety of species to yield copolymers. As an example, with sulfur dioxide, copolymer 5 with sulfone linkages in the main chain is formed. The polymer melts at 200°C under 500 atmospheres of pressure.²³



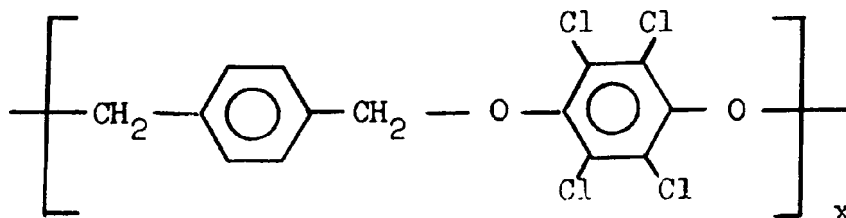
The treatment of 4 with a number of aromatic nitroso compounds affords low-melting copolymers.²³ With nitrosobenzene, for example, copolymer 6 is formed.



6

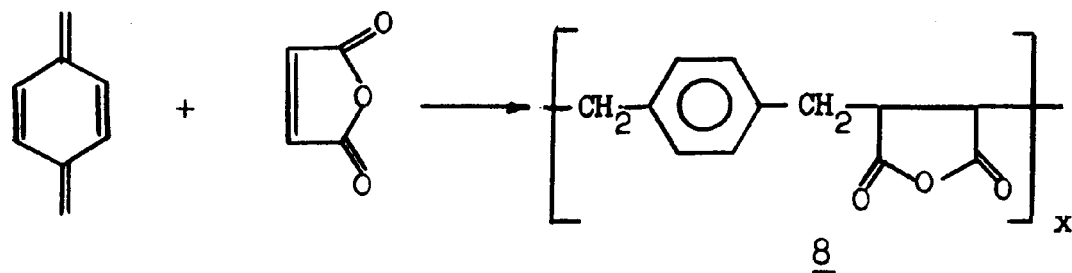
The polymers obtained are soluble in organic solvents and melt or soften at ca. 200°C.

With tetrachlorobenzoquinone, polymer 7, with a softening point at 195-200°C, is formed.²³



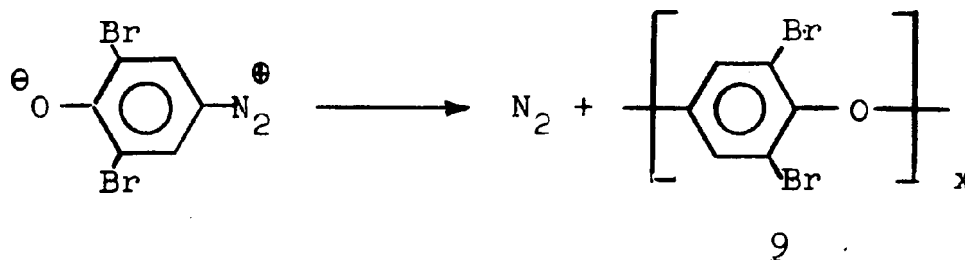
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Thermoplastic copolymers are also obtained by the interaction of 4 with maleic anhydride, diethyl maleate, acrylonitrile, n-butyl acrylate, and styrene. For example, with maleic anhydride, a polyanhydride, 8, is obtained.



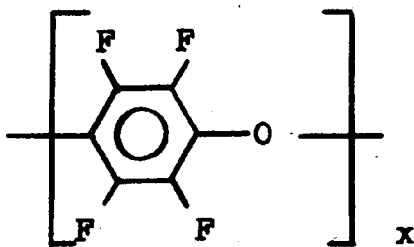
Other interesting copolymers derived from 4 have been reported. With phosphorus trichloride, a copolymer with phosphorus atoms in the main chain is produced. A number of these phosphorus-containing polymers have been investigated by Errede; they all have softening points at ca. 150°C .²⁹

Dewar and James²⁴ prepared polymers containing ether oxygen atoms in the main chain as well as rings by the decomposition of derivatives of benzene-1,4-diazooxide:

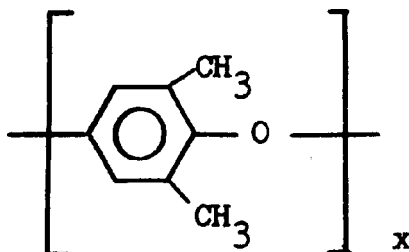


Polymer 9 has a softening point at $200\text{--}220^\circ\text{C}$.

An analog of 9 has been prepared by Wall²⁵ with the substitution of fluorine atoms for hydrogen atoms on the aromatic ring. The polymer, 10, is an elastomer.

10

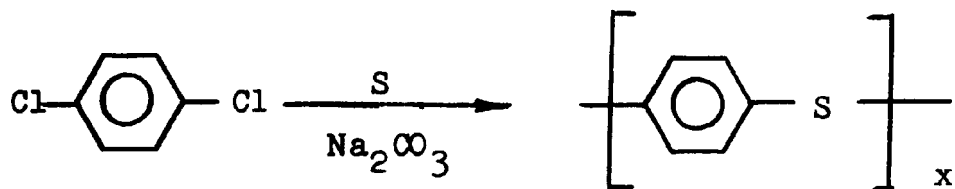
Staffin and Price prepared polymers of 2,6-disubstituted phenylene ethers by the treatment of 2,6-dimethyl-4-bromophenol with alkali followed by oxidation with lead dioxide.²⁶

11

Polymer 11 is soluble in most organic solvents and has a softening point at 260°C. The weight loss on heating the polymer at 420°C for 30 minutes in vacuo was 69%.²⁶

Polymers with sulfur atoms and benzene rings -- the aromatic thioethers -- are also known. Lenz and coworkers,^{27,28} prepared polyaromatic thioethers by the high temperature condensation of polyhalogen aromatic compounds with alkali or

alkali-earth sulfides:



12

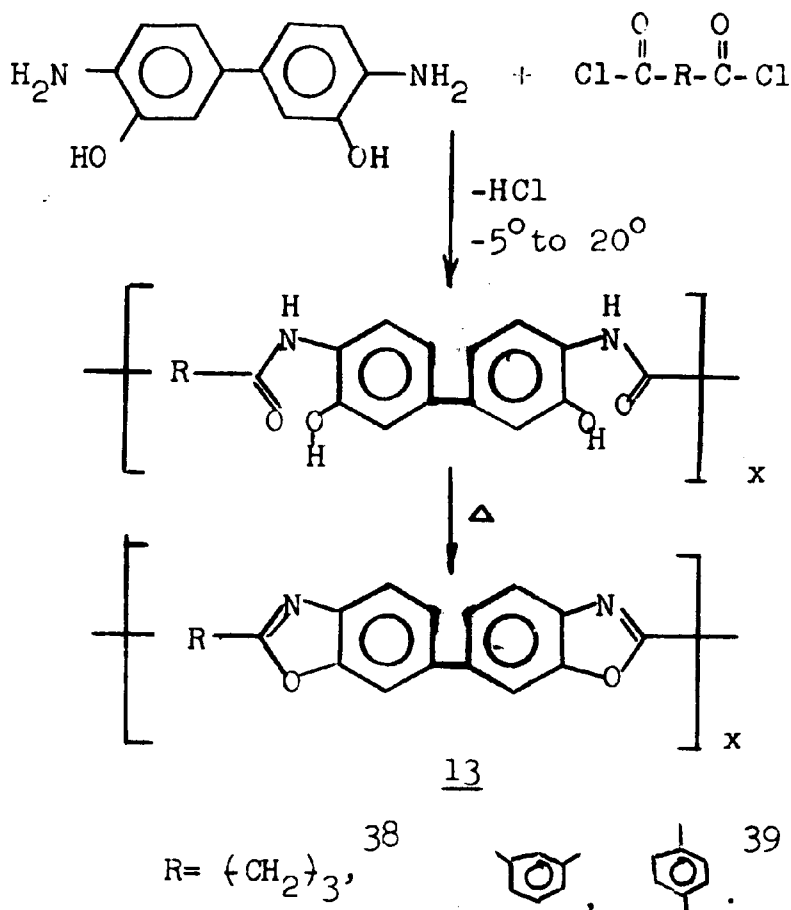
A number of polymers containing benzene rings and "modifying linkages" such as ester, amide, hydrazine, oxamide, and anhydrides has been prepared and investigated extensively. Most of them exhibit good thermal properties as well as useful fiber and film-forming properties. The subject has been discussed fully in excellent articles by Wallenberger¹⁴ and Koton.²⁹

The above data on poly(p-phenylene)-like polymers indicate that the "chain-modifiers" or "inserts" provide solubility and hence the possibility of preparing films and fibers; however, an attendant decrease in melting point and thermal stability also result. The most significant advances in the preparation of thermal polymers have been made since about 1955 with the development of novel polycondensation reactions which include interfacial polymerization^{30,31} and intramolecular post-cyclization reactions.³²⁻³⁵ Other methods of importance discovered recently include

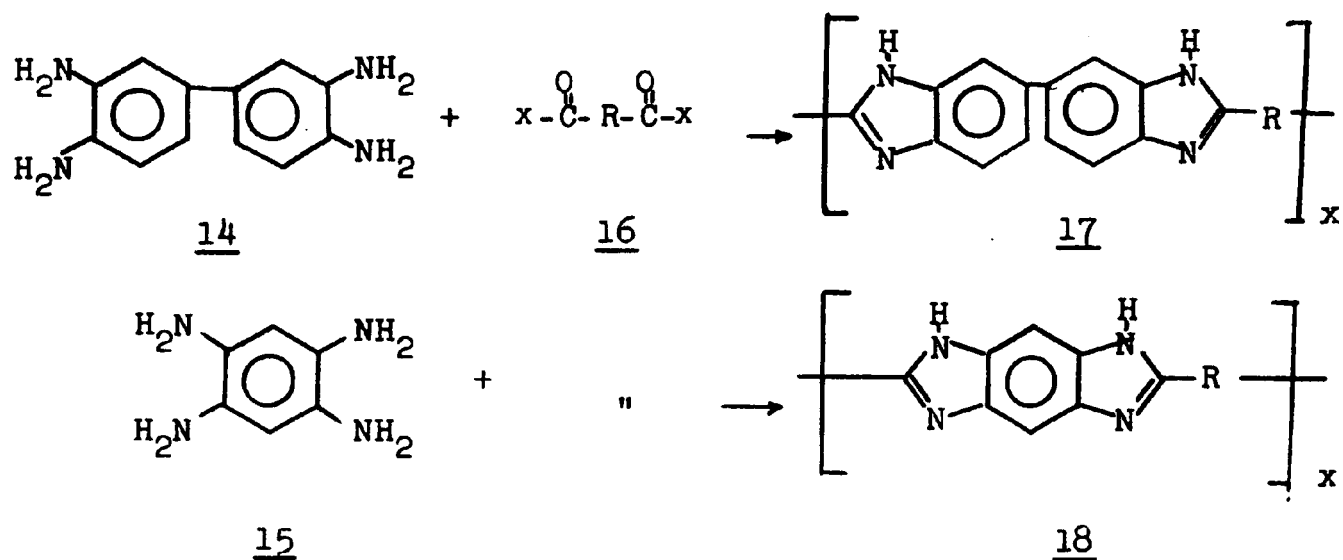
polyrecombination,³⁶ and cyclopolymerization.³⁷ The use of polycondensation reactions allows a number of structural analogues of poly(p-phenylene), especially those containing recurring heterocyclic and aromatic units, to be prepared, and reveals an area of unusual potential and diversity. Polymers of this type resulting from more recent work include polybenzoxazoles,^{38,39} polybenzimidazoles,^{40,41,42} polyoxadiazoles and polytriazoles,^{43,44,45} polypyromellitimides,⁴⁶ polythiazoles,⁴⁷ polybenzothiazoles,⁴⁸ polypyrimidine-quinazolones,⁴⁹ polyquinoxalines,⁵⁰⁻² polybenzborimidazolines,⁵³ poly-s-triazines,⁵⁴ and polyazopyrenes.⁵⁵

Polybenzoxazoles with aliphatic and aromatic linkages in the main chain were first reported in a patent assigned to the DuPont Company.³⁸ Recently, Kubota and Nakanishi³⁹ prepared fully aromatic polybenzoxazoles utilizing the benzoxazole synthesis of Ladenburg.⁵⁶ Polycondensation of a bis(o-aminophenol) with a dibasic acid chloride yields a polyamide intermediate which undergoes cyclodehydration at 220-230°C forming polybenzoxazole 13.

Polymer 13 has excellent thermal stability; no decomposition occurs at 500°C in air; weight loss was 27% at 900°C in a nitrogen atmosphere, or 35% in air.

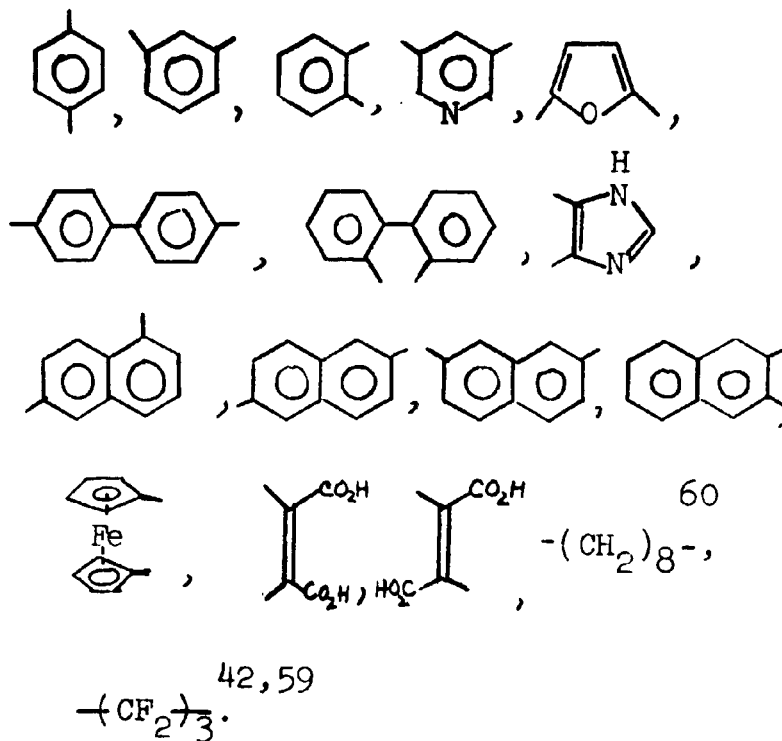


Aliphatic and aromatic polybenzimidazoles have been synthesized by Brinker and Robinson,³⁵ and by Vogel and Marvel,⁴⁰⁻⁴² and several other workers,⁵⁷⁻⁶¹ utilizing the polycondensation of bifunctional carboxylic acids or their derivatives and suitably substituted aromatic tetramines such as 3,3',4,4'-tetraaminobiphenyl and 1,2,4,5-tetraamino-benzene. In general, melt condensations are used;^{35, 40-42, 58,60-61} however, the polymerization can also be successfully carried out using polyphosphoric acid as the catalyst.



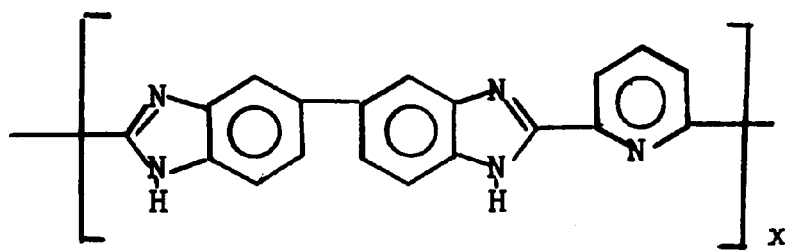
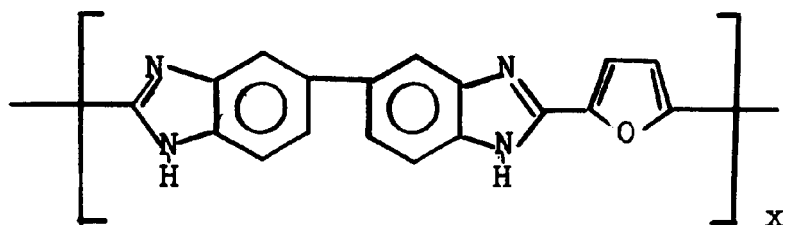
Where $x = -\text{OH}, -\text{OCH}_3, \text{O}^\circ$;

R =



All the polymers studied by Marvel and his colleagues are colored and soluble in sulfuric as well as formic acids. Some are highly crystalline, as indicated by the x-ray

powder patterns. Polymers whose "R" linkages are aromatic moieties have excellent thermal stability. Mixed aliphatic-aromatic polybenzimidazoles from isophthalic acid and 1,2,4,5-tetraaminobenzene(15) or 3,3',4,4'-tetraaminobiphenyl(14) begin to volatilize at 600°C in a nitrogen atmosphere, losing about 30% of their weight at 900°C. Interesting properties are also possessed by poly-2,2'-(pyridylene-2", 6")-5,5'-bibenzimidazole(17a) and poly-2,2'-(furylene-2", 5")-5,5'-bibenzimidazole (17b).

17a17b

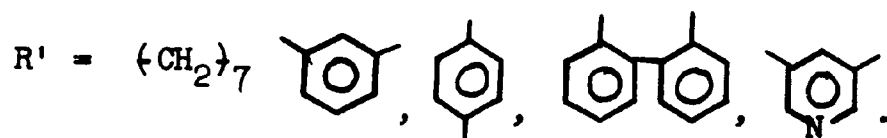
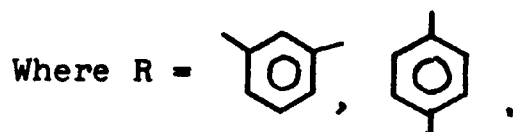
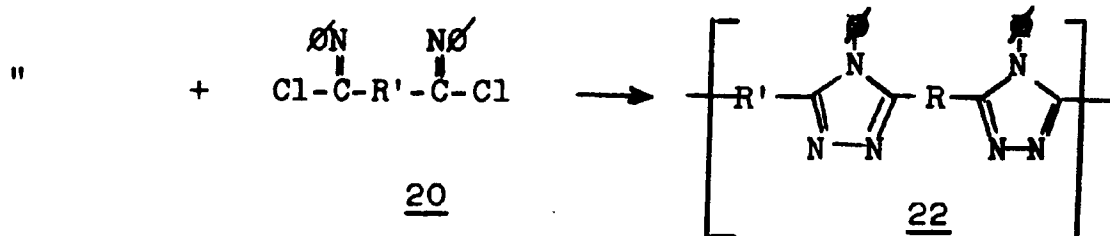
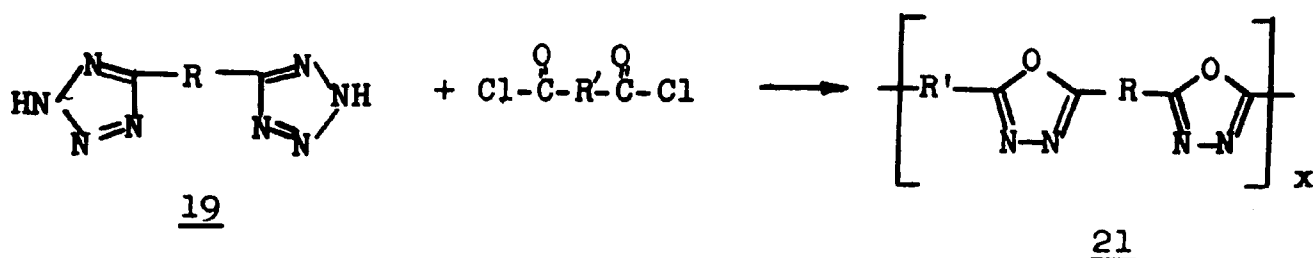
Polymer 17a has outstanding thermal stability; weight loss occurred only above 500°C. Polymer 17b is orange in color and softens at 480°C with little decomposition.⁴⁰

An attempt has been made by Marvel to increase the thermal stability of the polybenzimidazoles by the replacement of the hydrogen atoms by phenyl substituents on the benzimidazole rings.⁴¹ Studies indicate that no appreciable improvement results.

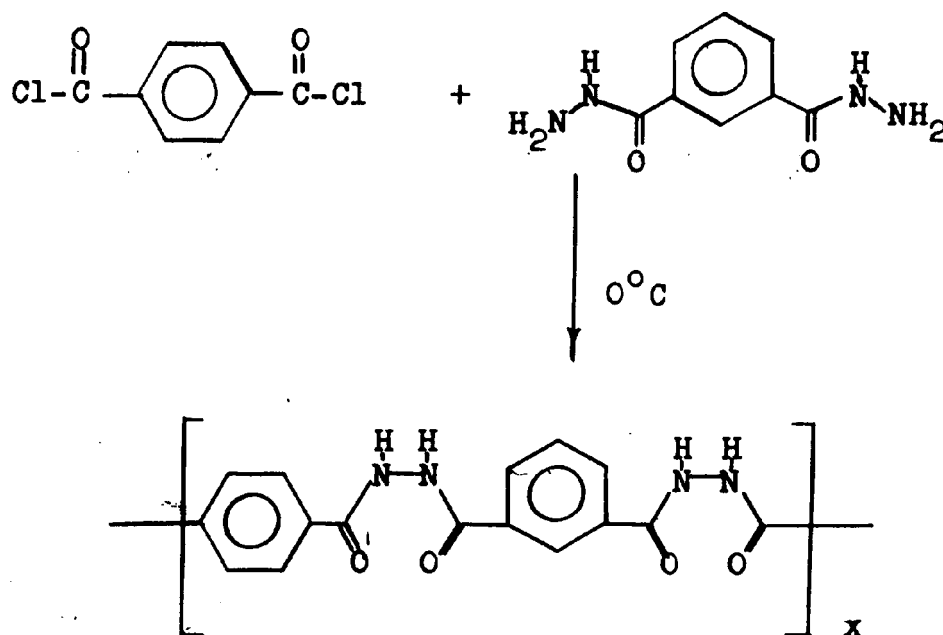
Some of the polybenzimidazoles studied are fiber and film-forming material. One outstanding property noted is that the tensile strength at near 300°C is essentially the same as at room temperature.⁴⁰ Most of the polymers are remarkably stable towards hydrolysis by acids or bases. The polybenzimidazoles, as a class, represent one of the most successful thermal polymers reported thus far.

A discussion concerning the mechanism of formation of the polybenzimidazoles has recently been reported by Wrasidlo and Levine.⁶¹

An elegant method of preparation of polyoxadiazoles and polytriazoles has been reported by Abshire and Marvel⁴³ extending Huisgen's triazole synthesis⁶² to bifunctional compounds. The reaction of a bistetrazole (19) with a dicarboxylic acid chloride in pyridine yields polyoxadiazoles with molecular weights of approximately 6,000. Bistetrazole (19) with bisimide chlorides (20) under similar conditions yields polytriazoles. The softening points of polyoxadiazoles occur at ca. 320°C, and of polytriazoles, at ca. 240°C. Both classes of polymers exhibit some solubility in formic and sulfuric acids.

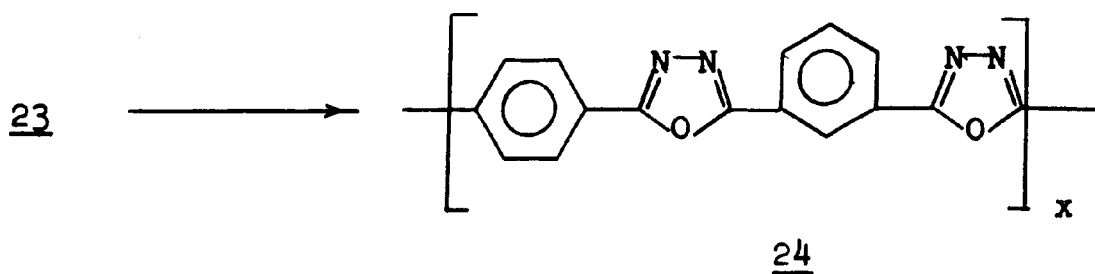


Recently, Frazer and Wallenberger^{44,45} reported a novel procedure for the preparation of polyoxadiazoles via the cyclodehydration of polyhydrazides. A number of high molecular weight aromatic polyhydrazides and heteroaromatic polyhydrazides with melting points between 320°C and >420°C were prepared from aromatic diacid chlorides and aromatic dihydrazides in hexamethylphosphoramide.⁴⁴ For example:

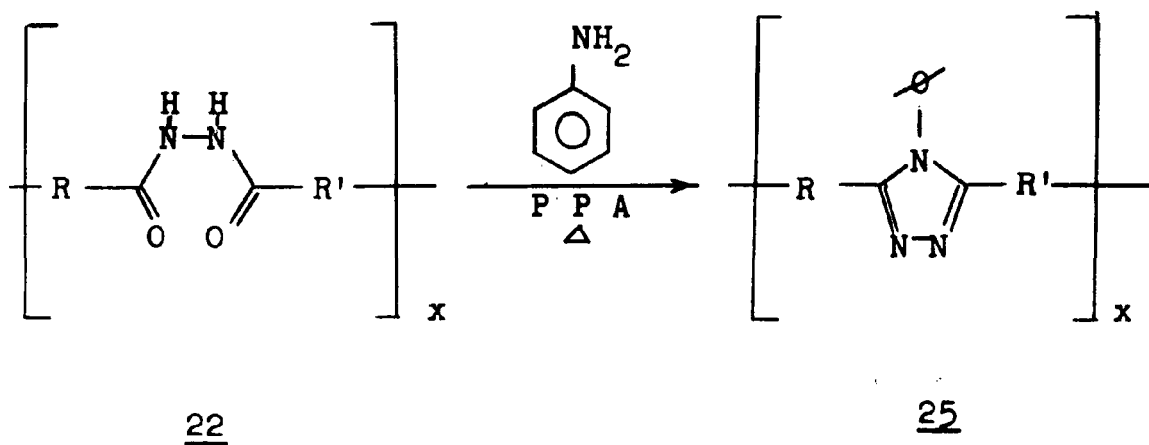


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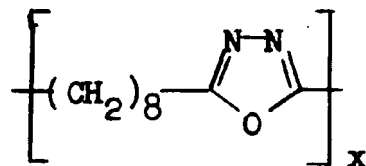
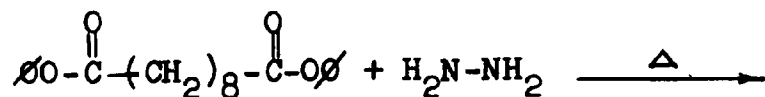
A number of these aromatic-aliphatic polyhydrazides has been converted to high molecular weight poly-(1,3,4-oxadiazoles) by thermal cyclodehydration at 170-280°C.⁴⁵ The resulting polymers have a high inherent viscosity in sulfuric acid and high crystallinity. They resist oxidation and decompose between 450-500°C.⁴⁵



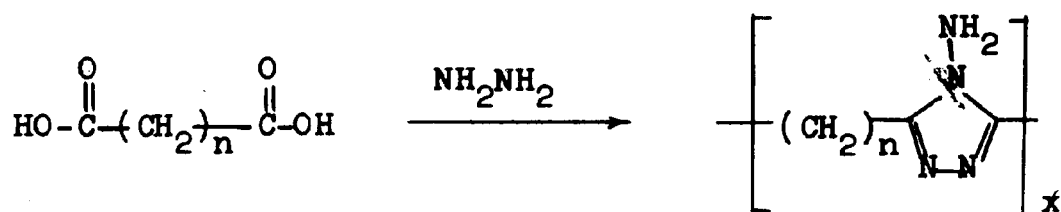
If polyhydrazides are heated with aniline and polyphosphoric acid at 250-265°C, high molecular weight poly(phenylenetriazoles) are obtained.⁶³ Thermogravimetric analysis studies indicate that weight loss was 10% between 470-530°C, under a nitrogen atmosphere.



Hasegawa and Unishi⁶⁴ prepared polyoxadiazole by heating diphenyl sebacate and hydrazine in dimethylformamide at 150°C, followed by thermal treatment at 220-240°C for 14 hours. The polymer is a fiber-former with a melting point at 95-100°C.



Fisher,⁶⁵ and later, Korshak, Chelnokova and Shkolina⁶⁶ prepared well-defined polyaminotriazoles from two moles of hydrazine and one mole of dibasic acid at elevated temperatures and pressures. The polymers are stable to $>300^\circ\text{C}$.

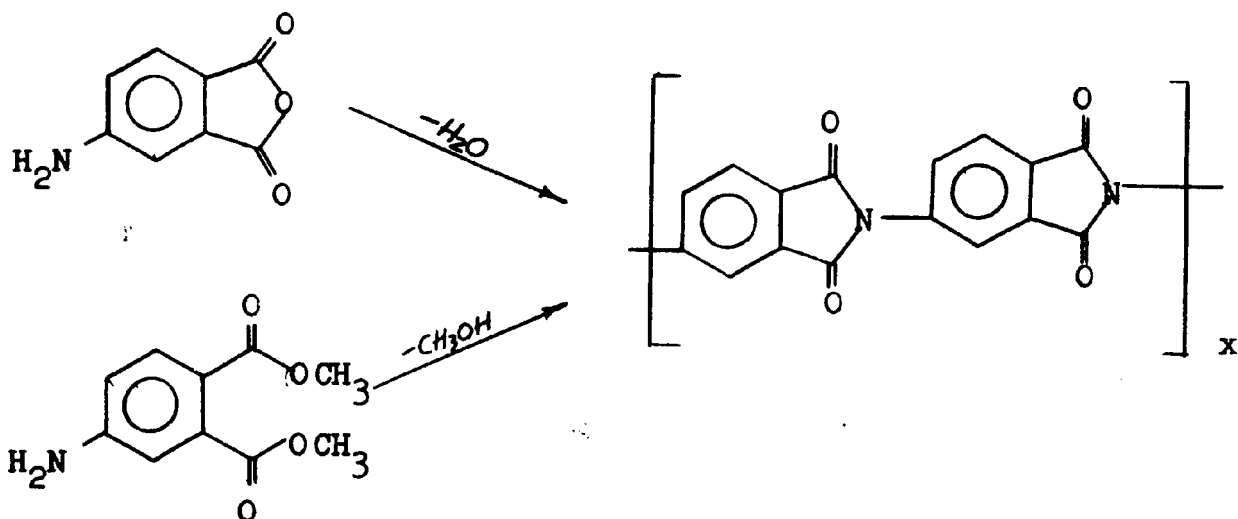


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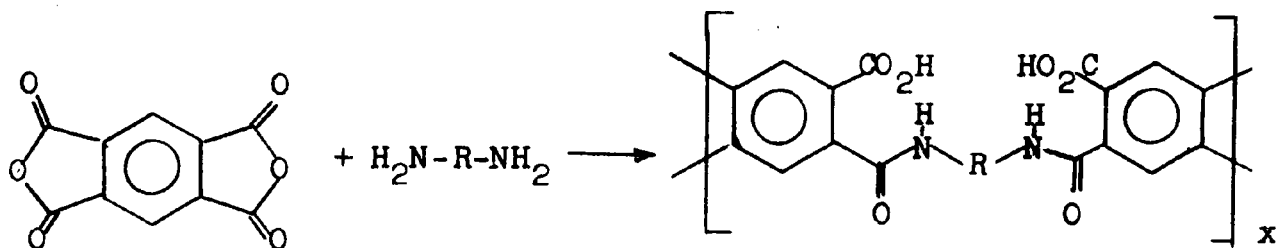
where $n = 2, 3, 4, 7, 8$ and 20 .

The polypyromellitimides represent another class of thermally stable polymers. Films cast from these polymers are stable to 800°C , highly resistant to oxidation, extremely tough and exhibit excellent flame and radiation resistance.⁶⁷⁻⁷³ The first recorded synthesis of a polyimide is that of Bogert and Renshaw,⁶⁷ who observed that 4-aminophthalic anhydride and dimethyl-4-amino phthalate, on heating eliminate water

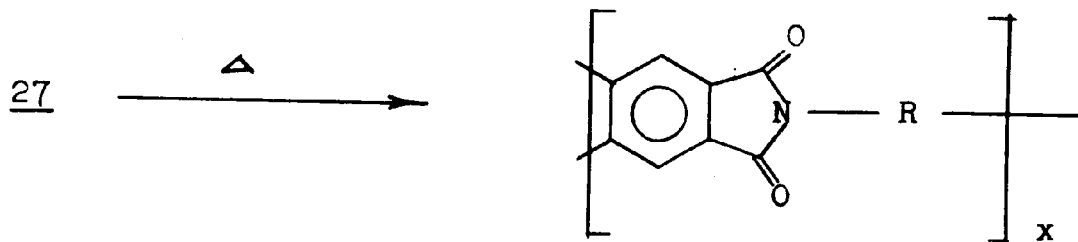
and methanol respectively, yielding polymeric imides.



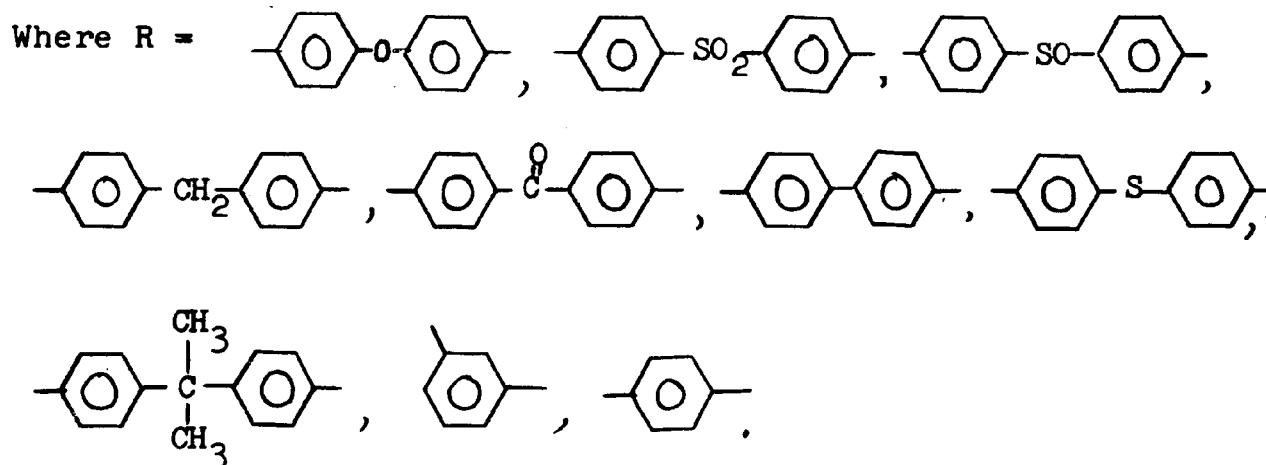
A more recent approach involves the reaction of the commercially available pyromellitic dianhydride and aromatic diamines in a molar ratio of 1:1 in dimethylformamide or dimethylacetamide.⁴⁶



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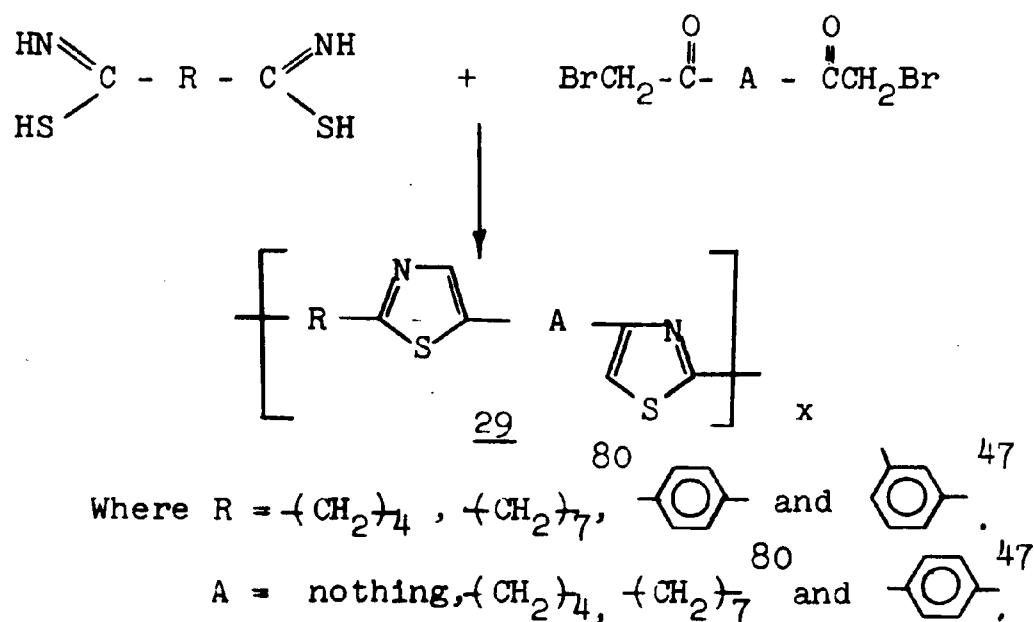
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Films cast from polymer 27 underwent cyclodehydration on heating at 200-250°C to yield the insoluble polypyromellitimide 28.

The mechanism of the polymerization reaction has recently been discussed by Wrasidlo.⁷⁴

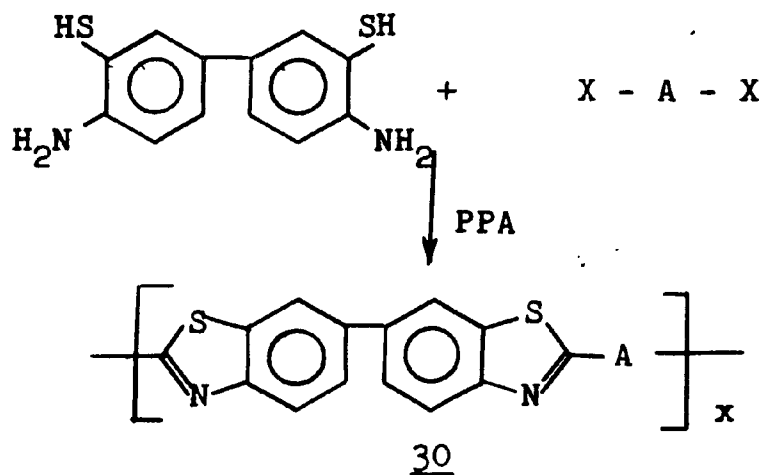
Polymers containing benzene and thiazole rings have been reported by Erlenmeyer and co-workers⁷⁵⁻⁸⁰ utilizing the Hantzsch thiazole synthesis.⁸¹ No detailed characterization of the structures nor studies of the thermal stability of the presumably polymeric material were reported. Mulvaney and Marvel synthesized a number of polymers in the molecular weight range of 5,000-6,000 containing benzene and thiazole rings.⁴⁷ The assignment of structures was based on spectral evidences by comparison with model compounds. Most of the polymers show fair stability at 300°C.



In recent years, a number of investigators have attempted to prepare polybenzothiazoles. Work by Rudner and Brumfield⁸³ failed to yield high molecular weight polybenzothiazoles; this apparently was due to the impurities in the 3,3'-dimercaptobenzidine employed in their preparation. Investigations by Morton and co-workers⁸⁴ utilized the well-known dye reaction which occurs when toluidines are heated with sulfur to prepare benzothiazole polymers. In 1961, Kiprianov and Mushkalo⁸⁵ attempted to obtain polybenzothiazoles by the homopolymerization of 3-mercapto-4-amino benzoic acid or its ester. Difficulties were encountered due to the decomposition of the monomer during the condensation.

A more recent report of Hergenrother and co-workers⁴⁸ describes the preparation of polybenzothiazole (30) via

the reaction of 3,3'-dimercaptobenzidine with an aromatic dicarboxylic acid, or benzothiazole-forming dicarboxylic acid derivatives. The reaction proceeds according to the following general scheme:



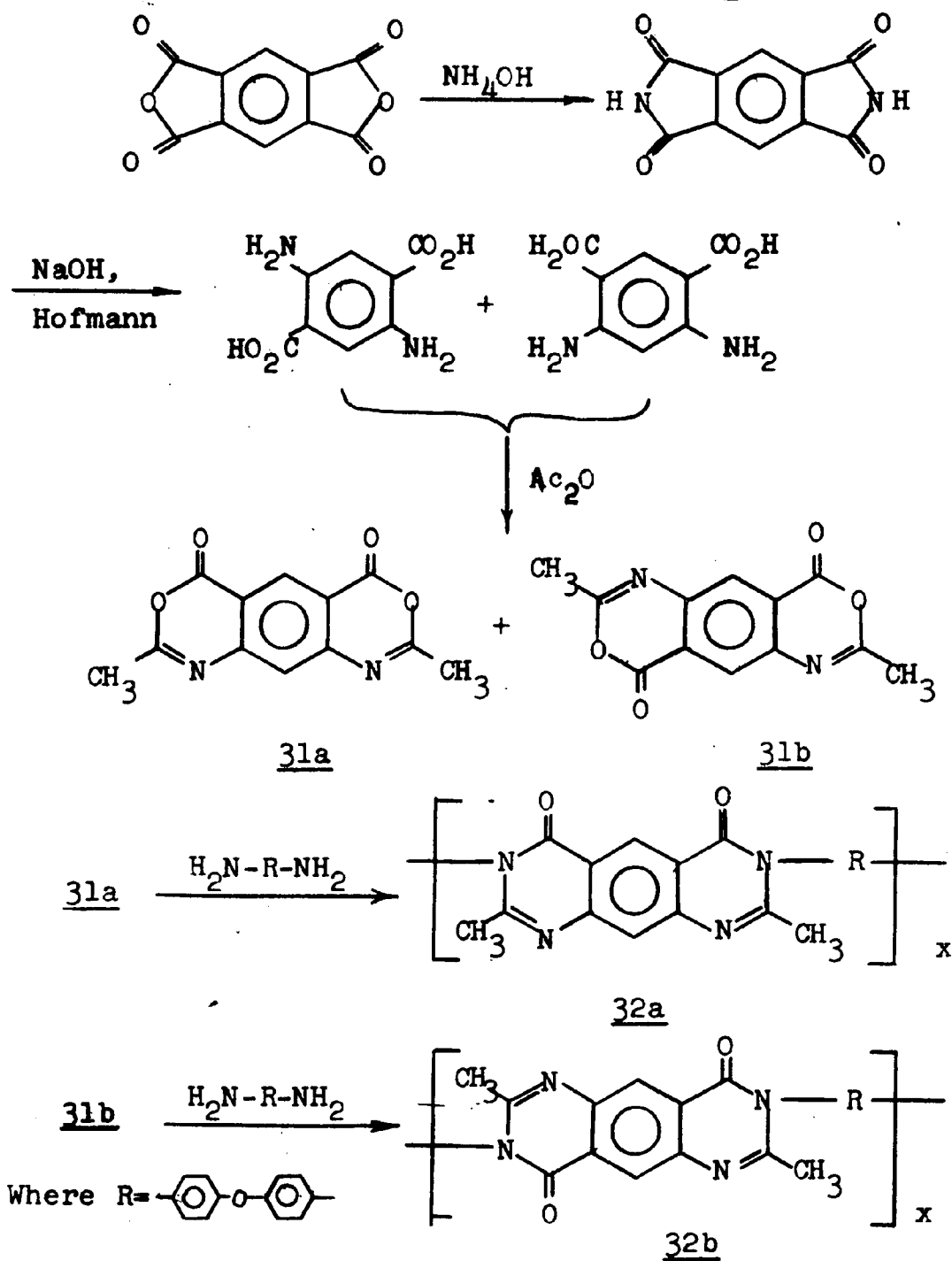
Where $x = -\text{CO}_2\text{H}$, $-\text{CO}_2\text{R}$, $-\text{CONH}_2$, $-\text{COCl}$, $-\text{C}(\text{NH})_2$, etc.

$A =$, etc.

The polybenzothiazoles have excellent oxidative stability. Thermogravimetric analysis studies indicate stability to 593°C in air. The absence of changes in polymer structures at that temperature is substantiated by infrared spectral studies.

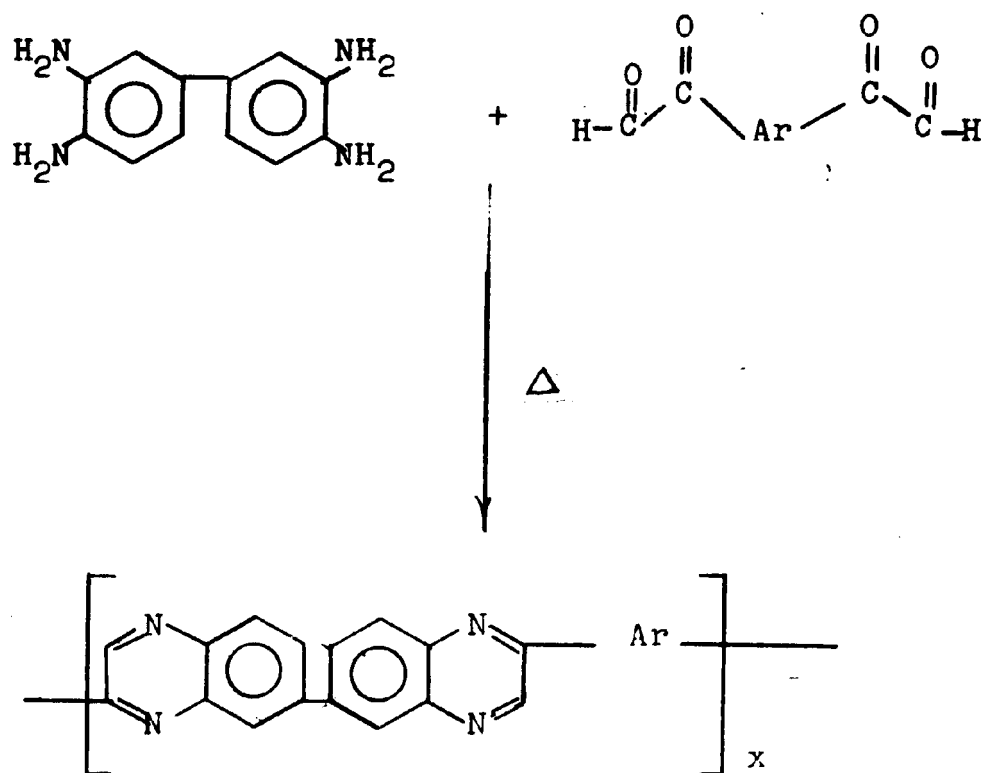
A new class of linear heterocyclic polymers, the polypyrimidonequinazolones, has been reported by Serlin and Markhart.⁴⁹ Pyromellitic dianhydride was treated with excess aqueous ammonia to produce pyromellitic diimide which was subjected to hydrolysis and Hofmann

degradation, followed by treatment with acetic anhydride to form two isomeric benzdi(methyloxazinones) (31a and b). The oxazinones were then treated respectively with 3,3',4,4'-tetraaminobiphenyl in a solid state polymerization to produce the polypyrimido[4,5-g]quinazolones (32a and b).

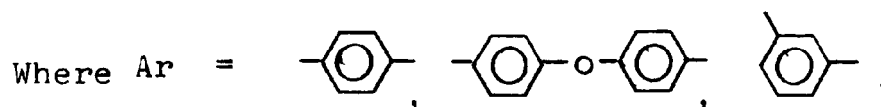


Polymers 32a and b are infusible, but readily dissolve in cresylic acid. A 50% weight loss was observed when the polymers were heated to 300°C in air for 100 hours.

Stille⁵⁰ and de Gaudemaris^{51,52} independently reported the reactions of aromatic tetraamines with certain tetracarbonyl compounds affording polyquinoxalines (33) in nearly quantitative yields.

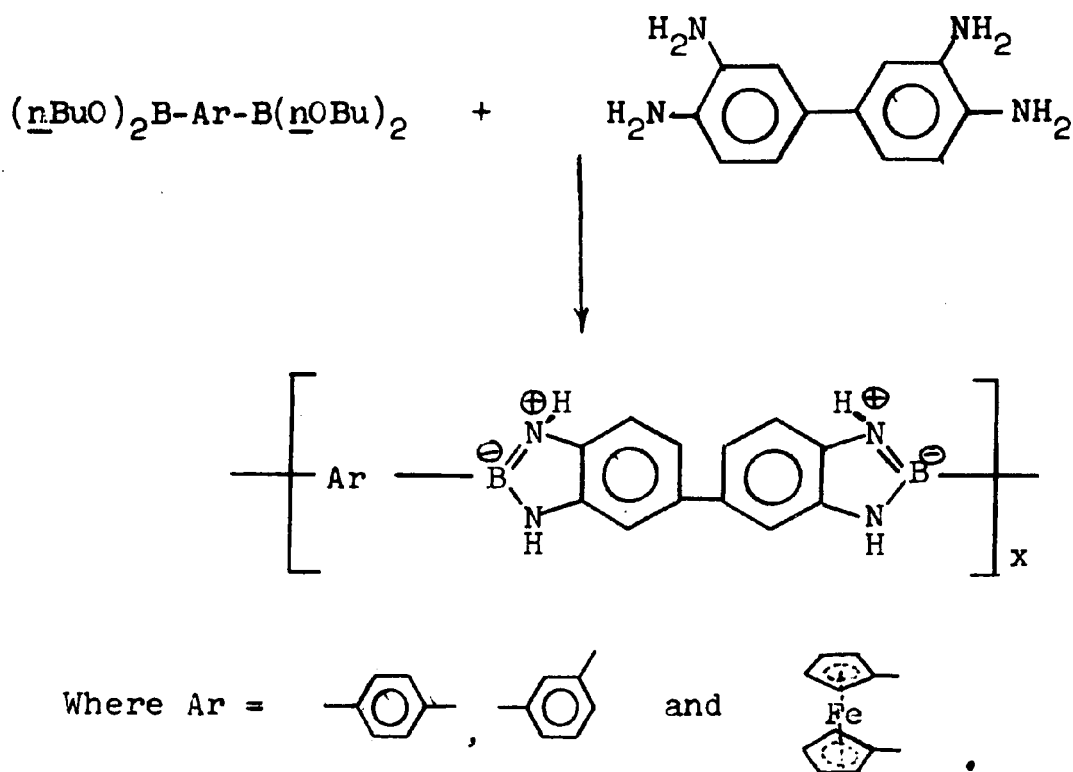


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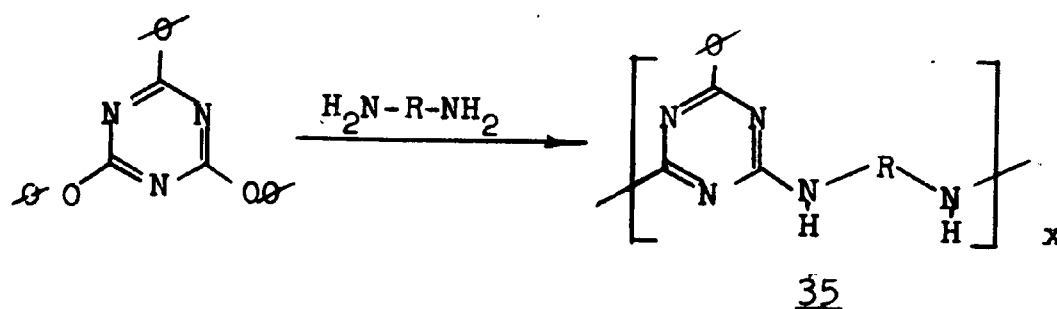
The polymers were insoluble in common organic solvents. Thermogravimetric analysis studies show stability to 500°C in air and 800°C in a nitrogen atmosphere.

Mulvaney, Bloomfield and Marvel⁵³ obtained polybenzborimidazolines using the polycondensation of aromatic tetra-*n*-butyl diboronates with 3,3',4,4'-tetraaminobiphenyl. Solution and melt polymerization techniques were used.



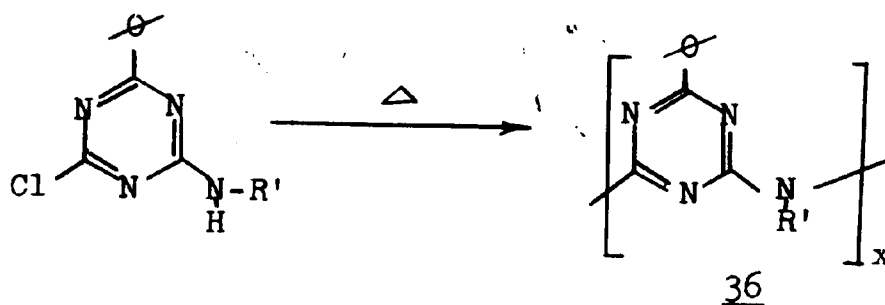
All three polymers prepared were soluble in polar solvents and had inherent viscosities in the range of 0.05 to 0.35. Polymers containing 1,4-phenylene and 1,3-phenylene nuclei were stable to 500-600°C and the ferrocene-containing polymer decomposed at 300-400°C.

Polymers with the s-triazine ring in the main chain have been investigated by Reimschuessel.⁸⁶ Ehlers and Ray⁵⁴ continued and expanded the previous work⁸⁶ and prepared a number of poly-s-triazinyleneamines of the types:



Where R = , , and .

and



Where R' = -CH₃, -CH₂CH₃, C₆H₆-, H, and .

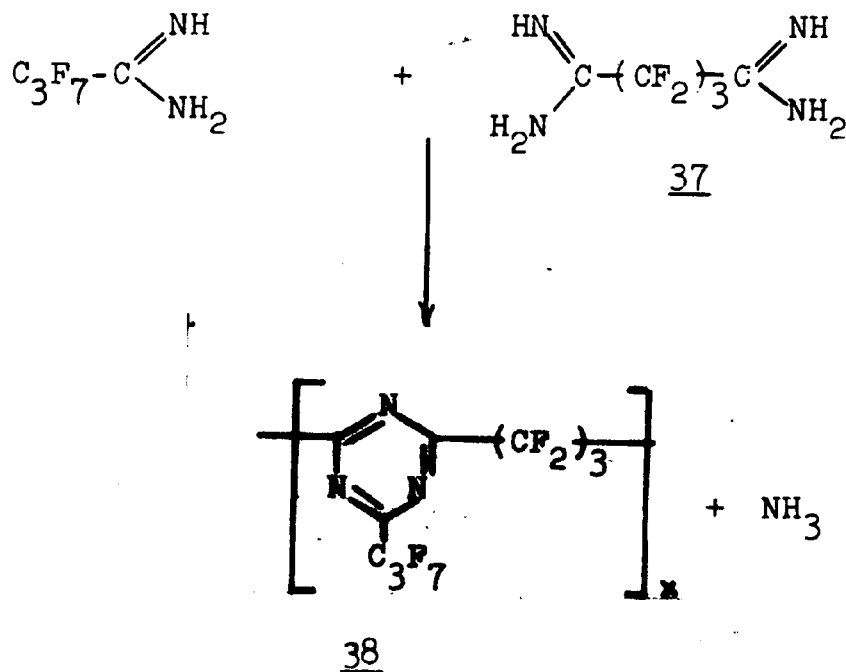
Polymers of the type of 35 were obtained via the melt condensation of 2-phenyl-4,6-diphenoxys-s-triazine with diamines under nitrogen at 250°C for 20 hours. The polymers were soluble in dimethylformamide and methyl ethyl ketone. Molecular weights, based on inherent viscosity data, are

estimated to be between 1300-3000. Thermogravimetric analysis studies (nitrogen atmosphere) show inversion points at 400-450°C.

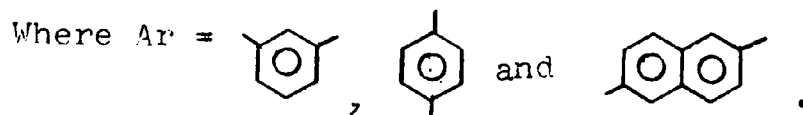
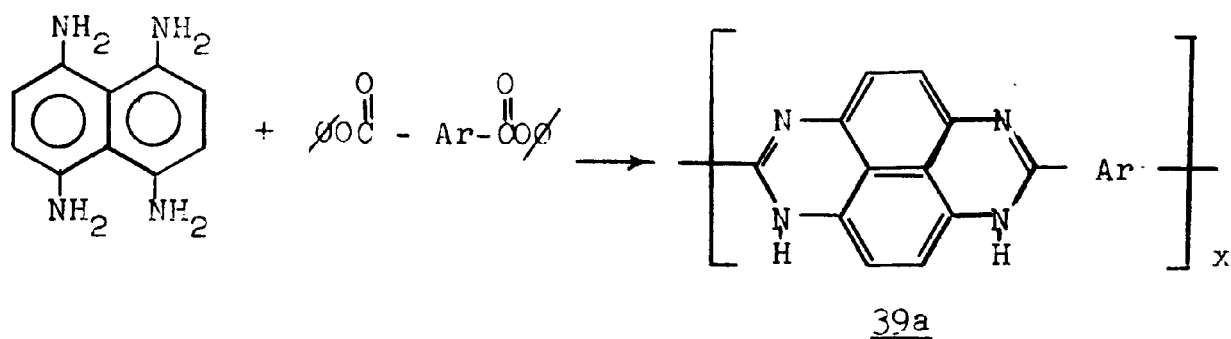
Polymers of the type of 36 were prepared by the melt condensation of amino and chloro-substituted s-triazines or between amino or phenoxy derivatives of s-triazines. Thermogravimetric analysis studies (nitrogen atmosphere) indicate inversion points at 400-450°C.

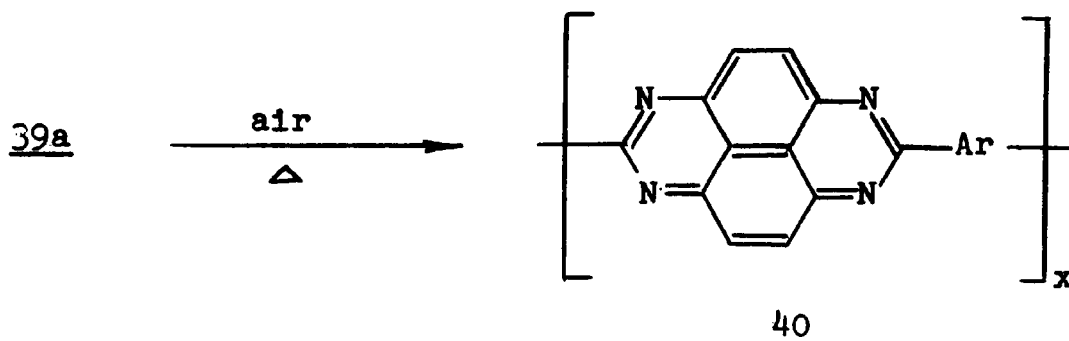
A number of polymers containing both the s-triazine rings and perfluoroalkyl groups in the main chain have been reported by Brown.^{87,88} They were obtained by the condensation of perfluorobutyroamidine and perfluoroglutaric (or adipic) diamidines affording ~~excellent~~ ~~polymers~~ with very high thermal stability. On heating for seventy-two hours at 350°C, the polymer, (38), for example, does not lose weight. It is stable at 400°C and only at 470°C does the weight loss in 30 minutes amount to 30-50%. The polymer also shows unusual chemical resistance. Thus, on boiling with nitric acid for 24 hours, the polymer did not change its properties.

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More recently, with the continuing interest in thermally stable material, Marvel⁵⁵ prepared polymers based on 2,7-disubstituted-1,3,6,8-tetraazopyrene. Polycondensation of 1,4,5,8-tetraaminonaphthalene with various diphenyl esters of bifunctional aromatic acids in diglyme, followed by heating at 300°C for 2 hours gave 40.

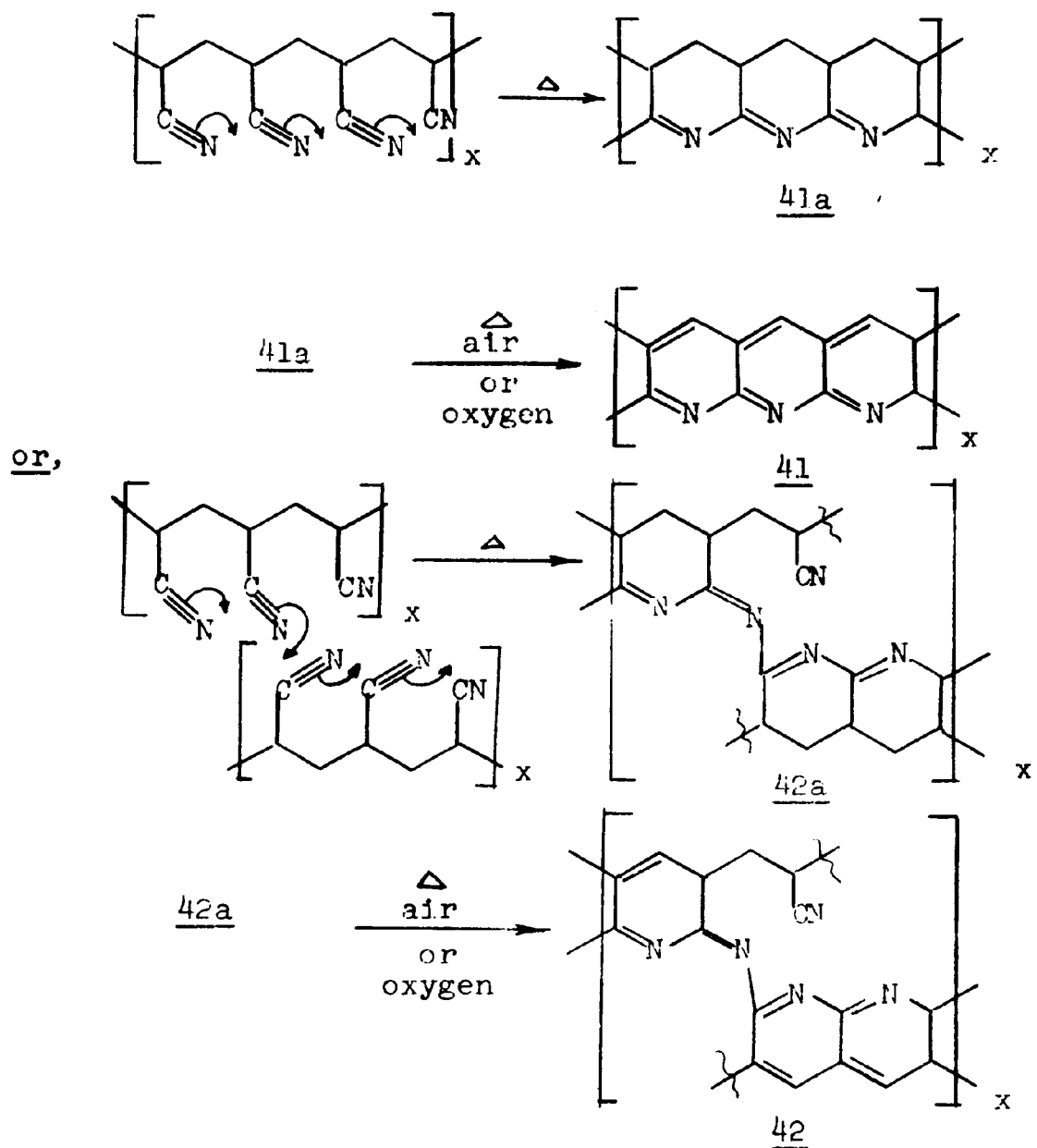




Polymers of the type of 40 show excellent stability to ca. 450-500°C, and with a weight loss of 22% at 840°C in a nitrogen atmosphere. In air, the polymers showed rapid weight loss above 425°C.⁵⁵

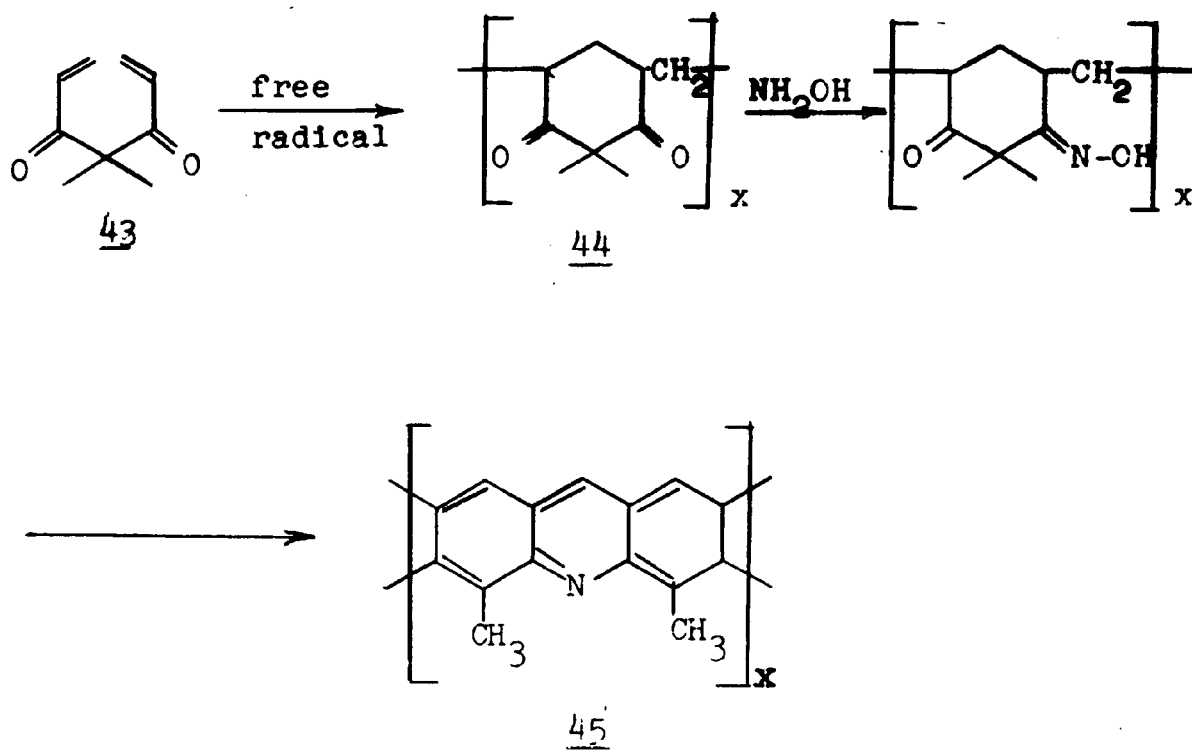
The studies in heteroaromatic polymers indicate that by the use of heterocyclic rings as "inserts" of poly(p-phenylenes), solubility and hence tractability is greatly improved; in addition, there is little sacrifice in thermal stability. Recently, it has been suggested by Marvel⁵⁵ that one approach to obtaining thermally stable organic polymers lies in the development of synthetic routes to the so-called ladder polymers or polymers of two-strand structures, with fully aromatic units, especially those with hetero-atoms -- the heterocyclic analogues of the poly(acenes) and poly(phenes). Preliminary studies by Brown⁸⁹ in silsesquioxane substantiated this speculation. In addition, when polyacrylonitrile is heated, after the evolution of gaseous products, a black powdery material

results. Structures such as 41⁹³ or 42⁹⁴ have been proposed for the product, presumably by a random cyclization mechanism.



This polymer (41 or 42) is extremely stable thermally; no decomposition was observed when the film cast from it was heated to 800°C.

Marvel and co-workers⁵⁵ attempted to prepare a ladder-polymer of this type (41) by starting with diene 43, using free radical polymerization to produce polymer 44 in 95% yield. An attempt to convert the carbonyl groups to dioximes with hydroxylamine failed; only poly(monoöximes) were obtained. Using the Knoevenagel pyridine synthesis, polycyclization of the poly(monoöxime) gave a black, shiny product, soluble in dimethylformamide. Spectral studies indicate that cyclization was not complete. Thermal studies are still in progress.



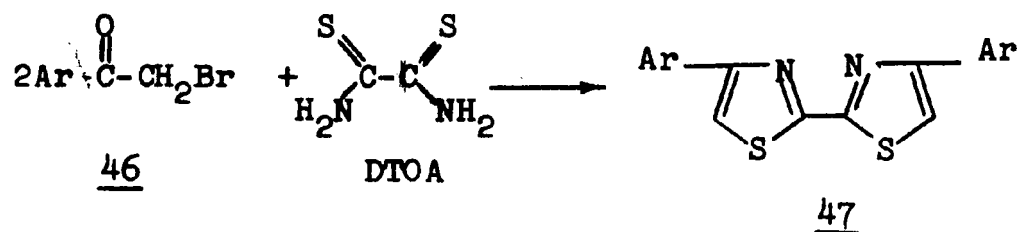
The above discussion attempts to summarize synthetic routes to organic polymers of high thermal stability. Particular attention has been given to the relationship between properties and polymer structures. In addition to the "organic" approach described here, much effort has also been directed towards the use of inorganic polymers and co-ordination polymers as possible solutions. Both of these approaches have been discussed in excellent review articles by Krause,⁹⁵ Rode,⁹⁶ and Eilar.⁹⁷

II. INTRODUCTION

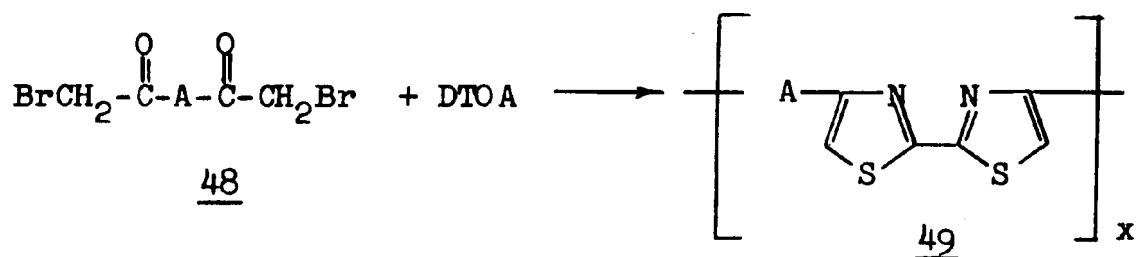
Recent investigations indicate that polymers possessing heteroaromatic or mixed aromatic-heteroaromatic units in the main chain show outstanding thermal stability and reveal an area of unusual potential and diversity. It was the purpose of this research to develop organic reactions that would afford new heteroaromatic or mixed aromatic-heteroaromatic moieties, with the aim of generating thermally-stable polymerizates. One reaction which appeared to be attractive was the condensation of halomethyl ketones with the commercially available dithiooxamide, an application of the Hantzsch thiazole synthesis.⁸¹ This reaction was of particular interest because it would allow the preparation of requisite monomers of great structural diversity. The correlation of gross polymer properties with controlled structural variations, e.g. extent of conjugation, presence of flexible and hetero-atom linkages, etc., would then be feasible.

Aryl bromomethyl ketones (46) and dithiooxamide (DTOA) afford 4,4'-diaryl-2,2'-bithiazoles (47) with useful yields (>80%) and of high melting points: 47, Ar= phenyl,⁷⁵ β -naphthyl⁹⁸ and p-biphenyl⁹⁹; m.p. 222°, 278° and 347° respectively. The use of 1,4-dibromobutane-2,3-dione⁷⁶ and 1,3,5-tris-(bromoacetyl)-benzene¹⁰⁰ in the condensation have been reported to yield "brown, amorphous, high molecular weight condensation products", however, the resulting

material, presumably polymeric in nature, was not characterized.



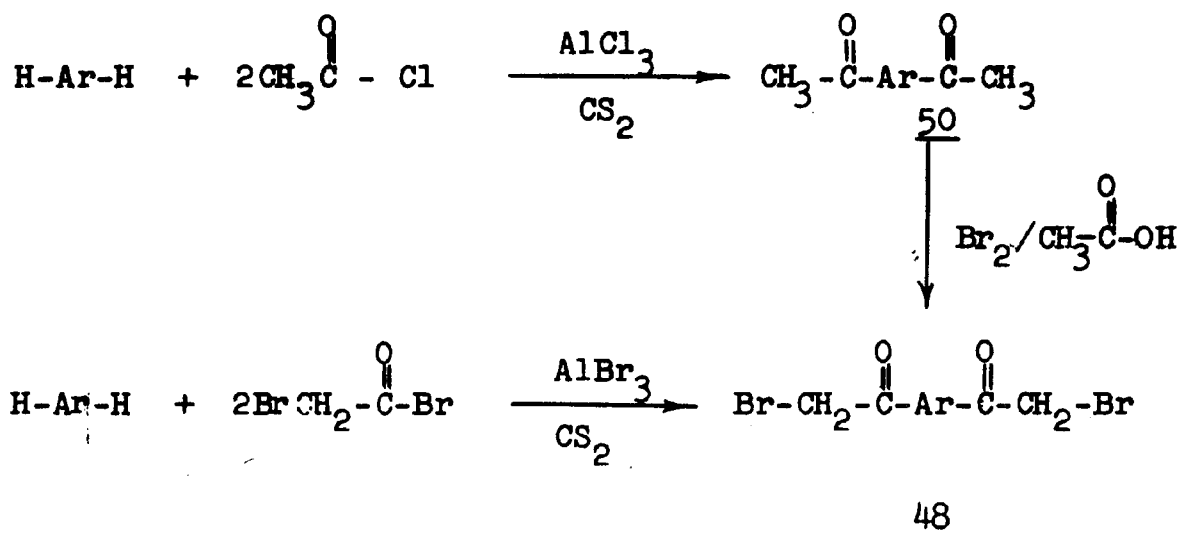
For polymerization purposes, the requisite bifunctional aryl halomethyl ketones would in general be accessible via the Friedel-Crafts acylation of the corresponding aryl compounds. This approach allows desired structural variations of the type:



A = Ar, (Ar)_n, ArRAR, ArOAr, heteroaromatic, etc.

A. AROMATIC POLYBITHIAZOLES

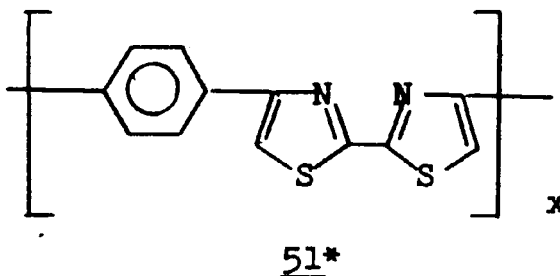
Bifunctional aryl bromomethyl ketones (48) were prepared by the bisacetylation of the appropriate aromatic substrates to produce diketones 50. Bromination of 50 afforded monomers 48. In certain cases, aromatic substrates were bisbromoacetylated using bromoacetyl bromide and aluminum bromide to produce monomers 48 in one step.



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of DMF (153°) affording, within fifteen minutes, a finely divided polymer precipitate. Purification of the resulting polymers was by a continuous extraction (Soxhlet) technique using DMF, ethanol, and ether in that order. The residual polymer, after being dried in vacuo, was used for yield calculation and subsequent characterization.

The use of p-bis(bromoacetyl)benzene as comonomer generated poly-4,4'-(p-phenylene)-2,2'-bithiazole (51) which was obtained in 88% yield as yellow-brown solids.



As a prototype in the series, this polymer was examined most extensively. It is insoluble in a variety of organic solvents including (at 90°) dimethyl sulfoxide, dimethylacetamide, formic acid, phenyl ether, diphenylmethane and quinoline; however, it readily dissolves in cold concentrated sulfuric acid, as do all polymers in this series. The polymer is highly refractory; it does not melt when heated to 520°C in a sealed tube; a 5 mg. sample heated with a full flame of a grid burner and in an open crucible

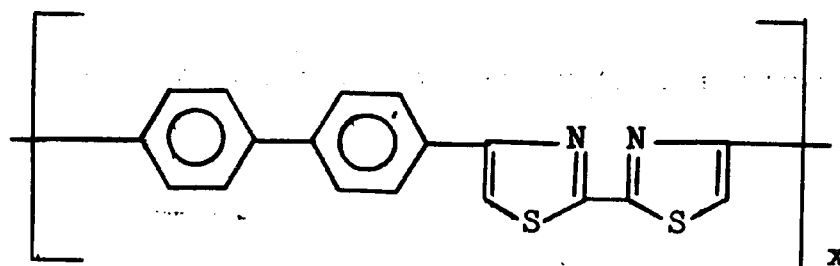
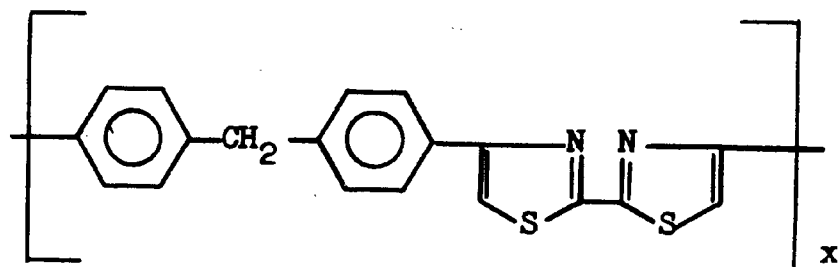
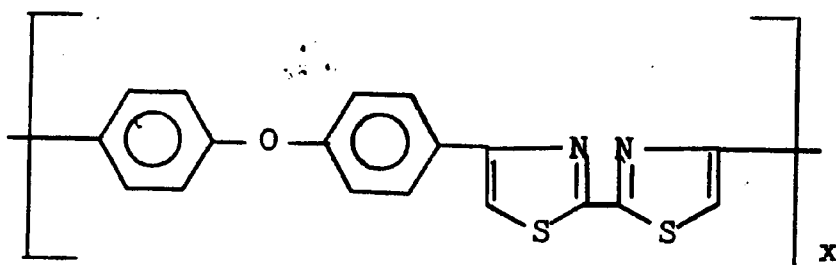
*51a refers to poly-4,4'-(p-phenylene)-2,2'-bithiazole prepared using DMF solvent.

*51b refers to poly-4,4'-(p-phenylene)-2,2'-bithiazole prepared using diglyme solvent.

required three minutes for complete combustion, showing no melt and leaving no residue. The combination of insolubility and infusibility suggested the formation of a highly cross-linked polymerizate, however, subsequent chemical and structural work negated this possibility. Debye-Scherrer powder patterns reveal that 51a is highly crystalline. Elemental analyses (see Table I.) are quite good for the anticipated repeating unit and imply structural integrity and high molecular weight. The polymer has a number average molecular weight ($\bar{M}_n$) of about 12,000 or approximately 50 recurring units, based on bromine analysis and the assumption of an average of one bromine end group per polymer chain. It is difficult to assess the validity of the above assumption of the average of one bromine end group per chain. However, the complete analytical data on all polymers indicate that the molecular weights are indeed high. In addition, the relative molecular weights of all polymers in this series, based on bromine contents, are internally consistent with the physical data indicating some degree of accuracy. In this work, therefore, estimates of polymer molecular weights are based on end group analyses. Solution methods for molecular weight determinations are not applicable in all cases due to difficulties in the dissolution of the polymers.

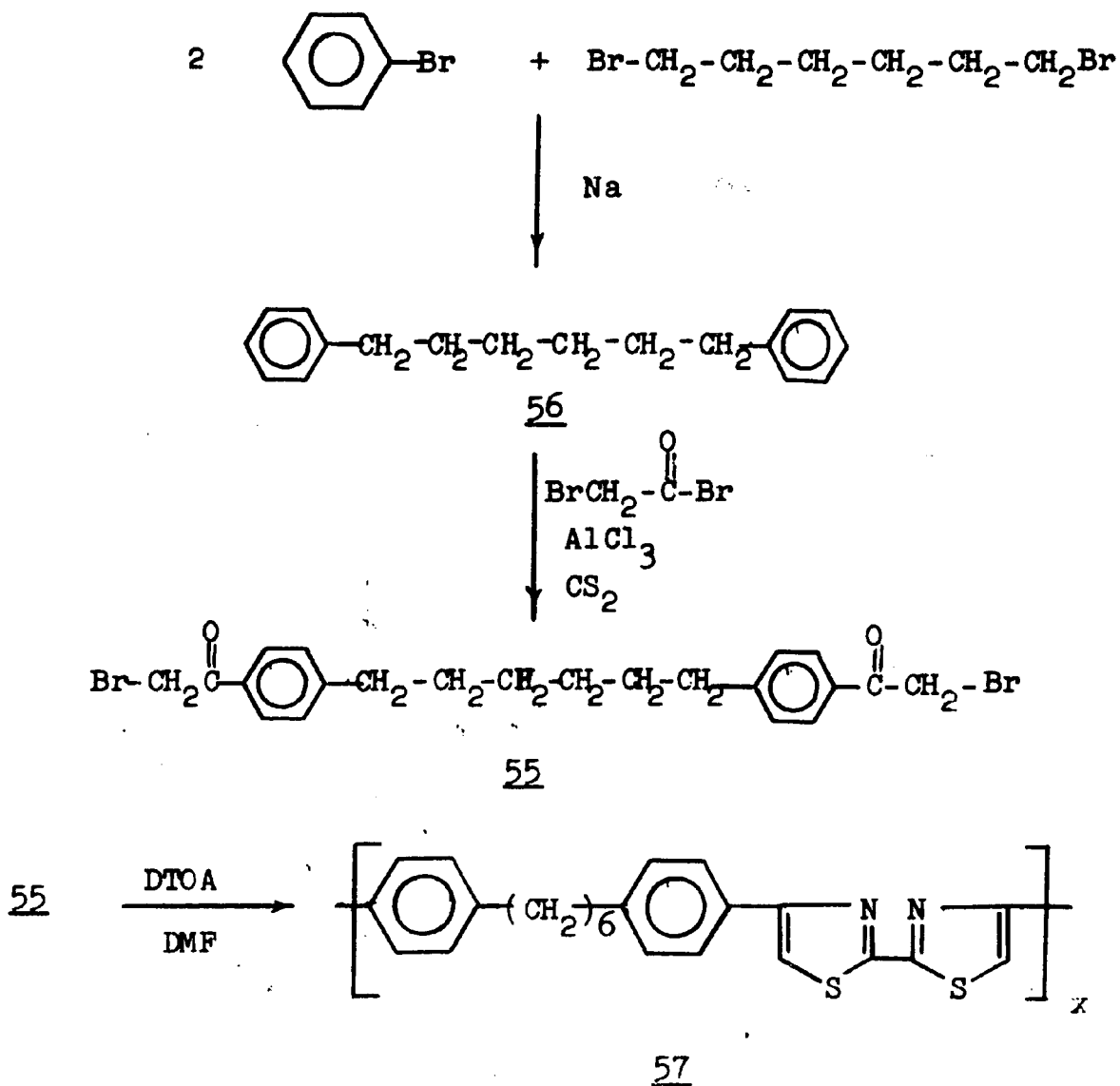
With the encouraging results of polymer 51a, studies were extended to the preparation and characterization of

polybithiazoles based on biphenyl, diphenylmethane and diphenyl ether substrates (polymers 52, 53, 54 respectively).

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As anticipated, these polymers are characteristically insoluble in common organic solvents, and do not melt at 520° in a sealed tube. Elemental analyses for these polymers are quite good, and again imply structural integrity and high molecular weights. Based on bromine end group analyses,

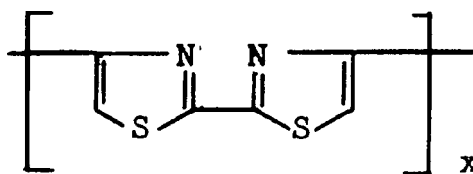
the molecular weights for 52, 53, and 54 are 84,000, 11,000 and 80,000, respectively. All three polymers are highly crystalline, as indicated by the x-ray powder patterns. In view of this crystalline character, it appeared unlikely that insolubility and infusibility were the result of the formation of extensively cross-linked polymerizates; however, this possibility was explored further. If the polycondensation reaction utilized here does indeed afford a linear polymerizate, a modification of the polymer structure such as the introduction of flexible linkages into the recurring unit should markedly alter the physical properties of the resulting polymers. The utilization of the bis-bromoacetyl derivative of 1,6-diphenylhexane as monomer provided such evidence. Using the procedure of Van Alphen,¹⁰² bromobenzene was treated with 1,6-dibromohexane in the presence of sodium to produce 1,6-diphenylhexane (56). Bis-bromoacetylation of 56 in the usual manner followed by purification using column chromatography (silica gel) yielded 55 in about 10% yield. Polymerization of 55 with DTOA produced polymer 57 in three fractions (total yield, 89%) based on solubility in dimethylformamide. (See Table I).



The fractions of 57 exhibit successively decreasing crystallinity, number average molecular weight and melting point with attendant increasing solubility. The major fraction of the polymer (Fraction A) is insoluble in hot dimethylformamide; it has a relatively sharp melting point and is highly crystalline. Fraction B, soluble in hot but

insoluble in cold dimethylformamide, and Fraction C, soluble in cold dimethylformamide, are quite similar to each other. Both display lower and wider melting ranges along with decreased crystallinity than Fraction A. The number average molecular weights based on end group analysis are 80,000, 12,000, and 11,000 for Fractions A, B, and C, respectively. The evidence obtained for polymer 57 appears to substantiate the assumption that the polymerization reaction utilized here indeed affords linear polymerzates.

An attempt has also been made to prepare a polymer consisting completely of thiazole rings (58).⁷⁶



58

Starting with the commercially available 2,3-butanedione, monomer 1,4-dibromobutane-2,3-dione was prepared. Condensation of this monomer with dithiooxamide in absolute ethanol⁷⁶ affords a dark brown powder in 18% yield, after purification (continuous Soxhlet extraction with ethanol and then ether). Elemental analyses are not good for the polymer recurring unit, however, Debye-Scherrer powder

patterns indicate some degree of crystallinity, in contrast to the report of Bischoff.⁷⁶ The same polycondensation was carried out utilizing dimethylformamide as the polymerization solvent; a black powder in 11% yield (after the standard purification technique) with fair elemental analyses for the anticipated recurring unit was obtained. Based on x-ray powder patterns, the polymer exhibits some degree of crystallinity. Due to the only fair elemental analyses for the recurring unit for polymer 58, no further work was done in regard to the properties and structural characterization.

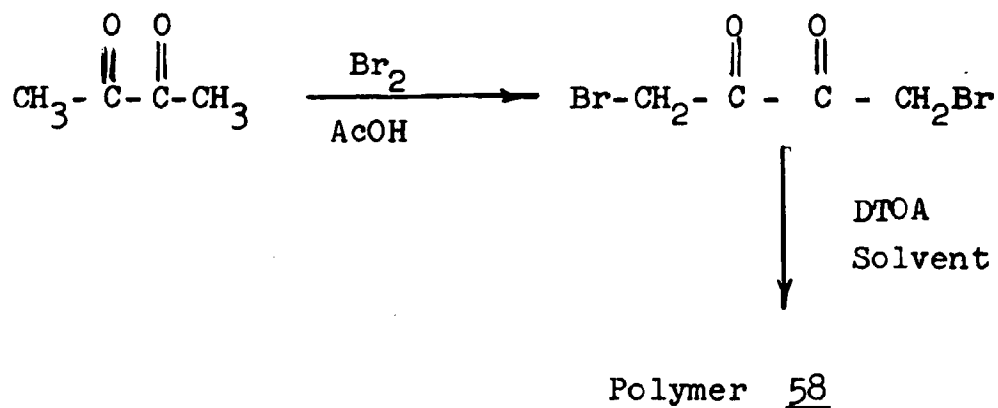
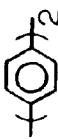
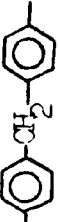
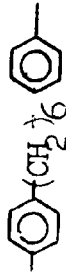


TABLE I

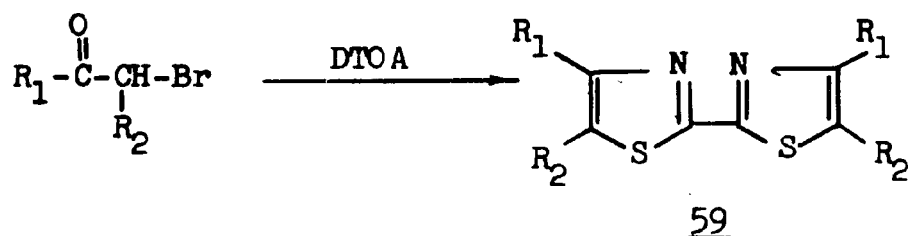
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES

Polymer	Unit A	% Yield ^a	η^b	$\bar{M}_n^c$	M.p. °C	Analyses, % Calcd.				
						(Found)				
						C	H	N	S	Br
51a		88	0.23	12,000	>520	59.48 (59.23)	2.49 (2.87)	11.56 (11.41)	26.47 (25.20)	0.00 (0.54) 0.76)
52		79	0.24	84,000	>520	67.89 (67.36)	3.17 (3.53)	8.80 (8.00)	20.14 (18.85)	0.00 (0.00) 0.19)
53		78	0.47	11,000	>520	68.64 (68.79)	3.64 (3.70)	8.43 (8.44)	19.29 (19.05)	0.00 (0.70)
54		79	0.38	80,000 ^d	>520	64.65 (64.24)	3.01 (3.47)	8.38 (8.36)	19.18 (18.81)	0.00 (0.0) 0.0).
57										
Fraction A		56	0.40	80,000 ^d	440-448	71.60 (71.60)	5.51 (5.69)	6.96 (6.85)	15.93 (16.19)	0.00 (0.0)
Fraction B		15	0.1	12,000	238-252	(71.02)	(5.71)	(6.85)	(...)	(0.66)
Fraction C		18	<0.1	11,000	218-235	(69.31)	(5.49)	(6.42)	(...)	(0.71)

^aYield of purified polymer (see Experimental). ^bInherent viscosity at 25.0° and at a concentration of 0.25g/100ml. in concentrated sulfuric acid. ^cNumber average molecular weight based on bromine content. ^dBased on 0.1% Br; Beilstein test indicates less than 0.1% Br. ^eMelting point refers to crystalline melting point.

B. STRUCTURAL CHARACTERIZATION

While the elemental analytical data for the polymers support the assignment of the recurring bithiazole units, confirmatory data for these structures were obtained from ultraviolet and infrared spectra. For use as models, a number of 2,2'-bithiazoles were prepared via the condensation of mono-bromomethyl ketones with dithiooxamide:



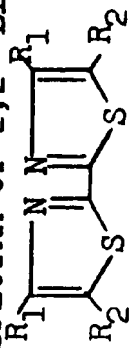
R_1 and R_2 = aromatic or aliphatic substituents.

Ultraviolet spectra of the model compounds were obtained using potassium bromide disks, a medium which proves to be very useful for the examination of the insoluble polymerizates described above. Simple thiazoles¹⁰³ generally exhibit a maximum absorption in the region 240-260 mμ with log ε above 3.6. There is little data available on the 2,2'-bithiazole system. However, based on the relatively small number of examples listed in Table II, certain characteristics are discernable. The 2,2'-bithiazole system with aromatic substituents displays a low wavelength band (ca. 230-250 mμ) of strong intensity and a high wavelength band of medium

intensity (ca. 340-360 m μ). The absence of aryl substituents causes a reversal of these relative intensities, i.e., the low wavelength band becomes the weaker (compounds 60 - 63) and the high wavelength band becomes the stronger. In addition, the position of the low wavelength band is rather sensitive to the nature of the aromatic substituent present while the high wavelength band appears to be rather stationary, appearing close to 360 m μ (e.g. compare 66, 67, 68).

The ultraviolet spectra of the poly-4,4'-diaryl-2,2'-bithiazoles are summarized in Table II. The polymers exhibit the anticipated low wavelength absorption of strong intensity and variable position and the high wavelength band of medium intensity close to 360 m μ . Polymer 52 is the only exception exhibiting a marked bathochromic shift at both high and low wavelengths. The closest chromophore match between model compounds and polymers exists in model 66 and polymers 53 and 57. Significantly, the spectra of these three species are quite similar. The spectra of all three fractions of polymer 57 are similar. Fraction C is sufficiently soluble in ethanol to yield a solution spectrum. In general, based on several examples (see Tables II and III), the spectra obtained using the potassium bromide disk technique and in solution are comparable; minor differences in extent of fine structure and exact location of maxima do occur. The close correspondence of solution and potassium bromide spectra indicates the usefulness of the latter medium for the examination of completely insoluble polymers.

TABLE II
ULTRAVIOLET SPECTRA OF 2,2'-BITHIAZOLES



Cpd.	R ₁	R ₂	Medium	Band ^a	
				Low λ	High λ
<u>60</u>	CH ₃	H	KBr	230m	332s, 337s, 344sh, 355sh, 364sh
<u>61</u>	CH ₃	CH ₃	C ₂ H ₅ OH	228(3.81)	330(4.34), 341sh(4.25)
<u>62</u>	CH ₃	OO ₂ C ₂ H ₅	KBr	239m	350s, 367sh
			KBr	252m	345s
			C ₂ H ₅ OH	248(3.73)	340sh(4.32), 348(4.37), 351(4.38), 361sh(4.25)
<u>63^b</u>	CH ₃	CH ₂ CH ₂ OH	?	< 240 ^c	360(4.25)
<u>64^d</u>	C ₆ H ₅	C ₆ H ₅	CHCl ₃	< 260s ^e	376m(4.26)
<u>65</u>	C ₆ H ₅	H	KBr	248s, 268sh	360m
			C ₂ H ₅ OH	248(4.59), 258sh(4.45)	350(4.10), 358sh(4.04)
<u>66</u>	p-C ₆ H ₅ CH ₂ C ₆ H ₄	H	KBr	249s, 269sh	359m
<u>67</u>	p-C ₆ H ₅ C ₆ H ₄	H	KBr	294s	364m
<u>68</u>	p-C ₆ H ₅ OC ₆ H ₄	H	KBr	266s	355m

^a s = strong absorption, m = medium absorption, sh = inflection point; log ε values in parentheses.

^b P. Karrer and M. C. Sanz, *Helv. Chim. Acta*, 26, 1778 (1943). ^c Spectrum not recorded below 240 mμ.

^d P. Karrer and F. Forster, *Helv. Chim. Acta*, 28, 315 (1945).

^e Spectrum not recorded below 260 mμ.

TABLE III
ULTRAVIOLET SPECTRA OF POLY-4,4'-DIARYL-2,2'-BITHIAZOLES

<u>Polymer</u>	<u>Medium</u>	<u>λ_{max}</u>	
<u>51a</u>	KBr	311s	360m
<u>52</u>	KBr	321s	375m
<u>53</u>	KBr	265s	365m
<u>54</u>	KBr	286s	359m
<u>57</u> ^a	KBr	258s	362m
	Ethanol	255s	355m

^a Fraction C

Absorption in the infrared region also proved helpful in characterizing the polymers. Spectra of the model compounds and polymers were obtained using potassium bromide disks. The spectra of the 4,4'-diaryl-2,2'-bithiazoles (65-68) (see Table II) exhibit three strong sharp bands in the region $740\text{-}940\text{ cm}^{-1}$. These bands, distinguishable from the aromatic hydrogen out-of-plane deformations in this region, appear very close to 749 , 884 and 942 cm^{-1} . The spectra of model bithiazoles without aryl substituents (60 - 62) lack one or more of these absorption bands. The lack of correlation between the number and position of the bands between $930\text{-}650\text{ cm}^{-1}$ region and the pattern of substitution in the simpler monothiazoles has been discussed,^{104, 105} although little information is available for the bithiazole system. Examination of the spectra of polymers 51a through 57 reveals that each displays the above three bands. In all nine models and polymeric 4,4'-diaryl-2,2'-bithiazoles these bands occur within the **remarkably** narrow ranges $940\text{-}944$, $882\text{-}887$ and $743\text{-}755\text{ cm}^{-1}$. The examination of additional examples of structures 47 and 49 will establish the diagnostic value of these bands for these systems.

C. POLYMER STABILITIES

1. Thermal Stability

The polybithiazoles exhibit unusual thermal stability. A thermogravimetric analysis (nitrogen atmosphere, heating rate of $150^{\circ}/\text{hr.}$)¹⁰⁶ of polymer 51a reveals that major weight loss occurs between 500° and 700° , with weight residues of 80% at 585° and above 50% at 900° (see Figure 1). A standardized static weight-loss technique was utilized to assess the relative thermal stabilities of the polybithiazoles. The method involved heating of a polymer sample under nitrogen, for one-hour periods, at successively increasing temperatures. A plot between the incremental weight loss of the sample with increasing temperature closely corresponds to the thermogravimetric curve obtained using a commercial instrument (compare Figures 1 and 2 for thermogravimetric analysis curves of polymer 51a). Using this static weight loss method, polymer 51a suffered a total weight loss of 20% after heating at 500° . Subsequent sample heating at 600° resulted in an additional 20% weight loss and left a black powdery residue of low nitrogen and sulfur content (relative to carbon). No attempt was made to examine the volatile decomposition products. The low residual sulfur content is in accord with the observation that both thiazole and benzothiazole afford hydrogen sulfide on vapor phase pyrolysis.¹⁰⁷ Examination of the infrared spectra, x-ray powder patterns and elemental analyses of the sample

during the course of the test procedure confirmed that gross structural changes occurred between 500° and 600°.

In a similar manner polymers 52, 53 and 54 exhibited total weight losses of 20% at temperatures of 400°, 400° and 525° respectively (see Figures 2 and 3). Although the mechanism of thermal decomposition of the polybithiazoles is unknown, the observed differences in polymer stabilities are presumably due to the nature of the aryl substituents in the recurring units. The greater stabilities of polymers 51a and 54 are in qualitative agreement with conclusions drawn from a study of the thermal stabilities of a variety of simple organic structures.¹⁰⁷ Heterocyclics, aromatics, perfluorinated ring compounds and aromatic silanes were found to be the most stable classes of compounds among a wide variety of structures studied.¹⁰⁷ The decomposition temperatures for benzene, biphenyl, diphenylmethane and diphenyl ether are 600°, 543°, 454° and 538° respectively.

2. Light Stability

On prolonged exposure to light, (daylight and artificial lights) the surfaces of the polymer samples, originally yellow-brown in color, assume a pink hue. This behaviour is exhibited, in varying degrees, by all model and polymeric bithiazoles described here. In one instance, an analytical sample (polymer 54) was re-analyzed after a three-month exposure to daylight and artificial lights.

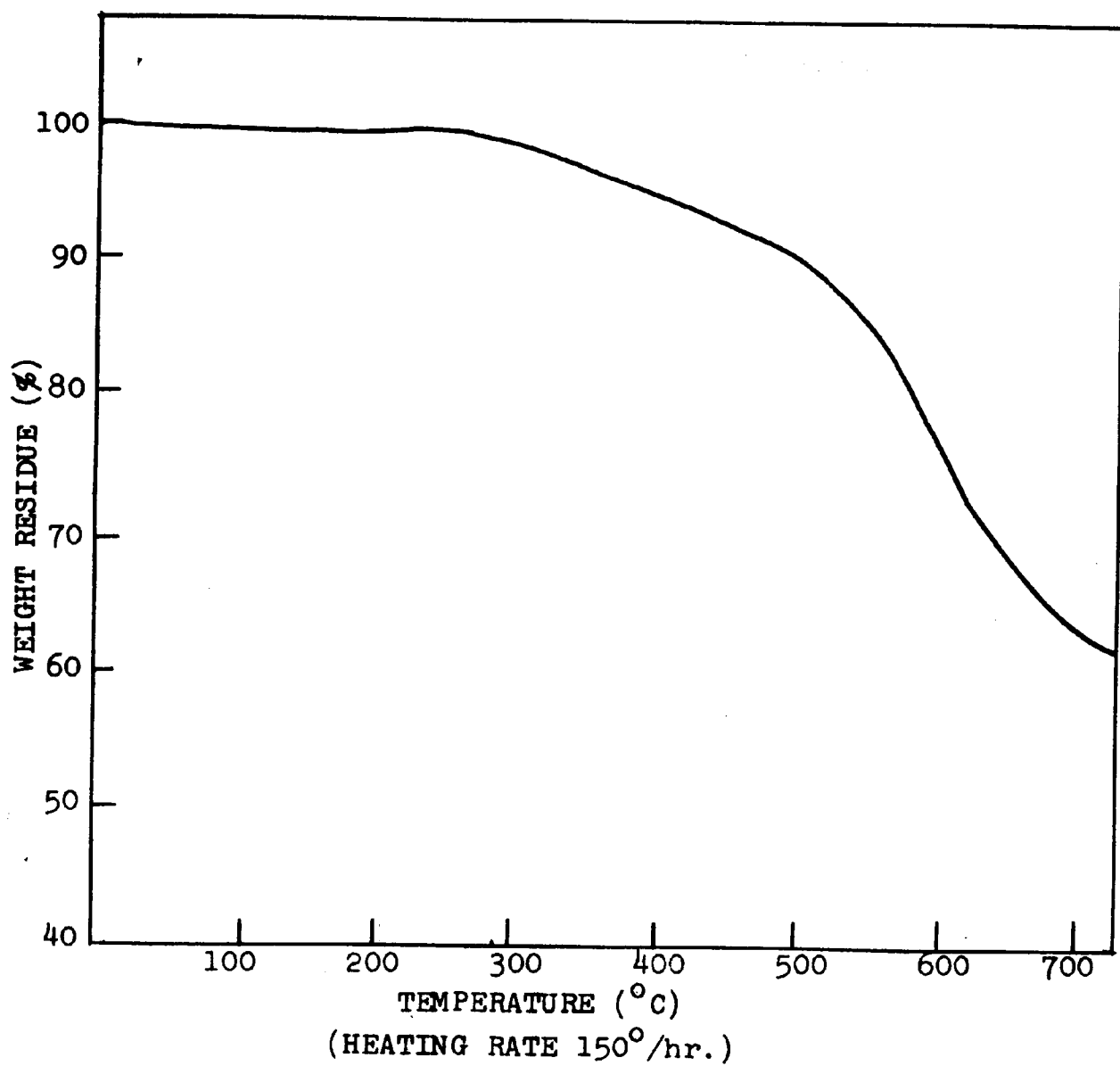
The carbon content had decreased from 64.2 to 62.7%, implying that a photooxidation process was involved.

3. Acid and Base Stabilities

No extensive studies have been done in connection with the stabilities of polybithiazoles towards acids and bases. A freshly prepared solution of polymer 51a in concentrated sulfuric acid (concentration ca. 0.25 g/100 ml. sulfuric acid) showed an inherent viscosity of 0.24 at 25°C. After standing for five hours at room temperature, the inherent viscosity was unchanged (see Table VI). An attempt was made to precipitate polymer 51a from the concentrated acid solution by pouring onto crushed ice. The infrared spectrum of the recovered material closely resembled that of the sample prior to acid treatment indicating no gross changes had occurred.

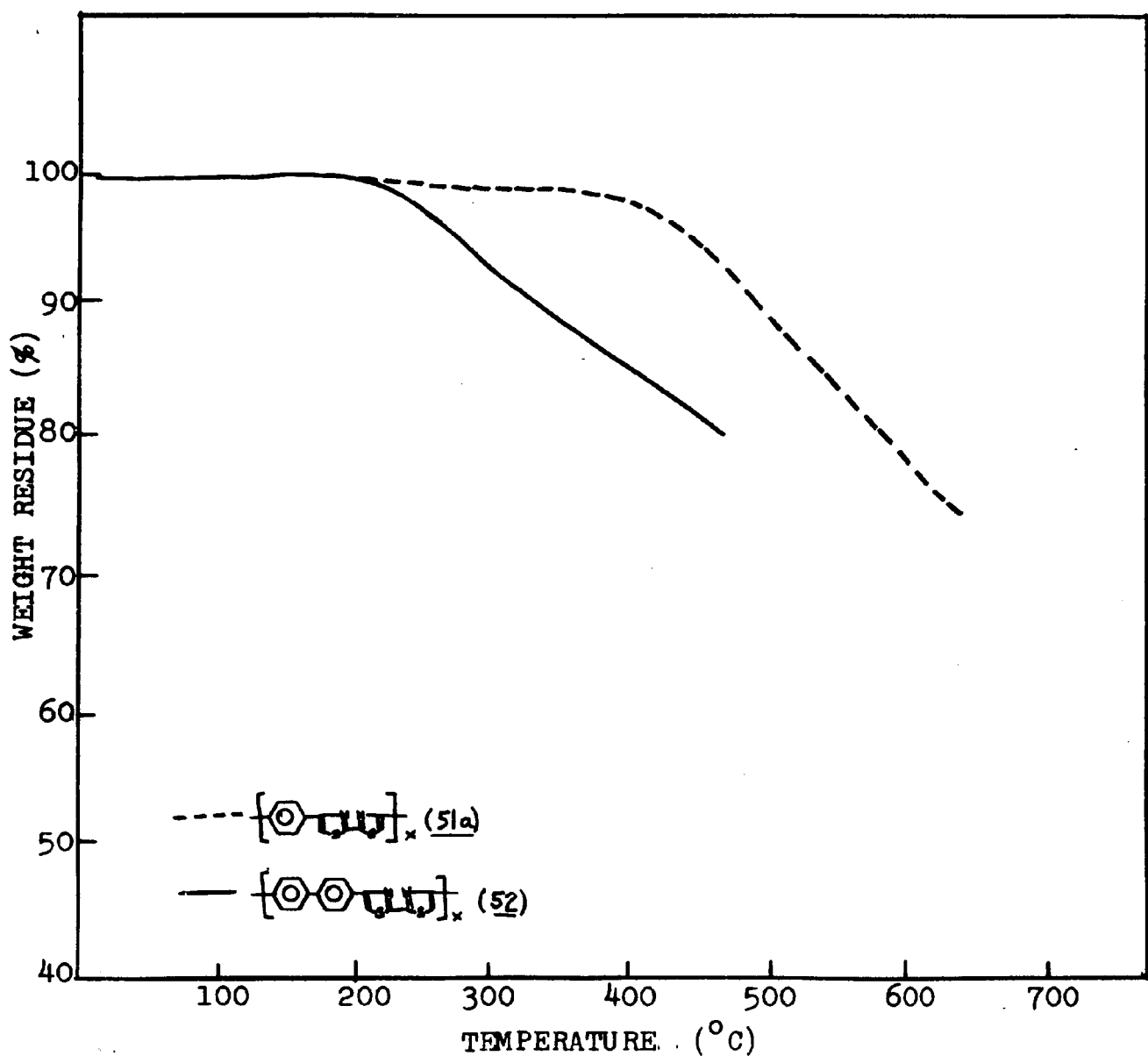
A suspension of polymer 51a and 10% sodium hydroxide solution was refluxed continuously for five hours. The infrared spectrum of the recovered material was identical to that of the material prior to base treatment. Elemental analyses of this material showed no apparent changes. It seems that 51a is stable towards base.

FIGURE 1



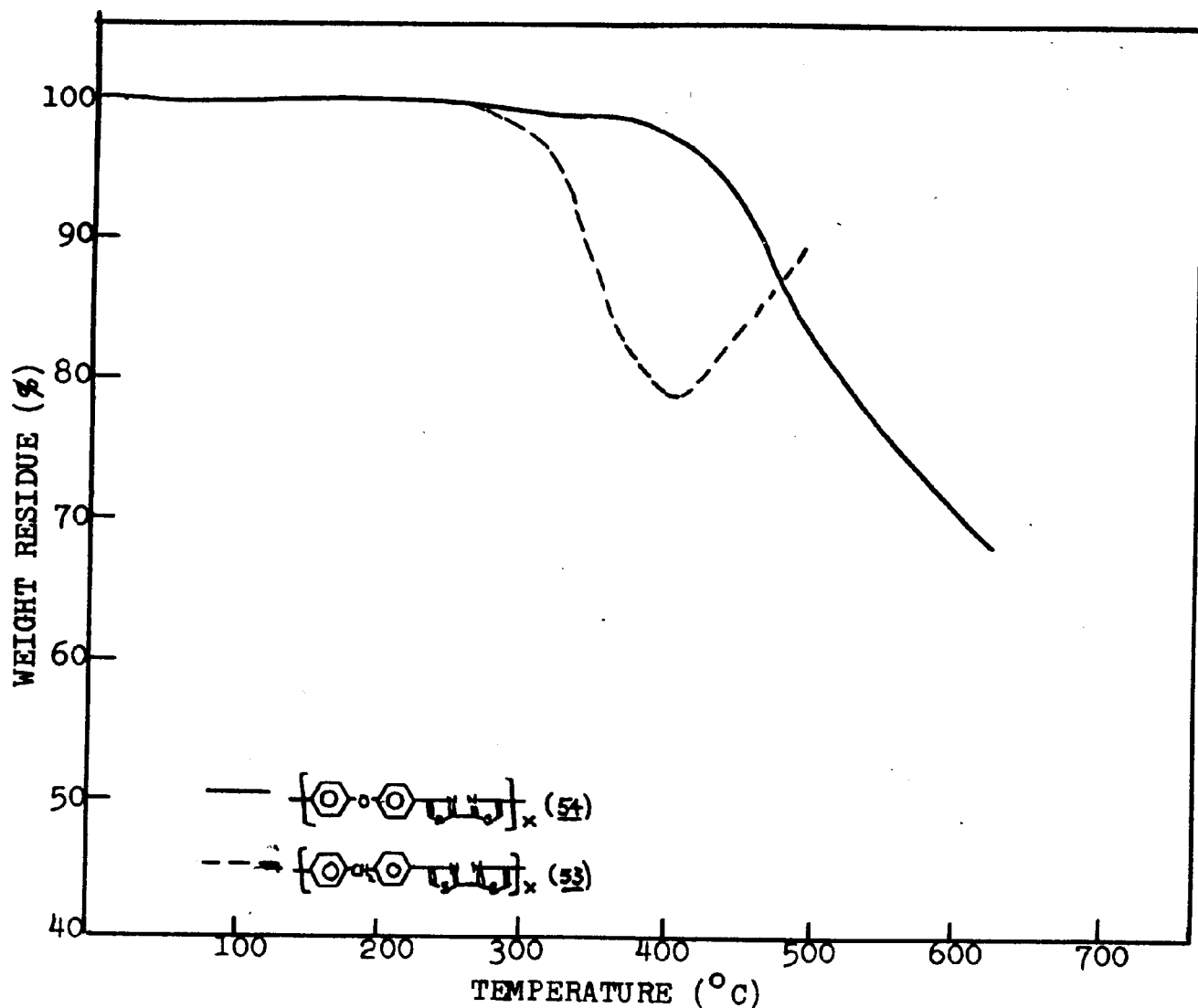
THERMOGRAVIMETRIC ANALYSIS CURVE (NITROGEN ATMOSPHERE)
of
POLY-4,4'-(p-PHENYLENE)-2,2'-BITHIAZOLE (51a)

FIGURE 2



THERMOGRAVIMETRIC ANALYSIS CURVES
 (STATIC METHOD, INCREMENTAL WEIGHT LOSS, N_2 ATMOSPHERE)
 OF
 POLY-4,4'-(p-PHENYLENE)-2,2'-BITHIAZOLE(51a)
 AND
 POLY-4,4''-(p-BIPHENYLENE)-2,2'-BITHIAZOLE(52)

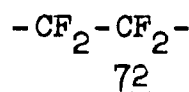
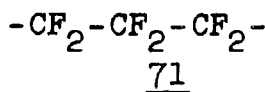
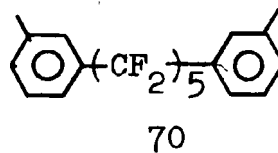
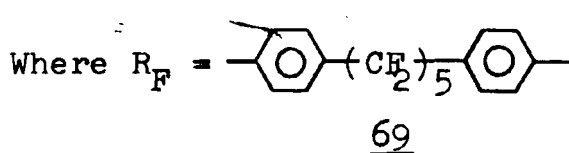
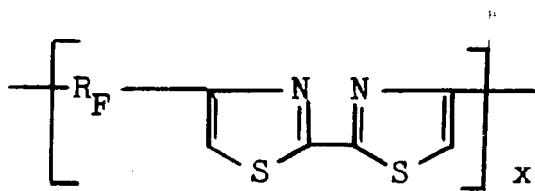
FIGURE 3



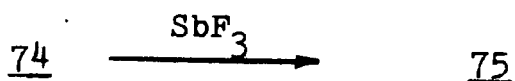
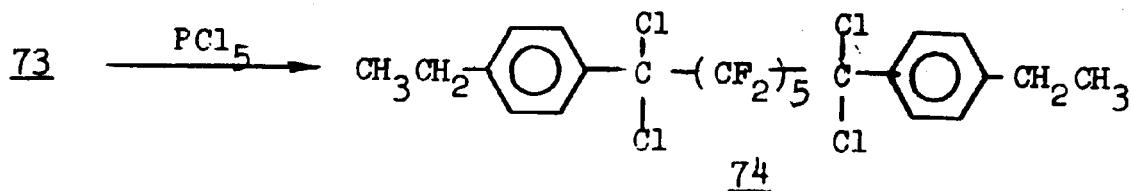
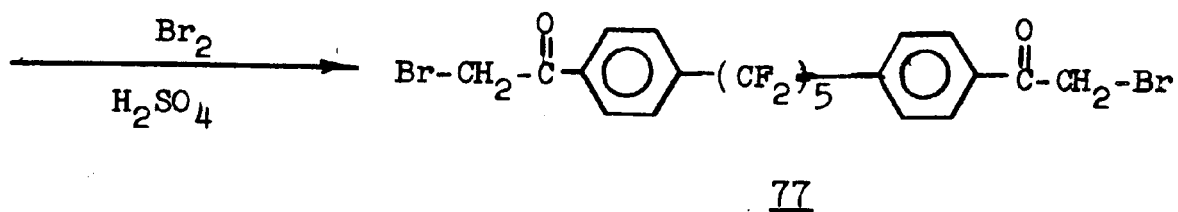
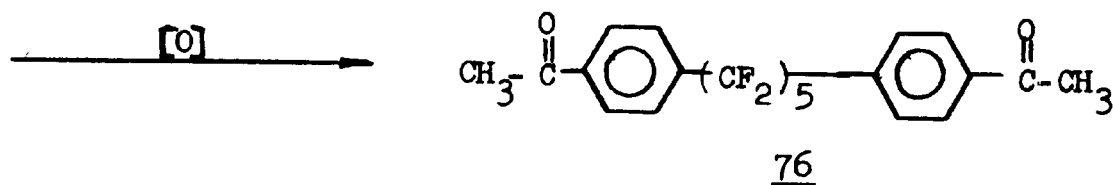
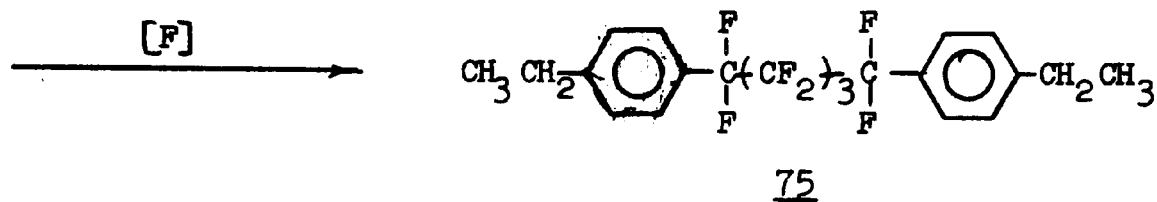
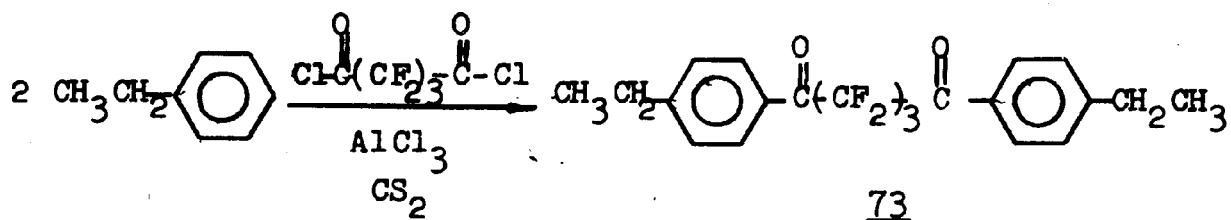
THERMOGRAVIMETRIC ANALYSIS CURVES
 (STATIC METHOD, INCREMENTAL WEIGHT ~~LOSS~~)
 QF
 POLY-4,4'-(p-DIPHENYLENEMETHANE)-2,2'-BITHIAZOLE (53)
 AND
 POLY-4,4'-(p-DIPHENYLENE ETHER)-2,2'-BITHIAZOLE (54)

D. ATTEMPTED SYNTHESIS OF BITHIAZOLE POLYMERS CONTAINING CARBON-FLUORINE BONDS

The encouraging results obtained from the above series of poly-4,4'-diaryl-2,2'-bithiazoles prompted attempts to utilize the polycondensation reaction described here to synthesize bithiazole polymers with perfluorinated chains. It has been demonstrated by Johns and co-workers¹⁰⁷ that among a number of organic structures evaluated, perfluorinated compounds exhibit the highest thermal stability. It has also been observed that polymers with perfluorinated aliphatic chains possess better thermal stability than the corresponding nonfluorinated analogs.¹⁰⁸ In addition, the studies of aromatic polybithiazoles just described seem to indicate a close correspondence between thermal stability of the polymer and the nature of the aryl substituents in the recurring units. Attempts were made to prepare the following polybithiazoles in the hope of generating thermally stable polymerizates with better tractability.



The following reaction schemes were considered for the synthesis of 77, the requisite monomer for polymer 69:



The diketone 73 may be prepared by the acylation of ethylbenzene with perfluoroglutaryl dichloride by the method of Fear.¹⁰⁹ The conversion of 73 to 75, in principle, could be accomplished in one step by the use of sulfur tetrafluoride.¹¹⁰ However, equipment necessary for such a reaction are not available at the University of Michigan, and, as an alternate route, diketone 73 could be converted to its tetrachloro derivative, 74, by phosphorus pentachloride. Displacement of gem-dichlorines by fluorines could lead to 75.¹¹¹ Oxidation of the benzylic hydrogens¹¹² of 75 would afford diketone 76, which upon bromination would give the requisite monomer 77.¹¹³

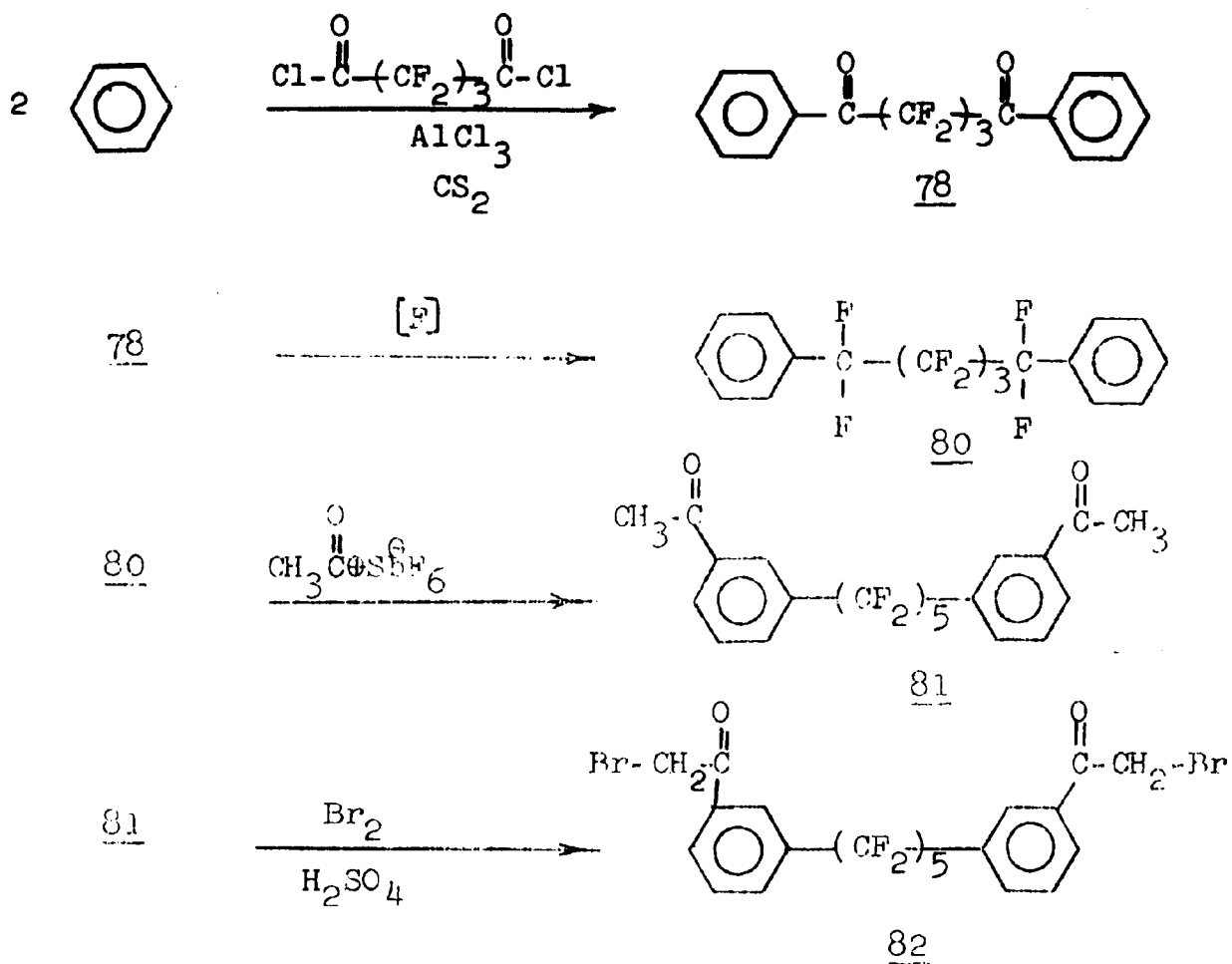
Treatment of ethylbenzene with perfluoroglutaryl dichloride in the Friedel-Crafts reaction afforded the diketone 73 in 60-68% yield. The structure of this heretofore unknown diketone was demonstrated in the following manner. The nuclear magnetic resonance spectrum in chloroform-D shows an aromatic hydrogen quartet in a typical A_2B_2 pattern at τ 2-3, a methylene quartet, τ 7.30 and a methyl triplet, τ 8.77; relative areas, 8:4:6. The infrared spectrum shows strong absorption at 1720 cm^{-1} (carbonyl), $1050\text{-}1350\text{ cm}^{-1}$ (C-F) and 960 cm^{-1} (ArH). Haloform-type cleavage^{115,116} by 10% sodium hydroxide yielded *p*-ethylbenzoic acid (63%) as the only product. The latter was identified by its melting point, $110\text{-}1^\circ$ (lit. $110\text{-}1^\circ$)¹¹⁷, its n.m.r. spectrum, and its amide, m.p. $160\text{-}1^\circ$ (lit. $161\text{-}2^\circ$)¹¹⁸. The

above spectral and chemical data adequately support the structural assignment.

The next step in the proposed synthesis was the conversion of diketone (73) to its tetrachloro derivative. Reactions of 73 with phosphorus pentachloride under various conditions including the use of benzene or a high-boiling fluorinated solvent, or the use of a sealed tube at 235° for 20 hours, were not successful. All attempts led either to the recovery of starting material or the production of tarry material. At this stage, it was decided to discontinue efforts to prepare 75 via the route just described. Had the preparation of the tetrachloride 74 been possible, the subsequent conversion to its fluoro-derivative 75 might be difficult. Although it has been reported that this method -- displacement of gem-dichlorines by fluorines -- is useful in the synthesis of fluorocarbons, there are enough well-documented examples in the literature to indicate the inefficiency and complexity of the reaction. For example, in 1947, McBee and co-workers¹¹⁹ attempted to prepare a number of fluorocarbons via the "displacement" route and observed that chlorine atoms in the benzylic position are extremely inert towards displacement reactions. Even under forcing conditions, reactions are incomplete and usually a complex mixture of products results with the expected fluorinated product in a low yield, generally of the order of 10-20%. It is felt that the only practical

method for the preparation of 75 will be by the sulfur tetrafluoride reaction,¹²⁰ or perhaps by the use of phenyl sulfurtrifluoride, the method of Sheppard.^{121,122}

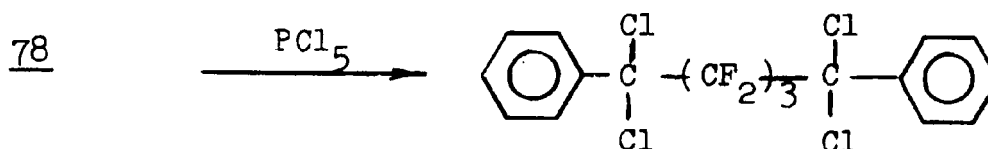
Concurrent with the attempted synthesis of monomer 77, an attempt was also made to synthesize monomer 82, the requisite monomer of polymer 70. The following scheme was proposed:



Benzene can be acylated using the method of Fear.¹⁰⁹
 Fluorination of the ketone functions to fluorocarbon 80

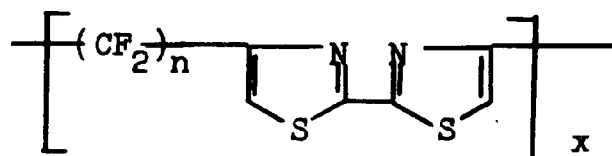
may be achieved by the methods described above. Acetylation with acetyl-antimonyhexafluoride¹²³ followed by bromination using the procedure of McBee¹¹³ should lead to the requisite monomer 82.

Treatment of benzene with perfluoroglutaryl dichloride in the Friedel-Crafts reaction afforded, after hydrolysis and purification, diketone 78 in 77% yield, with acceptable elemental analysis and consistent nuclear magnetic resonance and infrared spectra. Haloform-type cleavage^{115,116} with 10% sodium hydroxide afforded benzoic acid (identified by mixed melting point, and comparison of infrared spectra). Attempts were made to synthesize 79 according to the method and conditions utilized in the attempted synthesis of 74. All attempts failed. As in the previous case, reactions either led to the recovery of starting material or the production of tarry, intractable matter. Perhaps the most practical way to prepare 80 will be via the sulfur tetrafluoride reaction.¹²⁰



79

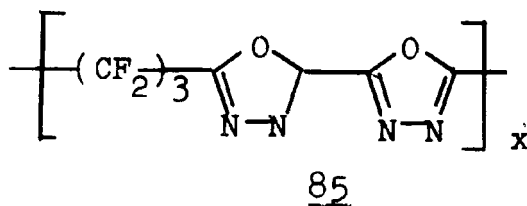
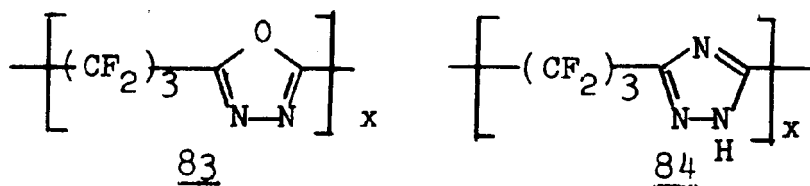
With the continuing interests in the syntheses of heterocyclic polymers containing carbon-fluorine bonds, efforts have been made to prepare the following polymers:



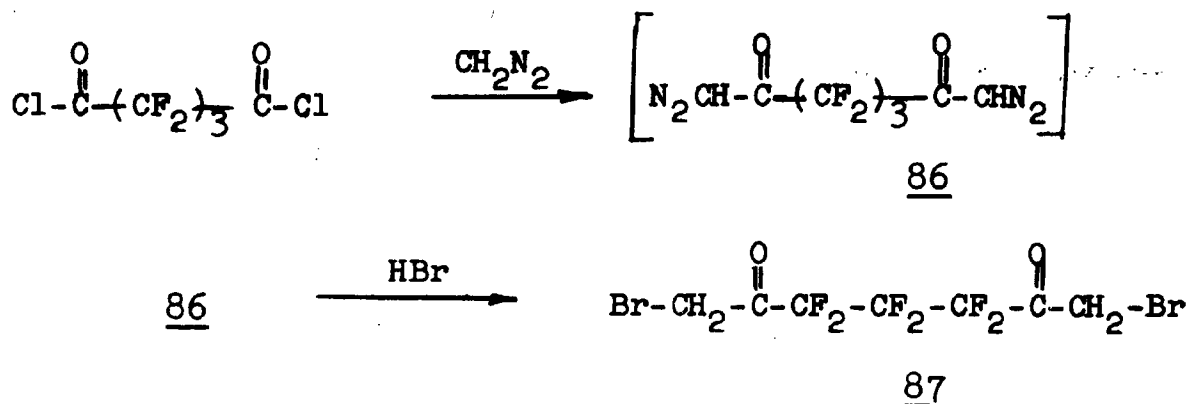
$$n = 2 \text{ (72)}$$

$$n = 3 \text{ (71)}$$

Polymers of this type would allow the study of effects on polymer properties resulting from the replacement of benzenoid aromatics by difluoromethylene units. Polymers of this type (structures 83-85) have recently been reported by Brown¹²⁴ and preliminary studies show promising thermal properties.



In our hands for use as starting material were perfluoroglutaryl dichloride and perfluorosuccinic acid. The following discussion summarizes the various approaches to the synthesis of 87, the requisite monomer for polymer 71.

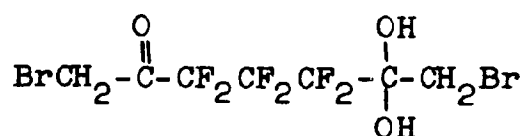


The action of hydrogen bromide or hydrogen chloride on diazoketones represents a general preparative method for pure halomethyl ketones.¹²⁵ The diazoketones are readily prepared from acyl halides and diazomethane.¹²⁶ Bromination using the special technique of McBee¹¹³ should afford the desired monomer 87.

Perfluoroglutaryl dichloride was added to an ethereal solution of diazomethane and an instantaneous evolution of nitrogen resulted. The bis(diazo)ketone so generated was not isolated, but was treated with anhydrous hydrogen bromide until the evolution of nitrogen ceased. The yellow-brown material obtained after the removal of ether was purified by fractional distillation, affording a low melting, white, crystalline compound. This material was recrystallized from carbon tetrachloride to give a melting point, 92-3°.

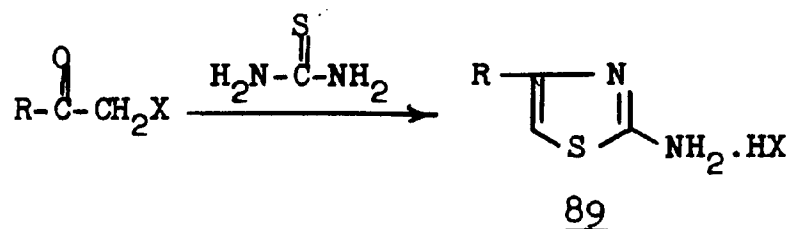
The infrared spectrum of this material (Nujol) shows strong absorption at 1780 cm.⁻¹ (carbonyl)¹¹⁴, 1050-1030 cm.⁻¹ (C-F) in addition to absorption of medium intensity at

3350 cm^{-1} (OH) and 700-900 cm^{-1} (weak). The unusually high absorption frequency of the carbonyl is caused by the strong electron withdrawing inductive effect exerted by the adjacent perfluoroalkyl group. The nuclear magnetic resonance spectrum of this compound in carbon tetrachloride exhibits signals at τ 3.45 (singlet) and τ 6.10 (doublet); relative areas 1:2. Deuterium exchange with deuterium oxide caused the peak at τ 3.45 to disappear rapidly while the peaks at τ 6.10 diminished in intensity and became constant in intensity after 15 minutes. The elemental analysis of this compound is not good for the expected structure, nor is it satisfactory for the structure of the gem-diol 88, which is consistent with the nuclear magnetic resonance and infrared spectral data. It has been observed¹¹⁶ that perfluorinated carbonyls form remarkably stable hydrates which can be distilled without decomposition.



88

It has been reported by Tomita¹²⁷ that reactions between halomethyl ketones and thiourea generate 2-aminothiazole hydrochlorides (89) which are excellent derivatives for halomethyl ketones.



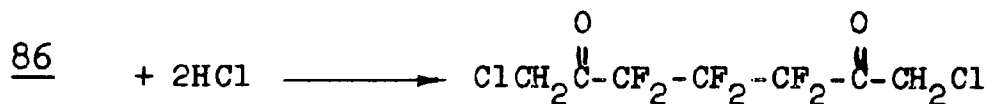
R = Aromatic or aliphatic Substituents

X = Br, Cl.

The reaction between the presumed dibromodiketone 87 and thiourea using the procedure of Tomita¹²⁷ did not yield a crystalline precipitate. No evidence for the formation of the heterocyclic system (89) was obtained.

An attempt has also been made to react 87 with dithiooxamide in ethanol. No indication of the formation of polymer was observed.

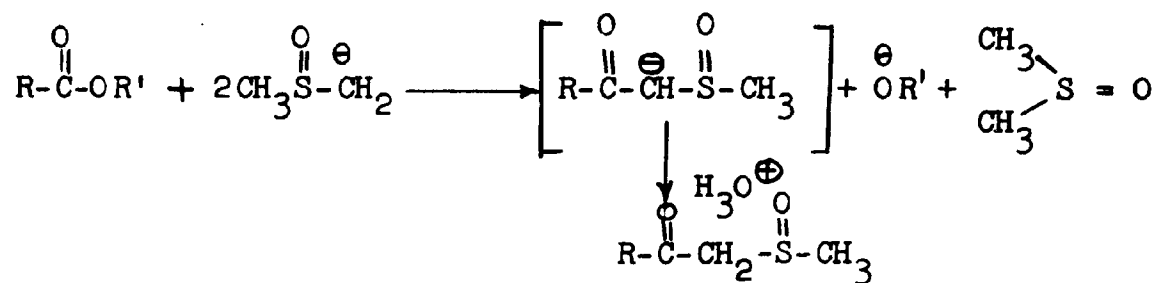
Attempts were made to treat 86 with anhydrous hydrogen chloride to generate 90. However, results were equally unsuccessful; no identifiable products were isolated.



90

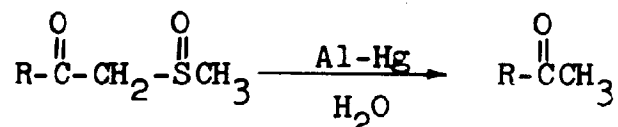
A novel method for the synthesis of methyl ketones has recently been reported by Corey and Chaykovsky.¹²⁸ It was discovered that the methylsulfinyl carbanion reacts

with a wide variety of esters to give β -ketosulfoxides in excellent yields:

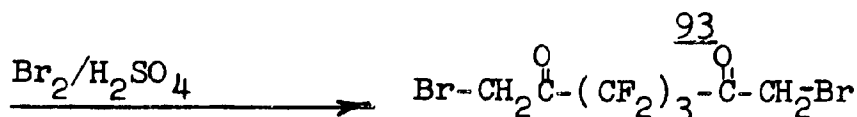
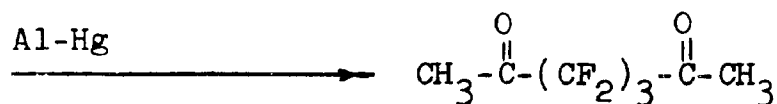
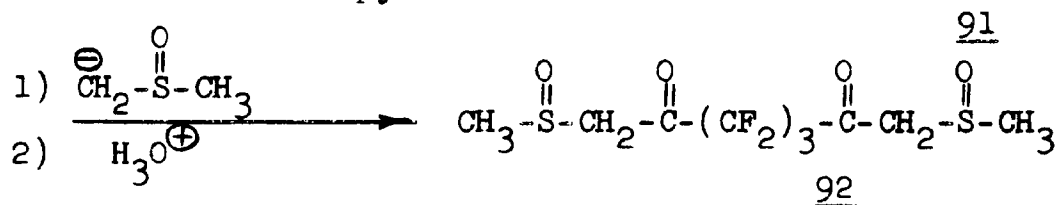
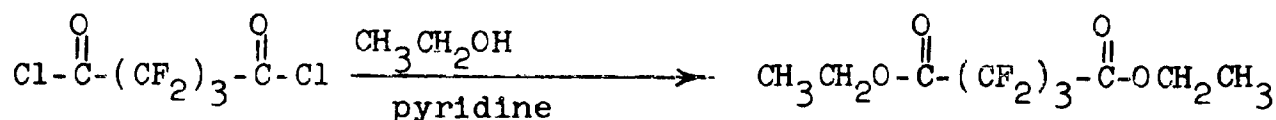


R' = methyl, ethyl.

The ketosulfoxides react rapidly and cleanly with aluminium amalgam in 90% tetrahydrofuran and 10% water mixture to yield ketones:

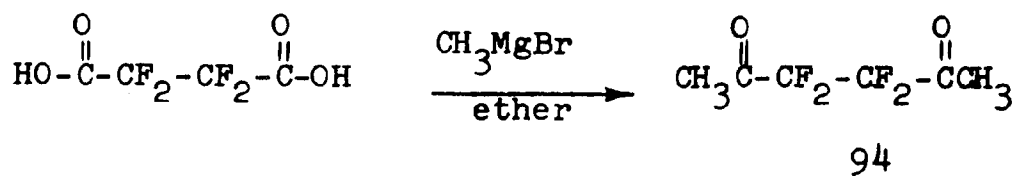


Accordingly, the following scheme was proposed for the synthesis of 93, a precursor of monomer 87.



Diethylperfluoroglutarate was prepared by the treatment of perfluoroglutaryl dichloride with ethanol in the presence of pyridine. Following the procedure of Corey and Chaykovsky¹²⁸ the diester was treated with methylsulfinyl carbanion in dimethyl sulfoxide, followed by acidic hydrolysis in an attempt to prepare the di(β -ketosulfoxide) 92. A dark brown mixture resulted from the above reaction. No characterizable products were isolated. This reaction was only attempted once in our laboratory. The influence exerted by the perfluoroalkyl groups towards the addition of methylsulfinyl carbanion is unknown. Special conditions may be necessary for the reaction.

It has been reported by Groth¹²⁹ that the reaction between perfluorosuccinic acid and excess methyl magnesium bromide yields, after hydrolysis, dimethylketone 94.



Using this procedure¹²⁹, perfluorosuccinic acid was treated with methyl magnesium iodide. After hydrolysis with saturated ammonium chloride solution and subsequent fractional distillation, a product boiling between 82-85°, which corresponds, presumably, to the forerun described by Groth¹²⁹ was obtained. The diketone (94) was reported to boil at 128°, however, no material boiling above 100°C was observed in our work. A similar organometallic reaction

--the reaction between methyl lithium and carboxylic acids-- which is known to give methyl ketones¹³⁰ has also been tried.



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After hydrolysis and fractional distillation, a small fraction boiling between 85-88° was obtained. The infrared spectrum of this material is identical with that obtained from the Grignard reaction described above. No material boiling above 100° was observed. In our hands, the treatment of perfluorosuccinic acid with organometallic reagents did not lead to the expected diketone (94) reported by Groth.¹²⁹

IV. SUMMARY AND CONCLUSIONS

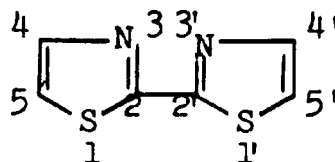
The polycondensation of dithiooxamide with bifunctional aromatic bromomethyl ketones affords a series of poly-4,4'-diaryl-2,2'-bithiazoles. Both high yields and molecular weights are obtained, presumably as a consequence of the enhanced reactivity of the thionamide function of dithiooxamide.¹³¹ The aromatic polybithiazoles exhibit outstanding thermal stability. They are characteristically infusible and highly crystalline. Synthetic routes to halomethyl ketones are sufficiently diverse that polymer recurring units can be varied greatly and in a controlled manner. Controlled structural variations within the polymer recurring unit allow for modifications of gross polymer properties. Monomers which allow the incorporation of heteroaromatic, organometallic, and perfluoroalkyl moieties are accessible. Attempts to prepare monomers with perfluoroalkyl groups have so far been unsuccessful and further work is necessary in this area. In addition, the use of aromatic methyl ketones less symmetrical than the ones reported here should lead to more tractable polymerizates with little sacrifice in thermal stability. Further effort should be devoted in this area to take advantage of this versatile bithiazole-forming polycondensation reaction in the synthesis of thermally stable polymerizates.

V. EXPERIMENTAL

All melting points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer Infracord or a Perkin-Elmer spectrometer, Model 21; the ultraviolet spectra with a Cary spectrometer, Model 11; the n.m.r. spectra with a Varian A-60 instrument, with tetramethylsilane used as internal reference. We are indebted to Mr. B. E. Wenzel and Mr. F. Parker for much of the spectral work. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Materials: Unless otherwise indicated, commercially available solvents and reagents were redistilled or recrystallized prior to use. Dimethylformamide was distilled over barium oxide; dithiooxamide (DTOA)¹³² recrystallized from ethanol to give material which decomposes without melting at about 140°. Mallinckrodt's Analytical Reagent grade aluminum chloride was used in the Friedel-Crafts reactions.

A. PREPARATION OF MODEL BITHIAZOLES

1. 4,4'-Dimethyl-2,2'-bithiazole(60).

The reaction of chloroacetone and DTOA was utilized following essentially the procedure described.¹⁰⁰ The product, after sublimation at 75° and 0.2mm. (44% yield), was off-white in color and had m.p. 138-139° (lit.¹⁰⁰ m.p. 136°). The n.m.r. spectrum (CCl₄) has singlets at τ 3.12 (vinyl hydrogen) and 7.53 (methyl). The infrared spectrum (KBr disk) has bands at 3080m, 2915m, 1511s, 1444s, 1436s, 1403s, 1366m, 1165m, 1000s, 984s, 876s, 770s, and 675m cm⁻¹. The ultraviolet spectrum (KBr disk) shows λ_{max} at 230m, 332s, 337s, 344sh, 355sh and 364sh m μ .

2. 4,4',5,5'-Tetramethyl-2,2'-bithiazole (61).

A solution of 2.1g. (0.018 mole) of DTOA and 5.0g. (0.033 mole) of technical grade 3-bromo-2-butanone in 100 ml. of absolute ethanol was refluxed for 7 hr. At the end of this time solvent was removed under diminished pressure and the residue taken up in benzene. The solution was filtered through a short column of alumina and the solvent then removed to give 2.9g. (74%) of crude product,

m.p. 130-170°. A portion of the crude product was purified by subliming out unidentified impurities at 70° and 0.2mm. The residue was recrystallized three times from acetonitrile to afford an analytical sample, m.p. 196.5-197.5°.

Anal. Calcd. for $C_{10}H_{12}N_2S_2$: C, 53.53; H, 5.39; N, 12.49.
Found: C, 53.75; H, 5.56; N, 12.78.

The n.m.r. spectrum ($CDCl_3$) displays a lone singlet at τ 7.60. The infrared spectrum (KBr disk) has peaks at: 2918m, 2850w, 1533s, 1404s, 1373m, 1108w, 974w, 922s, 842w, and 699m cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max} at 350s, 367sh, and 239m m μ .

3. 4,4'-Dimethyl-5,5'-dicarbethoxy-2,2'-bithiazole (62).

Using the literature procedure,¹⁰⁰ the condensation of crude ethyl α -chloroacetoacetate¹³³ and DTOA afforded a very low yield (ca. 5%) of 62. The product, after two recrystallizations from 95% ethanol, was obtained as colorless needles, m.p. 191-192° (lit.¹⁰⁰ m.p. 186°).

The n.m.r. spectrum ($CDCl_3$) displays a quadruplet at τ 5.63 (methylene), a singlet at 7.25 (methyl) and a triplet at 8.62 (ester methyl) with satisfactory relative integrated areas. The infrared spectrum (KBr disk) exhibits ester bands at 1716s and 1261s cm^{-1} . Additional bands occur at 2973m, 2918w, 1520m, 1394s, 1371s, 1314s, 1115s, 1095s, 850m, 820w and 760s cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max}

at 345s and 252m μ .

4. 4,4'-Diphenyl-2,2'-bithiazole (65).¹³⁴

This model was prepared as previously described⁷⁵ from phenacyl bromide and DTOA. After recrystallization from absolute ethanol it had m.p. 220-221.5° (lit.⁷⁵ 220-222°). The infrared spectrum (Nujol) has bands at 3130w, 1605w, 1585w, 1420m, 1300m, 1075m, 1055m, 1025m, 940s, 885s, 778m, 740s, 690s, 678m, and 668m cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max} at 248s, 268sh and 360m μ . An n.m.r. spectrum was not obtained due to solubility difficulties.

5. 4,4'-Bis(p-benzylphenyl)-2,2'-bithiazole (66).

a. Preparation of p-Benzylacetophenone.

Acetylation of diphenylmethane was carried out essentially as described below in the preparation of p-phenoxyacetophenone. From 16.8g. (0.100 mole) of diphenylmethane, 26.6g. (0.200 mole) of aluminum chloride and 10.2g. (0.100 mole) acetic anhydride, there was obtained by distillation 4.95 g. diphenylmethane and 5.95 g. (40%) of p-benzylacetophenone, b.p. 139-165° (0.6 mm). The major portion of the product had b.p. 139-144° at 0.6 mm. (lit.¹³⁵ b.p. 188-190° at 5 mm.) and n_D^{28} 1.5845. The n.m.r. spectrum (CCl_4) displays an A_2B_2 multiplet (J 8 c.p.s.) at τ 2.25 and 2.88 (C_6H_4), and singlets at 2.87 (C_6H_5), 6.13 (CH_2), and 7.66 (CH_3) with

satisfactory relative integrated areas.

b. Preparation of p-Benzylphenacyl Bromide.

Bromination¹³⁵ of p-benzylacetophenone afforded crude p-benzylphenacyl bromide as an oil. This oil was not purified before use in the next step.

c. Preparation of 4,4'-Bis(p-benzylphenyl)-2,2'-bithiazole.

Condensation of the oil obtained above with DTOA in absolute ethanol gave crude 66, m.p. 199-202°, in a yield of 33% based on p-benzylacetophenone. Recrystallization from acetonitrile gave golden plates, m.p. 211-212°.

Anal. Calcd. for $C_{32}H_{24}N_2S_2$: C, 76.76; H, 4.83; N, 5.60. Found: C, 76.91; H, 5.15; N, 5.67.

The n.m.r. spectrum ($CDCl_3$) displays an A_2B_2 multiplet (J 8 c.ps.) at τ 2.15 and 2.60 (C_6H_4) and singlets at 2.76 (vinyl and aromatic hydrogens) and 5.98 (CH_2) with satisfactory relative integrated areas.

The infrared spectrum (KBr disk) has bands at 3097w, 2022w, 1895w, 1600w, 1494m, 1480s, 1454m, 1430m, 1418m, 1056m, 943s, 885s, 882m, 753s, 741s and 697s cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max} at 249s, 269sh, and 359m $m\mu$.

6. 4,4'-Bis(p-biphenyl)-2,2'-bithiazole (67).

A solution of 5.7 g. (0.021 mole) p-phenylphenacyl bromide and 1.3 g. (0.011 mole) DTOA in 100 ml. dimethylformamide was refluxed for 1.5 hr., during which time a yellow solid was deposited. The reaction mixture was cooled and filtered, the solid washed with water, dried, and then recrystallized from cyclohexanone to give 4.0 g. (81%) of product as light yellow needles, m.p. 346-348°.

Anal. Calcd. for $C_{30}H_{20}N_2S_2$: C, 76.26; H, 4.24; N, 5.93. Found: C, 76.41; H, 4.08; N, 5.82.

The infrared spectrum (KBr disk) has bands at 3095w, 3043w, 1595w, 1478s, 1448m, 1412m, 1058m, 1008m, 941s, 887s, 849s, 772m, 750s, and 693s cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max} at 294s and 364m m μ .

7. 4,4'-Bis(p-phenoxyphenyl)-2,2'-bithiazole (68).a. Preparation of p-Phenoxyacetophenone.

p-Phenoxyacetophenone was prepared: to a mixture of 17.0 g. (0.100 mole) phenyl ether and 40 g. (0.30 mole) aluminum chloride in 100 ml. of carbon disulfide was added dropwise and with vigorous stirring, 10.2 g. (0.100 mole) of acetic anhydride. During the addition the reaction vessel was cooled intermittently. After total addition, the mixture was heated over steam for one hour, allowed to stand at room temperature for an additional 1.5 hr., and then cautiously poured into a liter of ice contain-

ing 50 ml. of concentrated hydrochloric acid. The mixture was warmed over steam and then extracted with benzene. Removal of solvent from the dried benzene solution afforded 19 g. (90%) of crude p-phenoxyacetophenone. Recrystallization from ethanol-water (ca. 3:1) resulted in little loss and gave material with m.p. 47-48° (lit.¹³⁶ m.p. 45°). The infrared spectrum (Nujol) is characterized by strong bands at 1682 (carbonyl), 1250 (ether), and 845, 760 and 690 cm^{-1} (all aromatic out-of-plane deformations).

The n.m.r. spectrum (CCl_4) displays a doublet at τ 2.10 and a multiplet centered about 2.60 - 3.10 (all aromatic protons) and a singlet at 7.52 (methyl) with satisfactory integrated relative areas. The ultraviolet spectrum (KBr disk) shows λ_{max} at 266s and 355m $\text{m}\mu$.

b. Preparation of p-Phenoxyphenacyl Bromide .

Bromination of the above product, using the literature¹³⁷ procedure, gave p-phenoxyphenacyl bromide (43% yield) as an oil, b.p. 168-178° at 0.5 mm. (lit.¹³⁷ b.p. 190-192° at 3 mm.). The infrared spectrum (neat) is characterized by strong bands at 1704 (carbonyl), 1259 (ether), 1215 (CH_2Br)¹³⁸, and 853, 769, and 700 cm^{-1} (all aromatic out-of-plane deformations).

c. Preparation of 4,4'-Bis(p-phenoxy-phenyl)-2,2'-bithiazole.

A solution of 1.4 g. (4.8 mmoles) of p-phenoxyphenacyl bromide and 0.29 g. (2.4 mmoles) of DTOA in 60 ml. of absolute ethanol was refluxed for one hour, during which time a yellow-orange solid was deposited. The mixture was filtered while hot to give 0.6 g. (50%) crude 68, m.p. 222-226°. Four recrystallizations from carbon tetrachloride followed by an additional two from benzene gave analytically pure material, m.p. 240.0-241.5°.

Anal. Calcd. for $C_{30}H_{20}N_2S_2O_2$: C, 71.42; H, 3.97; N, 5.55. Found: C, 71.42; H, 4.14; N, 5.48.

The infrared spectrum (KBr disk) includes bands at 3130w, 3070w, 1600vs, 1530s, 1500vs, 1480vs, 1415m, 1293s, 1255vs (ether), 1170s, 942s, 886s, 870s, 778m, 748vs, and 690s cm^{-1} . The ultraviolet spectrum (KBr disk) shows λ_{max} at 265s and 355m μ .

B. PREPARATION OF MONOMERS

1. p-Bis(bromoacetyl)benzene¹³⁴

Bromomination¹³⁹ of p-acetylacetophenone afforded crude monomer in near quantitative yield, m.p. 169-172°; recrystallization from 95% ethanol gave m.p. 173-174° (lit.¹³⁹ 177-178°). The infrared spectrum (Nujol) is characterized by strong bands at 1705 (carbonyl), 1205 (CH_2Br), and 810 cm^{-1} (aromatic out-of-plane deformation).

The n.m.r. spectrum (CDCl_3) displays singlets at τ 1.85 (ArH) and 5.52 (CH_2) with satisfactory relative integrated areas.

2. 4,4'-Bis(bromoacetyl)biphenyl.

a. Preparation of 4,4'-Bis(acetyl)biphenyl.

4,4'-Bis(a c e t y l)biphenyl was prepared according to the procedure of Sloan and Vaughan¹⁴⁰. The n.m.r. spectrum of this compound (CDCl_3) displays an A_2B_2 pair of doublets (J 8 c.p.s.) at τ 1.90 and 2.25 (aromatic) and a singlet at 7.37 (methyl) with satisfactory relative integrated areas. The infrared spectrum (Nujol) includes bands at 1690vs, 1610m, 1560w, 1400m, 1330w, 1280s, 1190w, 1140vw, 1120vw, 1080vw, 1020vw, 1000vw, 960s, 820vs and 720w cm^{-1} .

b. Preparation of 4,4'-Bis(bromoacetyl)-biphenyl.

To a solution of 9.6 g. (0.040 mole) of 4,4'-bis(acetyl)biphenyl in 400 ml. glacial acetic acid was added dropwise 16 g. (0.10 mole) bromine. A red-brown precipitate developed during the later stage of addition. After total addition the mixture was stirred for an additional 15 min. The precipitate (11.2 g.) had m.p. 214-216°. After standing overnight the reaction filtrate had deposited an additional 3.0 g. of crude product, m.p.

206-211°. The combined solids were recrystallized from ethyl acetate to afford, in two crops, 8.4 g. (53%) of colorless product, m.p. 219-221° dec. (sealed tube; lit.¹⁴¹ m.p. 226-227°).

Anal. Calcd. for $C_{16}H_{12}O_2Br_2$: C, 48.51; H, 3.05; Br, 40.35. Found: C, 48.44; H, 3.31; Br, 40.38.

The infrared spectrum (Nujol) is characterized by very strong bands at 1700 (carbonyl) and 1205 cm^{-1} (CH_2Br).

3. 4,4'-Bis(bromoacetyl)diphenylmethane.

a. Preparation of 4,4'-Bis(acetyl)diphenylmethane.

4,4'-Bis(acetyl)diphenylmethane, the precursor of 4,4'-bis(bromoacetyl)diphenylmethane, was prepared according to the procedure of Sloan and Vaughan¹⁴⁰ and had m.p. 90-92° (lit.¹⁴⁰ 93.5-94.5°). The n.m.r. spectrum ($CDCl_3$) of this compound displays an A_2B_2 pair of doublets (J 8 c.p.s.) at τ 2.08 and 2.70 (aromatic) and singlets at 5.92 and 7.47 with satisfactory relative integrated areas. The infrared spectrum (Nujol) includes bands at 1700vs (carbonyl), 1480vs, 1460s, 1390m, 1380vs, 1320w, 1280vs, 1220w, 1200m, 1120m, 1090w, 1040m, 970s, 875s, 860w, 828vs, 806s, 770w, 755w and 725w cm^{-1} .

b. Preparation of 4,4'-Bis(bromoacetyl)diphenylmethane.

The general bromination procedure¹⁴² of

Lutz et.al. was unsatisfactory in our hands for the bromination of 4,4'-bis(acetyl)diphenylmethane. To a solution of 7.6 g. (0.030 mole) of 4,4'-bis(acetyl)diphenylmethane in 150 ml. of glacial acetic acid was added, dropwise and with vigorous stirring, a solution of 9.6 g. (0.060 mole) bromine in 50 ml. of glacial acetic acid. After total addition the mixture was heated at the reflux temperature for two hours, at the end of which time the evolution of hydrogen bromide had ceased and the bromine color discharged. The reaction mixture was cooled, poured onto ice and the yellow precipitate removed, washed with 5% sodium bicarbonate solution and water, and then dried. The crude product was dissolved in benzene and chromatographed (silica gel, benzene) to give colorless needles, (8.7 g., 71%), m.p. 139-140° (lit.¹⁴² 137.5-138.5°).

Anal. Calcd. for $C_{17}H_{14}O_2Br_2$: C, 49.78; H, 3.44.
Found: C, 49.64; H, 3.74.

The n.m.r. spectrum (acetone- d_6) displays an A_2B_2 pair of doublets at 7.95, 2.52 (aromatic), and singlets at 5.30 (CH_2Br) and 5.78 (CH_2) with satisfactory relative integrated areas.

The infrared spectrum (Nujol) is characterized by bands at 1715 (carbonyl) and 1220 cm^{-1} (CH_2Br).

4. 4,4'-Bis(bromoacetyl)diphenyl Ether.

To a vigorously stirred mixture of 34 g. (0.20 mole) diphenyl ether, 93 g. (0.70 mole) aluminum chloride, and 200 ml. dry carbon disulfide was added over a one-hour period 121 g. (0.600 mole) of reagent grade bromoacetyl bromide. After total addition the mixture was stirred for 30 min., then refluxed for an additional 2 hr. and finally poured into 3 l. of crushed ice containing 25 ml. of concentrated hydrochloric acid. The resulting semi-solid mass was dissolved in chloroform and this solution added to the chloroform extracts of the aqueous layer. After drying, solvent was removed to leave crude product as a purple-gray mass. After seven recrystallizations from methanol (with Norit) followed by column chromatography (silica gel, ether), 11.1 g. (13%) of colorless needles were obtained, m.p. 120-121° (lit.¹⁴³ 121°).

Anal. Calcd. for $C_{16}H_{12}O_3Br_2$: C, 46.63; H, 2.94; Br, 38.78. Found: C, 46.62; H, 2.84; Br, 38.33.

The n.m.r. spectrum (acetone- d_6) displays an A_2B_2 pair of doublets (J 9 cps.) at τ 1.82 and 2.74 (aromatic) and a singlet at 5.27 (CH_2Br) with satisfactory relative integrated areas.

5. p,p'-Bis(bromoacetyl)-1,6-diphenylhexane (55).a. Preparation of 1,6-Diphenylhexane.

1,6-Diphenylhexane (56) was prepared essentially according to the method of Van Alphen.¹⁰² Thinly sliced sodium (38.0 g., 1.65 g-atoms) was covered with 150 ml. anhydrous ether, and to this mixture was added, in the course of 12 hr., a mixture containing 1,6-dibromohexane (97.5 g., 0.400 mole) and bromobenzene (140 g., 0.890 mole). Agitation was provided by a mechanical stirrer. Most of the sodium had disappeared at the end of the addition period. The ethereal solution was filtered; the residue treated with absolute alcohol and eventually dissolved in water. The aqueous solution was extracted with ether and the extracts were combined with the original ethereal solution. This combined ether solution was dried over Na_2SO_4 . Removal of drying agent and solvent left a residue, 97.4 g. Distillation of this material under reduced pressure yielded several fractions. The first fraction (7.7 g), boiling between $48-74^\circ$ (0.07 mm) consisted largely of starting material, 1,6-dibromohexane (identified by VPC retention time by comparison with authentic material). The second fraction, boiling between $89-98^\circ$ (0.05 mm) was a mixture of 1,6-diphenylhexane and 1-bromo-6-phenylhexane. The n.m.r. spectrum of the neat liquid displays a singlet at $\tau 2.82$ (aromatic), a triplet at 6.85 (CH_2Br), a multiplet at 7.50 (ArCH_2-) and a broad multiplet centered around 8.70

(tetramethylene). The major fraction boiled between 98-124° (0.05 mm.) with a constant boiling point at 115° (0.05 mm.). The n.m.r. spectrum of the neat liquid displays a singlet at τ 2.82 (ArH), a multiplet at 7.50 (ArCH₂-) and a multiplet centered at 8.70 (tetramethylene) with satisfactory relative integrated areas. This fraction (40.8 g, 45% yield, allowing for the recovery of starting material) was the desired 1,6-diphenylhexane based on its n.m.r. spectrum and boiling point. [115° (0.05 mm.), lit.¹⁰² 197° (14 mm.)].

b. Preparation of p,p'-Bis(bromoacetyl)-1,6-Diphenylhexane.

1,6-Diphenylhexane prepared above was bis-bromoacetylated in the manner described previously for diphenyl ether. The crude product which precipitated on hydrolysis of the reaction mixture was dissolved in benzene. The benzene solution was treated with Norit, dried, concentrated, and then subjected to column chromatography (silica gel, benzene). Fractions yielding crystalline material were combined and recrystallized twice from carbon tetrachloride, affording pure monomer (10% yield) as off-white needles, m.p. 136-137°.

Anal. Calcd. for C₂₂H₂₄O₂Br₂: C, 55.01; H, 5.04; Br, 33.28. Found: C, 54.91; H, 5.23; Br, 33.18.

The n.m.r. spectrum (CDCl₃) displays an A₂B₂ pair of doublets (J 8 cps.) at τ 1.96 and 2.61 (aromatic), a singlet at 5.51 (CH₂Br), a multiplet at 7.28 (ArCH₂), and a multiplet

centered at 8.5 (tetramethylene) with satisfactory relative integrated areas. The infrared spectrum has strong bands at 1705 (carbonyl) and 1210 cm^{-1} (CH_2Br).

6. 1,4-Dibromobutane-2,3-dione .

The method of Ruggli was used.¹⁴⁴ To a warm solution of 25 g. (0.29 mole) of 2,3-butanedione in 50 ml. anhydrous chloroform was added 96 g. (0.60 mole) of bromine dissolved in 30 ml. chloroform. Decoloration of bromine was rapid in the beginning, then became slower. The mixture was gently warmed during the addition period. When all the bromine had been added, the solution was warmed further until the color changed from red-brown to orange. Crystallization took place immediately upon cooling. The yellow leaflets were filtered off, and recrystallized from chloroform. A further crop was obtained upon shaking the mother liquor thoroughly with 100 ml. of 10% Na_2SO_3 solution. The combined material was dried at 55° (1.5 mm.) for eight hours. Yield: 25.4 g. (36%), m.p. $120-121^\circ$ (lit.¹⁴⁴ $116-117^\circ$).

The yield of the reaction was higher than reported above since a considerable amount was lost via sublimation during the drying process in vacuo, and further precipitation from the mother liquor upon prolonged standing.

Anal. Calcd. for $\text{C}_4\text{H}_4\text{O}_2\text{Br}_2$: C, 19.70; H, 1.65.
Found: C, 19.20; H, 1.67.

The infrared spectrum (Nujol) has strong bands at 1760

(carbonyl) and 1250 cm^{-1} (CH_2Br).

The n.m.r. spectrum (CDCl_3) displays a sharp singlet at $\tau 5.65$ (CH_2Br) consistent with the expected structure.

7. Attempted Preparation of *p,p'*-Bis(bromoacetyl)-1,5-diphenylperfluoropentane (77).

a. Preparation of 1,3-Di(*p*-ethylbenzoyl)-perfluoropropane (73).

1,3-Di(*p*-ethylbenzoyl)perfluoropropane was prepared essentially by the method of Fear.¹⁰⁹ Perfluoroglutaryl dichloride (9.30 g., 0.0335 mole) in 30 ml. anhydrous carbon disulfide was added dropwise to a stirred suspension of aluminum chloride (13.3 g, 0.100 mole), ethylbenzene (9.30 g., 0.0870 mole) and 300 ml. anhydrous carbon disulfide at 0° . After total addition, the mixture was stirred for 90 min. at room temperature and then poured onto crushed ice (ca. 100 g.) containing concentrated hydrochloric acid (40 ml.). After separation of layers, the aqueous phase was extracted three times with benzene, and the extracts combined with the carbon disulfide layer. The combined organic phase was then washed with 5% sodium bicarbonate followed by careful washings with water. Removal of solvent left a red residue which was distilled under vacuum. After a forerun boiling at $114\text{--}168^\circ$ (0.23 mm.), a major fraction boiling between $168\text{--}185^\circ$ (0.23 mm.) was obtained. Redistillation of this material yielded a product boiling at 155° (0.11 mm.). Yield: 8.35 g. (60%). (Repetition

of this reaction gave 68% yield of product).

Anal. Calcd. for $C_{21}H_{18}F_6O_2$: C, 60.58; H, 4.36.

Found: C, 60.61; H, 4.42.

The infrared spectrum (neat liquid) shows absorption maxima at 3005s, 1725vs, 1625vs, 1580w, 1475m, 1425m, 1305m, 1200m, 1175vs, 1060m, 1040w, 980 m-s, 910s, 855s, and 745m cm^{-1} .

The n.m.r. spectrum of this compound ($CDCl_3$) displays an A_2B_2 pair of doublets at τ 1.96 and 2.68 (J 8 c.p.s.) (aromatic), a quartet at 7.30 (methylene) and a triplet at 8.77 (methyl) with satisfactory relative integrated areas.

To 25.0 ml. of 10% NaOH solution was added 2.0 g. (0.048 mole) of the above diketone (73). The mixture was refluxed for two hours, cooled to room temperature and then extracted three times with ether (total 120 ml.). To the chilled aqueous layer was added 25 ml. concentrated hydrochloric acid. A fluffy yellow solid was formed and floated to the surface. Recrystallization of this solid from hot water gave 0.89 g. (63%) of *p*-ethylbenzoic acid, m.p. 110-111° (lit.¹¹⁷ 110-111°). Its amide had a melting point 160-161° (lit.¹¹⁸ 161-162°). The n.m.r. spectrum of the cleavage product displays an A_2B_2 pair of doublets at τ 1.96 and 2.80 (J 8 c.p.s.) (aromatic), a quartet at 7.33 (methylene), a triplet at 8.75 (methyl) and a singlet at -3.1 (carboxylic acid proton) with satisfactory relative integrated areas. The n.m.r. spectrum substantiates the assigned structure

of the cleavage product as p-ethylbenzoic acid.

Thin layer chromatography with alumina G of an analytical sample of the above diketone 73 gave only one visible spot, after elution with petroleum-ether followed by petroleum-ether-5% benzene solution.

b. Attempted Preparation of 1,5-Di(p-ethylphenyl)-1,1,5,5-tetrachloro-2,2,-3,3,4,4-hexafluoropentane (74).

1) The Use of Benzene as Solvent.

A solution containing 1.96 g.

(0.470 mmole) of 1,3-di(p-ethylbenzoyl)perfluoropropane (73), 4.0 g. (1.9 mmole) phosphorus pentachloride, and 50 ml. dry benzene was refluxed continuously for twelve hours. Acetone was added to destroy the excess phosphorus pentachloride. After removal of volatile material under diminished pressure (water aspirator) the mixture was distilled under vacuum. A fraction (1.2 g, 61%) b.p. 152-160° (0.05 mm), whose infrared spectrum was identical with the starting diketone, was obtained. A black, gummy residue remained in the distillation flask.

In a second attempt of this reaction the reflux time was extended to one week. Identical results, with the recovery of starting material, were obtained.

ii) The Use of 2-Phenyl-2,2-dichloro-1,1,1-trifluoroethane as Solvent.

2-Phenyl-2,2-dichloro-1,1,1-trifluoroethane was prepared by the method of Cohen in 97% yield.¹⁴⁵ It was hoped that this liquid (b.p. 78-83° at 25 mm.) would provide a sufficiently high reflux temperature for the reaction. A solution of 1.96 g. (0.470 mmole) of diketone 73, 4.0 g. (1.9 mmole) of phosphorus pentachloride, and 25 ml. of 2-phenyl-2,2-dichloro-1,1,1-trifluoroethane was refluxed continuously for four days. Acetone was added to the mixture to destroy the excess phosphorus pentachloride. Distillation under diminished pressure (water aspirator) afforded a fraction boiling at 68° (15 mm.) (solvent). Distillation under vacuum gave a material b.p. 168-175° (0.25 mm.). The infrared spectrum showed this material to be the starting diketone. Recovery: 1.5 g. (77%).

iii) Sealed Tube Reaction.

Diketone 73, (1.96 g., 0.470 mmole), phosphorus pentachloride (4.0 g., 1.9 mmole) were introduced into a combustion tube which was then sealed. The tube was inserted into a fiberglass explosion-proof tape, and heated at 235°C for 20 hours. The resulting mixture was a hard, black material. No characterizable product was isolated.

8. Attempted Preparation of *m,m'*-Bis(bromoacetyl)-1,5-diphenylperfluoropentane (82).

a. Preparation of 1,3-Di(benzoyl)perfluoropropane (78).

1,3-Di(benzoyl)perfluoropropane was prepared essentially according to the method of Fear.¹⁰⁹ Perfluoroglutaryl dichloride (7.73 g., 0.0280 mole) in 25.0 ml. anhydrous benzene was added dropwise to a stirred suspension of powdered anhydrous aluminum chloride (7.35 g., 0.0550 mole) and 100 ml. of absolute benzene at 0°C. After total addition, the reaction mixture was stirred for thirty minutes at room temperature, and then poured onto crushed ice (ca. 100 g.) containing 10.0 ml. concentrated hydrochloric acid. After separation of layers, the aqueous phase was extracted three times with benzene and the extracts combined with the original organic layer. The combined organic phase was washed with 5% sodium bicarbonate solution, followed by careful washings with water. The organic phase was then dried overnight over magnesium sulfate.

Separation of magnesium sulfate and removal of solvent afforded a black tarry residue. Crude yield: 7.66 g. (77%). Distillation in vacuo afforded a fraction b.p. 130-137° (0.4 mm), with a constant boiling point at 135° (0.4 mm). Yield: 7.46 g. (75%). The liquid solidified upon standing at room temperature, m.p. 52-53°.

Anal. Calcd. for $C_{17}H_{10}F_6O_2$: C, 56.68; H, 2.80.

Found: C, 56.62; H, 2.97.

The infrared spectrum of this compound (Nujol) shows bands at 1720vs, 1460vs, 1380m, 1320s, 1290w, 1270m-s, 1230s, 1170vs, 1110s, 1060m, 1030w, 1000w, 980w, 940w, 900s, 840w, 800s, 755s, 710s, 680s, 670s and 650m cm^{-1} .

The n.m.r. spectrum (CDCl_3) exhibits a multiplet at τ 1.80 and 2.70 (aromatic).

To 25.0 ml. of 10% sodium hydroxide solution was added 0.50 g. (1.4 mmoles) of the above diketone (78). After standing for two days at room temperature, the solution was chilled in an ice bath and acidified to pH=1 using concentrated hydrochloric acid. A white crystalline material was deposited. Sublimation of this material at 35-45° (0.2 mm.) gave a substance, m.p. 119-120°. Mixed melting point with authentic benzoic acid gave no apparent depression. The infrared spectrum of this material (Nujol) was identical with the spectrum of an authentic sample of benzoic acid. Likewise, its n.m.r. spectrum (CDCl_3) was identical with that of an authentic sample of benzoic acid.

b. Attempted Preparation of 1,5-Diphenyl-1,1,5,5-tetrachloro-2,2,3,3,4,4-hexafluoropentane (79).

1) The Use of Benzene as Solvent.

A solution of 3.60 g (0.0100 mole) of 1,3-di(benzoyl)perfluoropropane, 6.24 g. (0.0300 mole) phosphorus pentachloride in 20 ml. of dry benzene was

refluxed for 118 hours. The reaction was worked up using the method of Bachman and Hill.¹⁴⁶ Water and ice were added to the mixture and stirred vigorously until all the phosphorus oxychloride formed had decomposed. After separation of layers, the organic phase was washed with 2% sodium carbonate solution, and then with water. The organic layer was then dried over calcium chloride. Removal of calcium chloride and solvent benzene gave a residue. Distillation of this residue under vacuum afforded a colorless liquid, b.p. 123-125° (0.2 mm.). This liquid solidified upon standing at room temperature, m.p. 47.5-51°. Yield: 1.76 g. (49%). The infrared spectrum of this material was very similar to the starting diketone, and showed strong absorption at 1720 cm.⁻¹, assigned to the carbonyl function.

11) The Use of Phosphorus Oxychloride as Solvent.

Essentially the same procedure as described for the previous procedure was used except that 30 ml. phosphorus oxychloride was used as the solvent in place of benzene. After continuous reflux of the solution for 70 hours, solvent was removed and excess phosphorus pentachloride sublimed. The residue was distilled under vacuum affording a slightly yellow liquid, 1.67 g. (47%), b.p. 126-130° (0.25 mm.). The infrared spectrum of this liquid (neat) was very similar to that of the starting diketone.

111) The Use of 2-Phenyl-2,2-dichloro-1,1,1-trifluoroethane as Solvent.

A solution of 3.60 g (0.0100 mole) diketone 78, 8.5 g (0.041 mole) phosphorus pentachloride in 15 ml. of 2-phenyl-2,2-dichloro-1,1,1-trifluoroethane¹⁴⁵ was refluxed continuously for 21 hours. Acetone (30 ml.), was added to the cooled solution. After removal of volatile material under aspirator pressure (ca. 15 mm), the black residue was distilled under high vacuum affording 2.5 g. of a material, b.p. 125-140° (0.07-1.00 mm). The infrared spectrum of this material was very similar to that of the starting diketone with strong carbonyl absorption at 1720 cm.⁻¹ Recovery: 69.5%.

iv) Sealed Tube Reaction.

Diketone 78 (3.6 g., 0.010 mole) and phosphorus pentachloride (12.0 g., 0.0500 mole) were introduced into a combustion tube which was then sealed. The tube was inserted into a Fiberglas explosion-proof tape and heated for 8 hours at 235°. The resulting mixture was a thick oil whose infrared spectrum was very similar to that of the starting diketone with strong carbonyl band at 1720 cm.⁻¹

9. Attempted Preparation of 1,7-Dibromo-3,3,4,4,5,5-hexafluoroheptane-2,6-dione (87).

a. Reaction of Diazomethane and Perfluoroglutaryl Dichloride.

To a well stirred, ice cold, ethereal solution containing 0.2M diazomethane¹⁴⁷ was added, in the course of 90 minutes, 8.6 g. (0.031 mole) of perfluoroglutaryl dichloride dissolved in 50 ml. anhydrous ether. There was a vigorous evolution of nitrogen which ceased as soon as all the acid chloride has been added. The mixture was stirred at room temperature overnight. No attempt was made to isolate the bis(diazo)ketone generated in this reaction.

Solvent ether was removed under diminished pressure and 100 ml. of anhydrous chloroform was added to dissolve the yellow-brown residue. Anhydrous hydrogen bromide was then bubbled into the solution until the evolution of nitrogen ceased. Removal of chloroform gave a thick brown residue. Vacuum distillation of this residue afforded a material, b.p. 43.5-50° (4.0 mm). Yield: 2.48 g. The liquid crystallized upon prolonged standing in the refrigerator. Several recrystallizations from carbon tetrachloride gave a constant melting substance, m.p. 92-93°.

Anal. Calcd. for $C_7H_4O_2F_6Br_2$: C, 21.34; H, 1.02; Br, 40.57. Found: (Schwarzkopf) C, 23.26; H, 1.95; Br, 39.15.
(Spang) C, 22.86; H, 1.51.
C, 22.89; H, 1.66.

The analytical data do not support the assignment of the expected structure.

The infrared spectrum (Nujol) of this substance shows absorption maxima at 3320w, 1780s, 1490w, 1280w, 1270w, 1240w, 1220w, 1185s, 1160m, 1120m, 1085w, 1050w, 1020vw, 910w, 870w, 820w, 790w and 720w cm^{-1} .

The n.m.r. spectrum (CCl_4) exhibits a singlet at τ 3.45 and a doublet at 6.10 with relative intensities 1:2. The peak at τ 3.45 exchanged rapidly and completely with D_2O while the doublet at 6.10 exchanged slowly and the intensity remained constant after 15 min.

The structure of the above material has not been identified.

In other attempts, decomposition of the bis(diazo)-ketone in anhydrous ether with anhydrous hydrogen bromide, or the decomposition in ether with 35% hydrobromic acid gave similar results.

b. Attempted Preparation of 1,7-Di(methylsulfinyl)-2,6-dioxo-3,3,4,4,5,5-hexafluoroheptane.

1) Preparation of Diethylperfluoroglutarate.

Diethylperfluoroglutarate was prepared: to a well-stirred solution of 27.4 g. absolute ethanol (0.600 mole) and 32.0 g. (0.405 mole) reagent grade pyridine, was added, a drop at a time, 55.4 g. (0.200 mole) perfluoroglutaryl dichloride. The solution was stirred for 30 minutes after

total addition, and then poured onto 100 ml. of water. After separation of layers, the aqueous phase was extracted three times with ether, and the extracts added to the original organic layer. The combined organic phase was then washed with 5% sodium carbonate solution, followed by water, and then dried over magnesium sulfate. Removal of drying agent and solvent gave a light yellow residue. Vacuum distillation of this material afforded two fractions. The first fraction, b.p. 25° (19 mm) contained ethanol and pyridine, while the second fraction, b.p. $106.5-107^{\circ}$ (19 mm) contained the expected diester. Yield; 40 g. (68%) (lit.¹⁴⁸ b.p. 76° (30 mm), $203-206^{\circ}$ (760 mm)).

The infrared spectrum of this liquid (neat) exhibits absorption bands at 3000m, 1780vs, 1475w, 1450w, 1360m, 1320m, 1270m-w, 1250m, 1175s, 1140s, 1110m, 1050m, 1010m, 950m, 925m, 860m, 826m, 790w, 750m and 710w cm^{-1} .

The n.m.r. spectrum (neat) shows a quadruplet at $\tau 5.50$, (methylene), and a triplet at 8.60 (methyl) with satisfactory relative integrated areas.

11) Reaction of Diethylperfluoroglutarate and Methylsulfinyl Carbanion.¹⁴⁹

Sodium hydride (0.3 mole as a 53.5% dispersion in mineral oil) was washed with several portions of low-boiling petroleum ether to remove the mineral oil. The reaction flask was equipped with rubber stoppers, a reflux condenser with a mercury gas-trap-bubbler and a

magnetic stirrer. The system was filled with nitrogen; 150 ml. of dimethyl sulfoxide, previously dried over molecular sieves, was introduced via a syringe, and the mixture heated at 75-80° for ca. 45 min. The resulting solution of methylsulfinyl carbanion was cooled in an ice bath. To this solution was added 22.2 g. (0.0750 mole) of diethylperfluoroglutamate (91). After total addition, the mixture was stirred for 30 min. at ice temperature and then at room temperature for an additional 30 min. A solution of 50 ml. water and 50 ml. concentrated hydrochloric acid was added to the mixture until the pH of the system was approximately 6. The mixture was then extracted with chloroform. Removal of solvent left a gummy residue. Vacuum distillation of this material afforded a fraction, b.p. 84° (17 mm.) which was shown by its infrared spectrum to be dimethyl sulfoxide. A tarry residue remained in the distillation flask. It was not further investigated.

10. Attempted Preparation of 1,7-Dichloro-3,3,-4,4,5,5-hexafluoroheptane-2,6-dione (90).

Perfluoroglutaryl dichloride was reacted with diazomethane in exactly the same manner described previously for the preparation of 86. Anhydrous hydrogen chloride was passed into the ethereal solution containing the bis(diazo)-ketone until evolution of nitrogen ceased. Removal of solvent and distillation of the yellow-brown residue gave 1.1 g. of light yellow liquid, b.p. 68-78° (0.6 mm.). The

infrared spectrum shows strong absorption at 3450 (OH), 1780 (carbonyl),¹¹⁴ 1450 (C-H), 1350-1000 (multiple bands, C-F) cm^{-1} . The n.m.r. spectrum (CDCl_3) exhibits a multiplet centered around τ 5.60 to 6.20. None of these bands were effected by deuterium oxide treatment.

11. Attempted Preparation of 1,6-Dibromo-3,3,-4,4-tetrafluorohexane-2,5-dione (94).

a. Reaction of Perfluorosuccinic Acid and Methyl Magnesium Iodide.

The method of Groth¹²⁹ was used. Methyl magnesium iodide was prepared by the dropwise addition of 42 g. (0.29 mole) of redistilled methyl iodide to 7.2 g. (0.29 g-atom) magnesium in 50 ml. anhydrous ether (treated with lithium aluminum hydride and redistilled before use). Stirring was provided by a "Vibro-mixer". The Grignard reagent was added dropwise to a well-stirred solution containing 11.0 g. (0.0580 mole) of perfluorosuccinic acid. (The acid was previously dried over phosphorus pentoxide at room temperature at 0.01 mm.Hg for 24 hours). The mixture, after being stirred overnight at room temperature, was hydrolyzed with 20 ml. of saturated ammonium chloride solution. The resulting solid (magnesium salts) was filtered off and washed well with ether, and the washings added to the original ether solution. The combined organic layer was dried over sodium sulfate. Removal of drying agent and solvent ether afforded a small amount of yellow-

brown oil. Distillation of this oil gave a small yield (ca. 1 g.) of a light yellow liquid, b.p. 88° . Some tarry residue remained in the distillation flask but did not boil even at 230° (oil bath temperature). (The expected diketone boils at 128°).¹²⁹ The infrared spectrum of this liquid (neat) shows a weak absorption band at 1780 cm^{-1} (carbonyl).¹¹⁴ This material seems to correspond to the low boiling forerun described by Groth.¹²⁹

b. Reaction of Perfluorosuccinic Acid and Methyl-lithium.

Methyl-lithium was prepared by the method of Tegnér¹³⁰ except that lithium ribbons cut into fine strips were used instead of lithium dust and stirring was performed by a "Vibromixer". To 2.4 g. (0.35 g.-atom) of lithium metal covered with 100 ml. of anhydrous ether under a nitrogen atmosphere was added, a drop at a time and with vigorous agitation, 23.0 g. (0.160 mole) redistilled methyl iodide dissolved in 50 ml. anhydrous ether. When addition of methyl iodide was complete, the mixture was refluxed for 30 min. and then added dropwise to a solution of 5.82 g. (0.0306 mole) perfluorosuccinic acid in 100 ml. ether. The reaction was performed under a dry nitrogen atmosphere. The solution, which was clear in the beginning, became cloudy as methyl-lithium was added. When addition was complete, the solution was refluxed for 30 min. and then 100 ml. saturated ammonium chloride solution was added

slowly to hydrolyze the resulting dilithio salt. After separation of layers, the aqueous phase was extracted three times with ether, and the extracts added to the original ether layer. The combined layer was dried overnight over sodium sulfate.

Removal of sodium sulfate and ether gave a yellowish residue. Distillation and fractionation of this material yielded a fraction (ca. 1 g.) boiling at 82-85°. The infrared spectrum of this liquid (neat) was identical to that of the material obtained from the reaction of perfluorosuccinic acid with methyl magnesium iodide. A tarry residue remained in the distillation flask and did not boil even when the temperature of the oil bath was 230°.

VI. POLYMERIZATION AND POLYMER CHARACTERIZATION

A. GENERAL METHODS:

A solution containing equimolar amounts (ca. 3 mmoles) of the bis-bromomethyl ketone and DTOA in dimethylformamide was heated to reflux (153°) in a 500 ml., three-necked flask fitted with a reflux condenser and mechanical stirrer. Precipitation of polymer generally commenced ca. 15 min. after initial reflux; reflux maintained for a total of 1.5 hours. At the end of this time the mixture was filtered while hot and the resulting solids continuously extracted (Soxhlet) for 15 hours each with dimethylformamide, absolute ethanol and ether, in that order. The residual polymer, after being dried at 100° and 0.2 mm. for 5 hours, was used for yield calculation and subsequent characterization.

Inherent viscosities were determined, using a Cannon-Fenske Series 150 viscometer, at 25.0° and at concentrations of 0.25g/100 ml. in concentrated sulfuric acid (filtered solutions). X-ray powder patterns were obtained using a 114.7 cm. powder camera (North American Philips Co.) and using copper K_{α} radiation $\lambda = 1.542\text{\AA}$.

Polymer thermal stabilities were examined (nitrogen atmosphere) using a static method much like the one previously described.⁴⁰ After pre-drying at $140-145^{\circ}$ (0.2 mm.) for 30 min., samples were placed into an electrically-heated chamber and held at 300, 350, 400, 500 and 600° consecutively for

one-hour periods each. At the end of each hour of heating the sample was cooled under nitrogen and removed to determine weight loss. A plot between the incremental weight loss of the sample with increasing temperature closely corresponds to the thermogravimetric analysis curve obtained using a commercial instrument (compare Figs. 1 and 2 for thermogravimetric analysis curves for polymer 51a).

Infrared spectra were obtained in KBr disks using conventional sample preparation techniques; data on all model and polymeric bithiazoles are from calibrated spectra (polystyrene). Potassium bromide disks proved to be invaluable media for examining the insoluble polymers in the ultraviolet region; some care in disk preparation is required in order to obtain satisfactory spectra. Approximately 0.1 mg. of polymer and 300 mg. of infrared-grade KBr contained in a stainless steel capsule with two ball bearings are shaken for 30 seconds in a mechanical vibration-grinder. The use of a plastic capsule is generally unsatisfactory. A portion of the mixture, ca. 40 mg. is diluted with 260 mg. KBr and the resulting sample shaken for an additional 30 seconds; the necessary dilution factor is determined empirically. The sample is dried at 130° for 30 minutes and then transferred while still hot to the disk mold; failure to remove adsorbed moisture at this point results in the formation of opaque rather than transparent disks. The mold assembly is evacuated at ca. 1 mm. for no less

than 10 minutes; 4,000 psi. pressure is applied and held for 5 minutes, followed by 16,000 psi. for an additional 5 minutes. The pressure is released and the disk removed in the conventional manner.

B. PREPARATION OF POLYMERS.

1. Poly-4,4'-(p-phenylene)-2,2'-bithiazole.

a. The Use of Dimethylformamide as Solvent (51a).

A solution of 6.40 g. (0.0200 mole) of p-bis(bromoacetyl)benzene and 2.45 g. (0.0200 mole) DTOA in 400 ml. DMF was vigorously stirred and heated to reflux. Precipitation of polymer commenced 3 min. after initial reflux; reflux maintained for a total of 1.5 hr. At the end of this time the mixture was filtered while hot and a yellow-brown powder was obtained. Purification (Soxhlet extraction) and drying of this polymer according to the procedure described previously (under General Methods) afforded a light yellow-brown powder, 4.25 g. (88%).

Anal. Calcd. for $(C_{12}H_6N_2S_2)_x$: C, 59.48; H, 2.49; N, 11.56; S, 26.47; Br, 0.00. Found: C, 59.23; H, 2.87; N, 11.41; S, 25.20; Br, 0.54, 0.76.

The infrared spectrum (KBr disk) of this polymer exhibits absorption bands at 3100vw, 1680w, 1610m, 1475s, 1420mw, 1310w, 1275w, 1100w, 940s, 883m, 845m-s and 745s cm^{-1} .

The ultraviolet spectrum of this polymer (KBr disk) exhibits λ_{max} at 311s and 360m m μ .

b. The Use of Diglyme as Solvent (51b).

A solution of 3.20 g. (0.0100 mole) *p*-bis(bromoacetyl)benzene, 1.22 g (0.0100 mole) DTOA in 150 ml. diglyme was vigorously stirred and heated to reflux. Precipitation occurred 10 min. after initial reflux; reflux was maintained for a total of 1.5 hours. The solution was then filtered while hot and a green precipitate was collected. After trituration with 100 ml. hot diglyme, the polymer was extracted (Soxhlet) for 14 hours each with absolute alcohol and ethyl ether, in that order. After drying in vacuo at 100° for 4 hours, a green solid, 2.15 g. (89%) was obtained.

Anal. Calcd. for $(C_{12}H_6N_2S_2)_x$: C, 59.48; H, 2.49; N, 11.56; Br, 0.00. Found: C, 57.41; H, 2.67; N, 10.38; Br, 3.60, 3.27.

The infrared spectrum (Nujol) of this polymer has bands at 1690m, 1620m, 1420s, 1315mw, 1280mw, 1220w, 1190w, 1110w, 1060mw, 1020w, 940vs, 890ms, 850m, 820w and 750vs cm.⁻¹

The ultraviolet spectrum (KBr disk) exhibits absorption maxima at λ_{max} 310s and 370m mμ.

The infrared and ultraviolet spectra of this material (51b) are quite similar to those of polymer 51a.

c. Treatment of Poly-4,4'-(*p*-phenylene)-2,2'-bithiazole with 10% Sodium Hydroxide.

A suspension of 0.32 g. polymer and 25 ml. 10% sodium hydroxide was refluxed continuously for 5 hours,

and then allowed to stand at room temperature for an additional 12 hours. The suspension was filtered, and the residue washed repeatedly with water until the washings no longer were basic. The residual polymer, after being dried at 100° and 0.01 mm. for 5 hours, was used for subsequent studies. Recovery: 0.30 g. (94%).

Anal. Calcd. for $(C_{12}H_6N_2S_2)_x$: C, 59.48; H, 2.49; N, 11.56. Found: C, 58.85; H, 2.62; N, 11.68.

The infrared spectrum (KBr disk) of this material is identical to that of the material (51a) prior to base treatment.

d. Treatment of Poly-4,4'-(p-phenylene)-2,2'-bithiazole (51a) with Concentrated Sulfuric Acid.

A sample of polymer 51a (0.30 g.) was dissolved in 25 ml. of concentrated sulfuric acid at room temperature. A deep brown solution resulted. The solution was then poured immediately onto ca. 100 g. of crushed ice and a green solid precipitated. The solution was filtered. The precipitate was washed repeatedly with water, and then triturated with 25 ml. of 10% sodium hydroxide solution. The color of the solid changed from green to brown. The solid was then extracted with water (Soxhlet) continuously for 15 hours. The residual solid, after being dried at 100°C and 0.01 mm. for 5 hours, was used for subsequent studies. Recovery: 0.28 g. (93%).

Anal. Calcd. for $(C_{12}H_6N_2S_2)_x$: C, 59.48; H, 2.49; N, 11.56; S, 26.47. Found: C, 57.68; H, 2.80; N, 10.52; S, 24.80; Ash, 1.80.

The infrared spectrum (KBr disk) of this material is essentially the same as that of the material prior to acid treatment.

2. Poly-4,4'-(p-biphenylene)-2,2'-bithiazole (52).

A solution of 3.96 g (0.0100 mole) 4,4'-bis-(bromoacetyl)biphenyl and 1.22 g. (0.0100 mole) DTOA in 400 ml. DMF was vigorously stirred and heated to reflux. Precipitation of polymer occurred 10 min. after initial reflux; reflux was continued for an additional 1 hour. Purification (Soxhlet extraction) and drying in the manner described previously afforded 2.56 g. (79%) of product.

Anal. Calcd. for $(C_{18}H_{10}N_2S_2)_x$: C, 67.89; H, 3.17; N, 8.80; S, 20.14; Br, 0.00. Found: C, 67.36; H, 3.53; N, 8.00; S, 18.85; Br, 0.00, 0.19.

The infrared spectrum (KBr disk) of this polymer exhibits bands at 1685s, 1610s, 1480vs, 1430m, 1410m, 1275m, 1185w, 1055m, 1005m, 937vs, 885s, 825vs and 750vs cm^{-1}

The ultraviolet spectrum (KBr disk) shows λ_{max} at 321s and 375m μ .

3. Poly-4,4'-(p-diphenylenemethane)-2,2'-bithiazole (53).

A solution of 2.87 g. (7.00 mmoles) 4,4'-bis-(bromoacetyl)diphenylmethane and 0.85 g. DTOA (7.0 mmoles) in 200 ml. dry DMF was vigorously stirred and heated to reflux. Precipitation occurred 7 minutes after initial reflux; reflux was continued for an additional 1.5 hours. The solution was filtered while hot and purified and dried in the manner described previously. Yield: 1.81 g. (78%).

Anal. Calcd. for $(C_{19}H_{12}N_2S_2)_x$: C, 68.64; H, 3.64; N, 8.43; S, 19.29; Br, 0.00. Found: C, 68.79; H, 3.70; N, 8.44; S, 19.05; Br, 0.70.

The infrared spectrum of this polymer (KBr disk) exhibits absorption maxima at 1685vw, 1610vw, 1575vw, 1485vs, 1420m, 1310w, 1275w, 1185w, 1100w, 1050w, 1015w, 940vs, 880s, 810m, 785w and 750vs cm^{-1} .

The ultraviolet spectrum of this polymer (KBr disk) exhibits λ_{max} at 265s and 365m μ .

4. Poly-4,4'-(p-diphenylene ether)-2,2'-bithiazole (54).

A solution of 1.24 g. (3.00 mmoles) 4,4'-bis-(bromoacetyl)diphenylether and 0.37 g. (3.0 mmoles) DTOA in 200 ml. dry DMF was vigorously stirred and heated to reflux. Precipitation occurred 17 minutes after the initial reflux; reflux was maintained for an additional 1.5 hours. Purification and drying in the usual manner afforded a light

yellow solid, 0.80 g. (79%).

Anal. Calcd. for $(C_{18}H_{10}N_2S_2O)_x$: C, 64.65; H, 3.01; N, 8.38; S, 19.18; Br, 0.00. Found: C, 64.24; H, 3.47; N, 8.36; S, 18.81; Br, 0.00, 0.00.

The infrared spectrum (KBr disk) of this polymer exhibits absorption maxima at 1680w, 1605s, 1530s, 1510w, 1475vs, 1425m, 1320w, 1295wm, 1250vs, 1170s, 1105mw, 1050m, 1015m, 940s, 885s, 860s, 835s, 750s, 710w and 665w cm^{-1} .

The ultraviolet spectrum (KBr disk) exhibits λ_{max} at 286s and 359m μ .

5. Poly-4,4'-(hexamethylene-p-diphenylene-1,6)-2,2'-bithiazole (57).

A solution of 1.80 g. (3.75 mmoles) p,p'-bis-(bromoacetyl)-1,6-diphenylhexane and 0.455 g. (3.75 mmoles) DTOA in 200 ml. DMF was stirred and heated to reflux. Precipitation of polymer occurred 13 minutes after the initial reflux; reflux was maintained for an additional 1.5 hours. The solution was filtered while hot. The precipitate collected was coded Fraction A. It was purified and dried in the usual manner. Yield: 0.84 g. (56%).

Precipitation occurred when the filtrate from the above was chilled. After continuous Soxhlet extraction for 15 hours each with absolute ethanol and anhydrous ether, in that order, and drying in vacuo at 100° for 5 hours, a yellow-brown solid was obtained and was coded Fraction B.

Yield: 0.22 g. (15%).

The mother liquor from fraction B above was removed under diminished pressure leaving a yellow-brown residue. Soxhlet extraction for 15 hours each with absolute alcohol and anhydrous ether, in that order, and drying in vacuo at 100° for 5 hours afforded a light yellow solid. This was coded Fraction C. Yield: 0.26 g. (18%).

Anal. Calcd. for $(C_{24}H_{22}N_2S_2)_x$: C, 71.60; H, 5.51; N, 6.96; S, 15.93; Br. 0.00.

Found: (Fraction A): C, 71.60; H, 5.69; N, 6.85; S, 16.19; Br, 0.00.

(Fraction B): C, 71.02; H, 5.71; N, 6.85; Br, 0.66.

(Fraction C): C, 69.31; H, 5.49; N, 6.42; Br, 0.71.

The infrared spectra (KBr disk) of this polymer exhibits absorption maxima at:

Fraction A: 3120w, 2940m-s, 2860m, 1675w, 1610w, 1480s, 1425m-w, 1185m-w, 1050w, 1020w, 940vs, 880m-s, 825m-s and 750s cm^{-1}

Fraction B: 2870m-w, 1680m, 1610m-s, 1485vs, 1445w, 1425w, 1300w, 1275w-m, 1185m, 1050m-w, 1015w, 940vs, 880s, 825s and 750s cm^{-1}

Fraction C: 2950s, 2880m-w, 1680m, 1610ms, 1485vs, 1445w, 1425w, 1310w, 1255w, 1185m-w, 1125m-w, 1020w, 940vs, 880m-s and 750s cm^{-1}

The ultraviolet spectra (KBr disk) of this polymer

exhibits $\lambda_{\max}$ at:

Fraction A: 260s and 375m μ ; Fraction B: 258s and 360m μ ;

Fraction C: 258s and 362m μ .

The ultraviolet spectrum of Fraction C in 95% ethanol exhibits $\lambda_{\max}$ at 255s and 355m μ .

The melting points (crystalline melting point) of this polymer are: Fraction A, 440-448°; Fraction B, 238-252° and Fraction C, 218-235°.

6. Poly-4-4'-(bithiazole-2,2') (58).

a. The Use of Dimethylformamide as Solvent.

A solution of 4.88 g. (0.0200 mole) 1,4-dibromobutane-2,3-dione, and 2.45 g. (0.0200 mole) DTOA in 300 ml. dry DMF was vigorously stirred and heated to reflux. After a brief heating, the solution turned black. Reflux was maintained for 1.5 hours. The solution was filtered while hot and a black solid was obtained. It was then purified and dried in the manner described above. Yield: 0.35 g. (10.5%).

Anal. Calcd. for $(C_6H_2N_2S_2)_x$: C, 43.35; H, 1.21; N, 16.85; S, 38.58; Br, 0.00. Found: C, 42.54; H, 2.79; N, 15.71; S, 28.01; Br, 0.34.

b. The Use of Absolute Ethanol as Solvent.

A solution of 2.44 g (0.0100 mole) 1,4-dibromobutane-2,3-dione, and 1.22 g. (0.0100 mole) DTOA in 300 ml. absolute alcohol was heated to reflux. Reflux was

maintained for 1.5 hours. Filtering the mixture while hot have a dark brown material. Purification and drying in the usual manner afforded a dark brown solid. Yield: 0.30 g. (18%).

Anal. Calcd. for $(C_6H_2N_2S_2)_x$: C, 43.35; H, 1.21; N, 16.85; S, 38.58. Found: C, 40.05; H, 2.19; N, 14.09; S, 33.10.

APPENDIX I
X-RAY DIFFRACTION PATTERNS
OF SOME
2,2'-BITHIAZOLES
AND
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES

Unless otherwise stated only bands of medium and strong intensities are listed. The "d" spacings (in Å) are obtained from arc length measurements and computed from Tables of Interplanar Spacings.¹⁵⁰

TABLE IV

X-RAY POWDER PATTERNS OF SOME 2,2'-BITHIAZOLES.A. 4,4'-Diphenyl-2,2'-bithiazole. (65).

Line No.	"d"	Relative Intensity
1	7.31	s
2	5.79	w-m
3	5.47	m
4	4.48	w-m
5	4.63	s
6	4.36	s
7	3.83	s
8	3.69	s
9	3.22	m
10	3.15	s
11	2.94	s

B. 4,4'-Bis(p-biphenyl)-2,2'-bithiazole (67).

Line No.	"d"	Relative Intensity
1	7.44	m-s
2	5.73	m
3	4.65	s
4	4.43	m-s
5	4.12	m-s
6	3.89	s

B. (Continued)

Line No.	"d"	Relative Intensity
7	3.25	m-s
8	3.10	m-s
9	1.99	m

TABLE V.

X-RAY DIFFRACTION PATTERNS OF SOME POLY-4,4'-
DIARYL-2,2'-BITHIAZOLES.

A. Poly-4,4'-(p-phenylene)-2,2'-bithiazole (51a).

Line No.	"d"	Relative Intensity
1	6.13	w
2	4.77	s
3	4.10	m
4	3.71	s
5	3.19	m
6	1.99	w

B. Poly-4,4'-(p-phenylene)-2,2'-bithiazole (51b).

Line No.	"d"	Relative Intensity
1	4.75	m
2	4.16	m-w
3	3.72	m
4	3.16	w
5	1.99	m-w

C. Poly-4,4'-(p-phenylene)-2,2'-bithiazole(51a)
Heated at 350° for One Hour Under Nitrogen .

Line No.	"d"	Relative Intensity
1	6.17	w
2	4.80	s
3	4.29	m
4	3.74	s
5	3.21	m
6	1.99	w-m
7	1.74	w

D. Poly-4,4'-(p-biphenylene)-2,2'-bithiazole (52).

Line No.	"d"	Relative Intensity
1	6.81	w
2	4.72	s
3	4.23	m
4	3.84	s
5	3.19	m
6	1.99	w

E. Poly-4,4'-(p-diphenylenemethane)-2,2'-bithiazole (53).

Line No.	"d"	Relative Intensity
1	4.67	s
2	4.11	m
3	3.47	s
4	3.45	s
5	3.31	s
6	1.99	w

F. Poly-4,4'-(p-diphenylene ether)-2,2'-bithiazole (54).

Line No.	"d"	Relative Intensity
1	4.69	s
2	4.38	m
3	3.82	s
4	3.21	w-m
5	1.98	w

G. Poly-4,4'-(hexamethylene-p-diphenylene-1,6)-2,2'-bithiazole (57).Fraction A

Line No.	"d"	Relative Intensity
1	4.79	s
2	4.32	s
3	3.78	s
4	3.24	m-w
5	1.99	m-w

Fraction B

1	5.26	s
2	4.29	s
3	3.79	s
4	3.50	m
5	1.95	w

Fraction C

1	4.86	m
2	4.55	s
3	4.41	m
4	4.07	s
5	1.99	w

H. Poly-4,4'-(bithiazole-2,2') (58).Polymer Prepared in Dimethylformamide Solvent:

Line No.	"d"	Relative Intensity
1	6.11	m
2	3.85	s
3	3.43	s
4	2.53	w
5	2.00	w

Polymer Prepared in Ethanol Solvent:

Line No.	"d"	Relative Intensity
1	4.57	m
2	3.88	m
3	3.42	s
4	2.29	s
5	2.00	m-w

APPENDIX II
INHERENT VISCOSITY MEASUREMENTS
OF SOME
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES

TABLE VI.
INHERENT VISCOSITY MEASUREMENTS
OF SOME
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES.

<u>Polymer</u>	<u>Concentration</u> (g/100 ml.)	<u>η_{inh}</u>
<u>51a</u>	0.500	0.24
	0.250	0.24, 0.24*
	0.125	0.21
<u>51b</u>	0.500	0.23
	0.250	0.23
	0.125	0.22
<u>52</u>	0.500	0.24
	0.250	0.24, 0.24*
	0.125	0.25
<u>53</u>	0.500	0.46
	0.250	0.47, 0.47*
	0.125	0.46
	0.0625	0.46
<u>54</u>	0.500	0.39
	0.250	0.38, 0.38*
	0.125	0.36
	0.0625	0.33

* η_{inh} of polymer solution after standing for 5 hours at 25°C.

<u>Polymer</u>	<u>Concentration</u> (g/100 ml.)	<u>η_{inh}</u>
<u>57</u> <u>Fraction A</u>	0.250	0.36, 0.45
<u>57</u> <u>Fraction B</u>	0.250	0.13
<u>57</u> <u>Fraction C</u>	0.250	0.057

APPENDIX III.
INFRARED SPECTRA OF SOME 4,4'-DIARYL-2,2'-BITHIAZOLES
AND
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES.

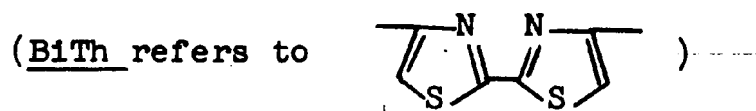


Figure 4.

INFRARED SPECTRA OF 4,4'-DIPHENYL-2,2'-
BITHIAZOLE AND POLY-4,4'-(p-PHENYLENE)-
2,2'-BITHIAZOLE.

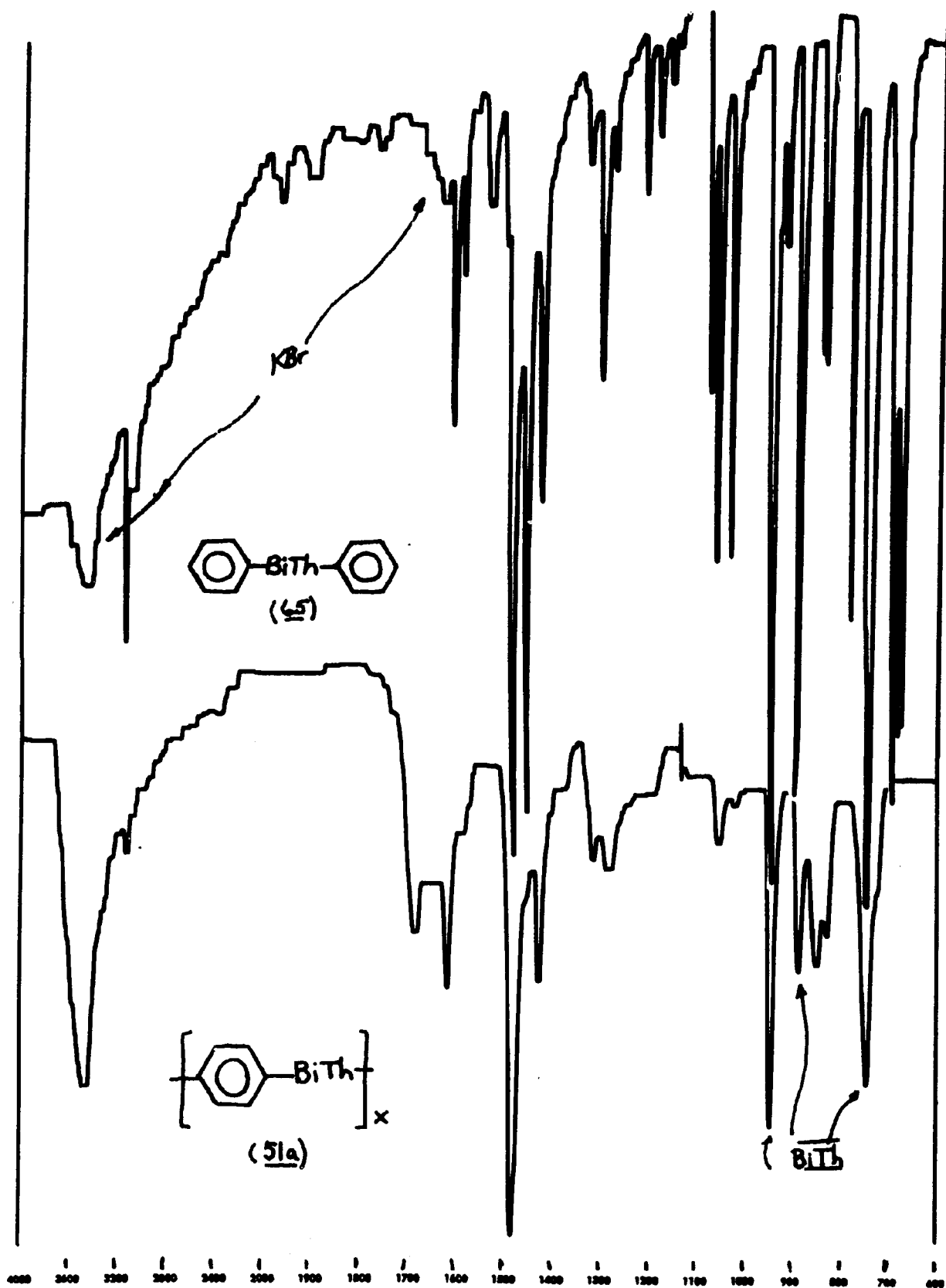


Figure 5.

INFRARED SPECTRA OF 4,4'-BIS(*p*-BIPHENYL)-
2,2'-BITHIAZOLE AND POLY-4,4'-(*p*-BIPHENYLENE)-
2,2'-BITHIAZOLE.

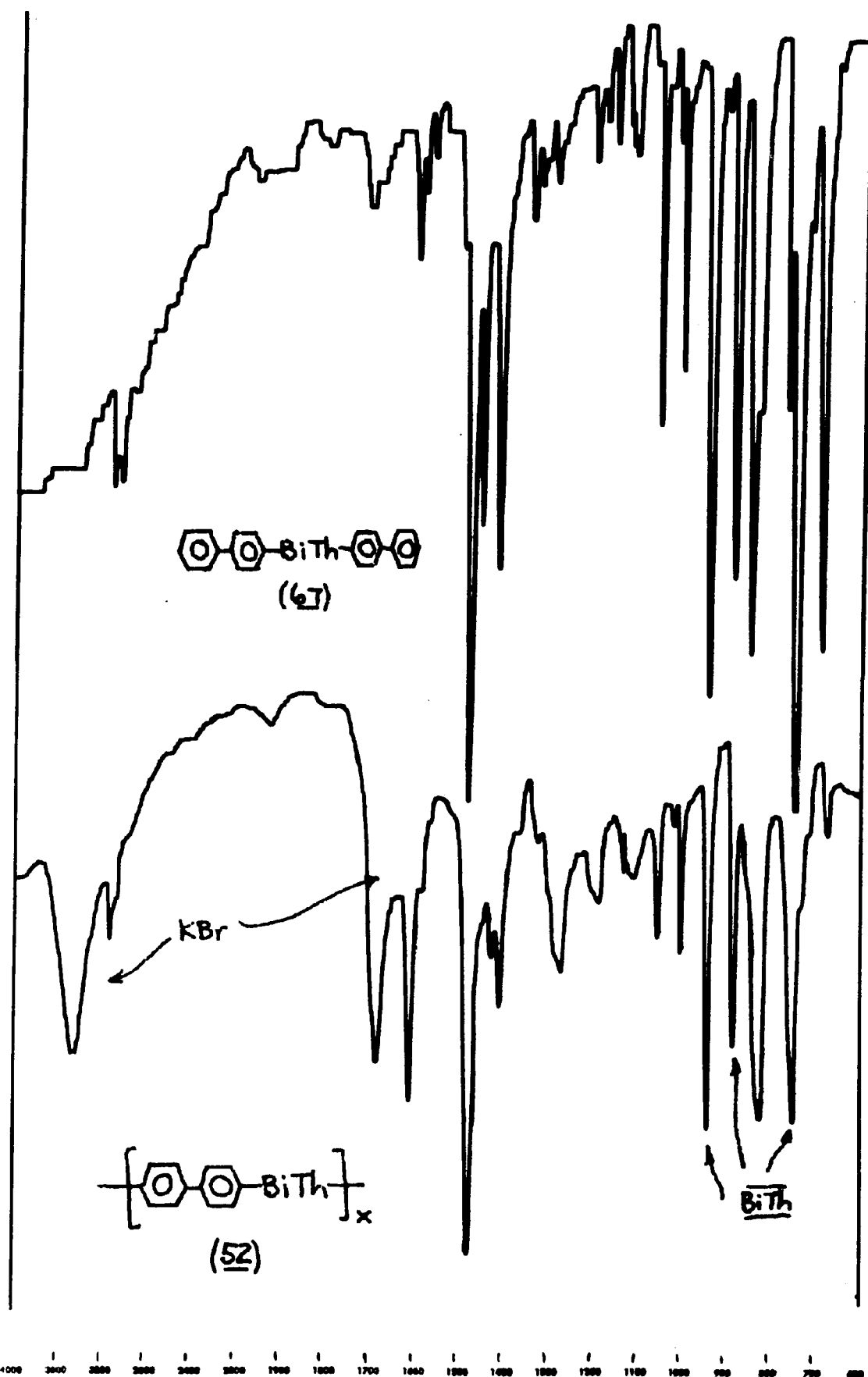


Figure 6

INFRARED SPECTRA OF 4,4'-BIS(p-BENZYLPHENYL)-
2,2'-BITHIAZOLE AND POLY -4,4'-(p-DIPHENYLENE-
METHANE)-2,2'-BITHIAZOLE

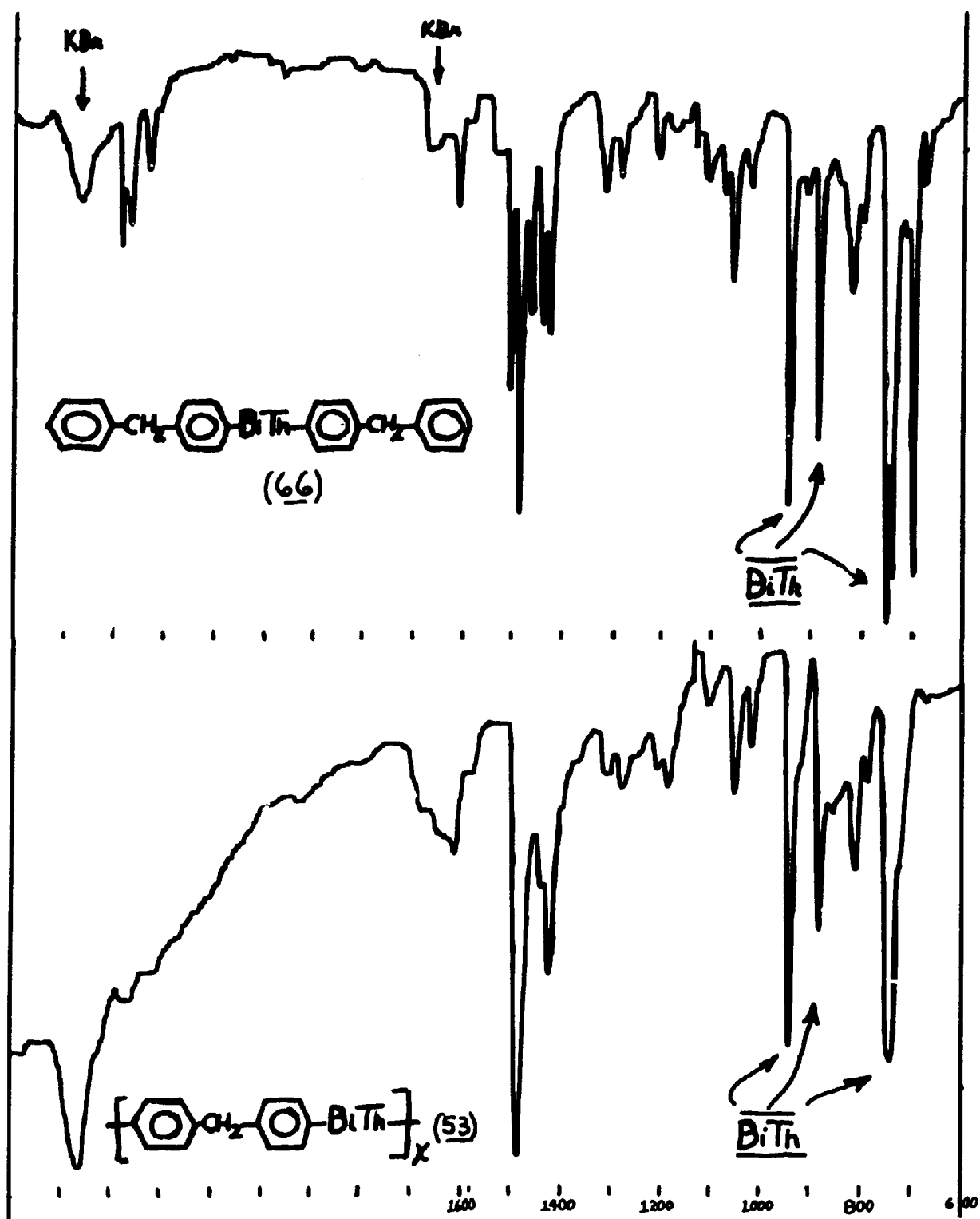


Figure 7.

INFRARED SPECTRA OF 4,4'-BIS(*p*-PHENOXYPHENYL)-
2,2'-BITHIAZOLE AND POLY-4,4'-(*p*-DIPHENYLENE
ETHER)-2,2'-BITHIAZOLE.

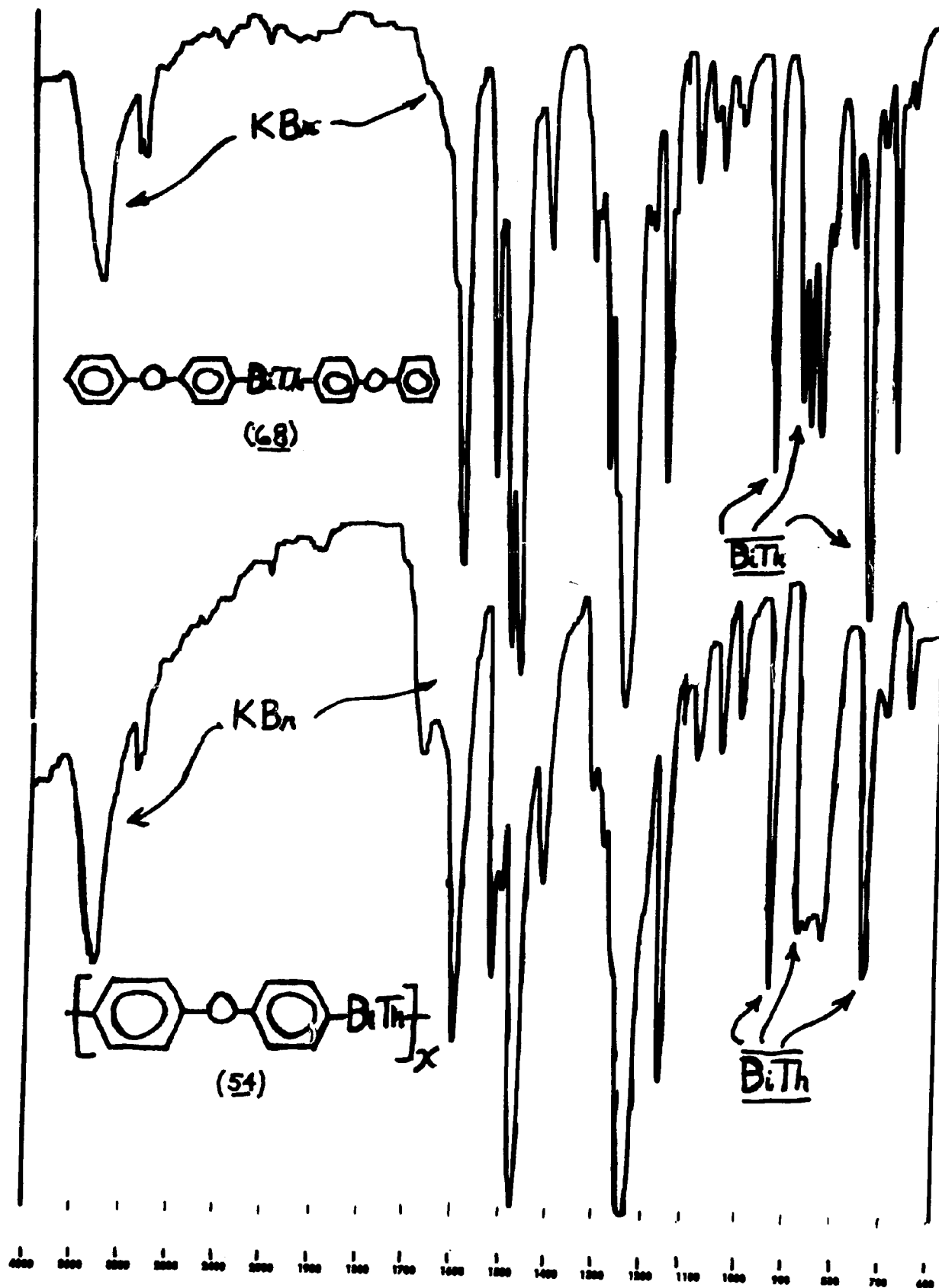
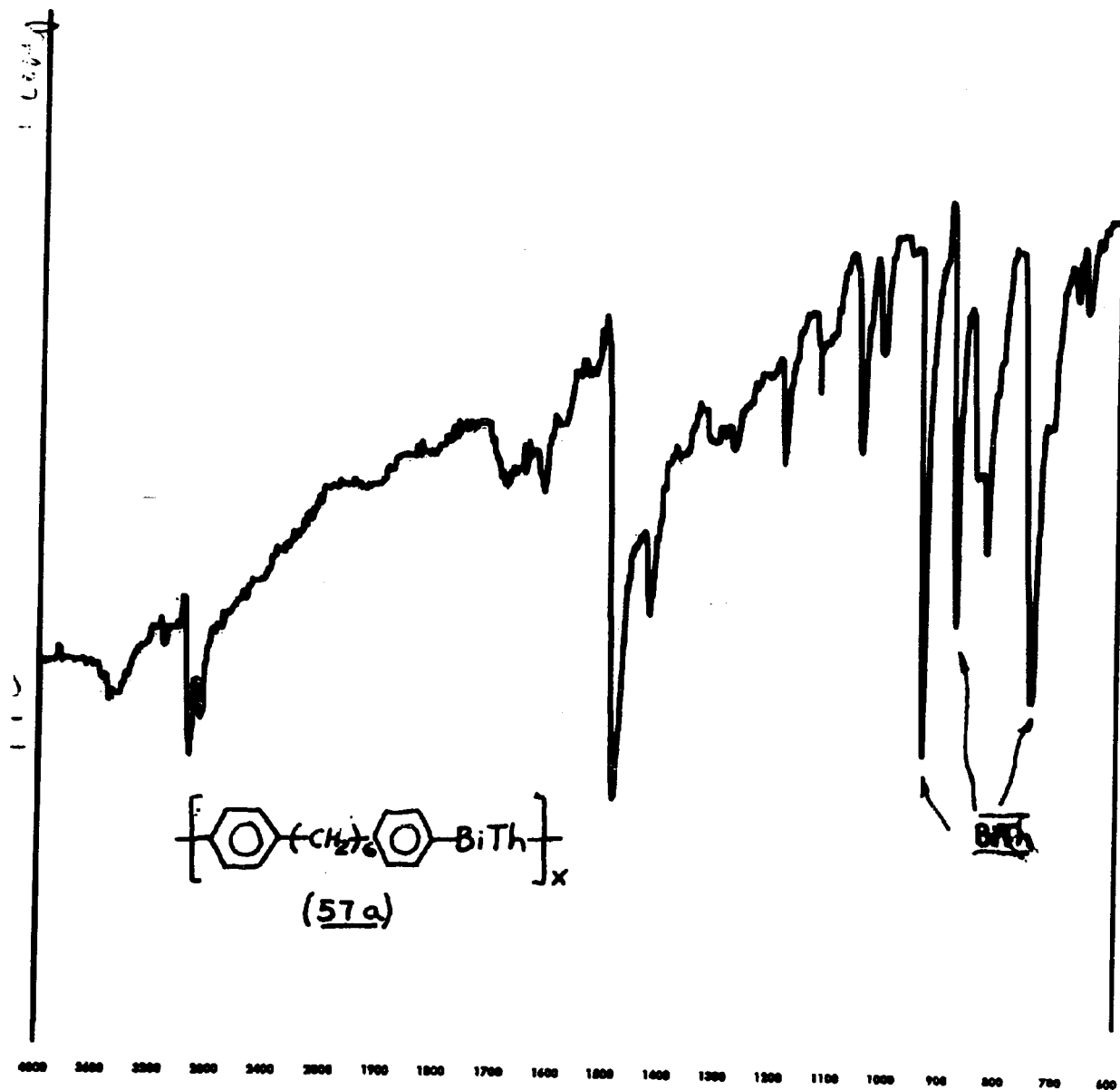


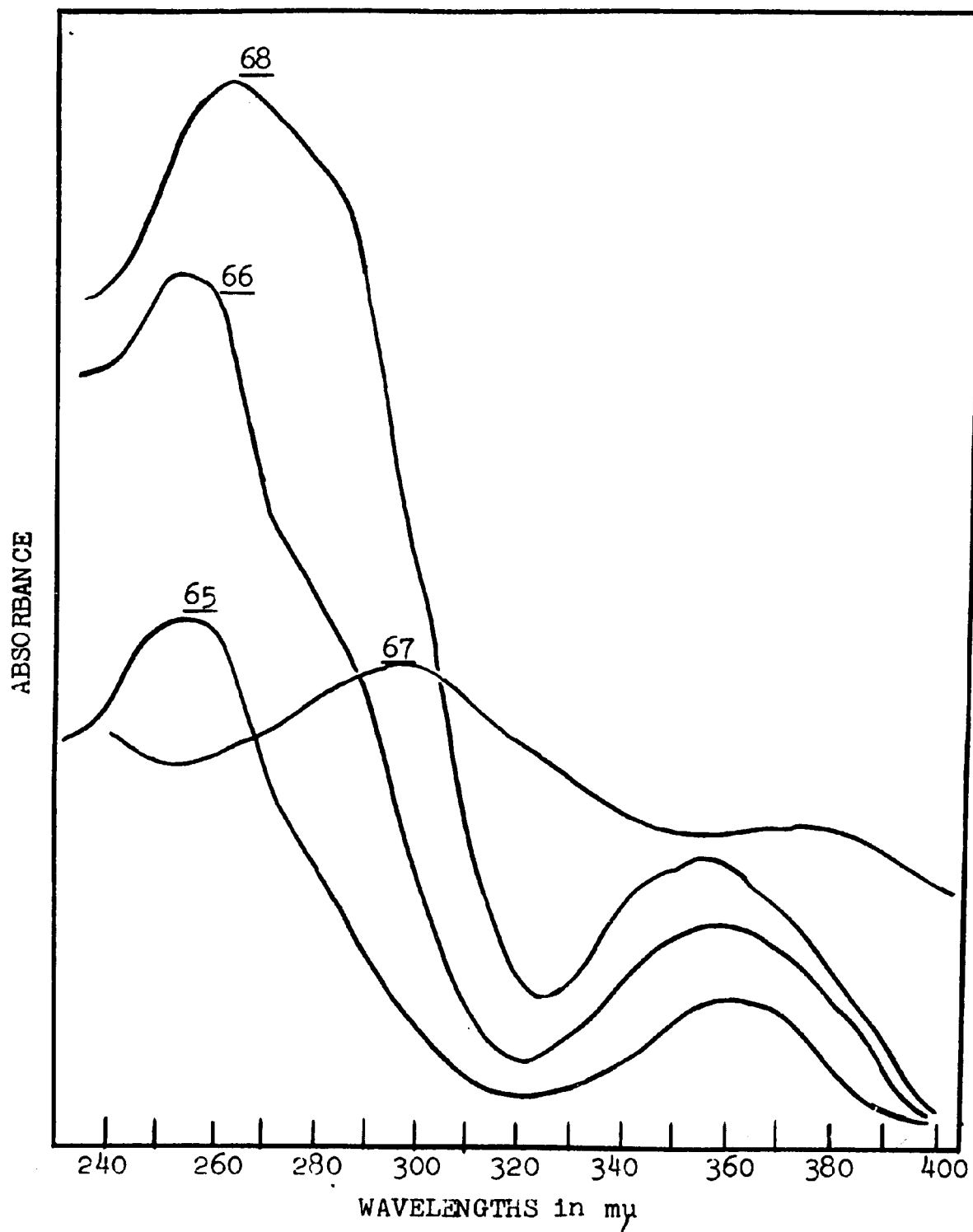
Figure 8.

THE INFRARED SPECTRUM OF POLY-4,4'-(HEXAMETHYLENE-*p*-DIPHENYLENE-1,6)-2,2'-BITHIAZOLE.



APPENDIX IV.
ULTRAVIOLET SPECTRA
of
SOME 2,2'-BITHIAZOLES
AND
POLY-4,4'-DIARYL-2,2'-BITHIAZOLES.

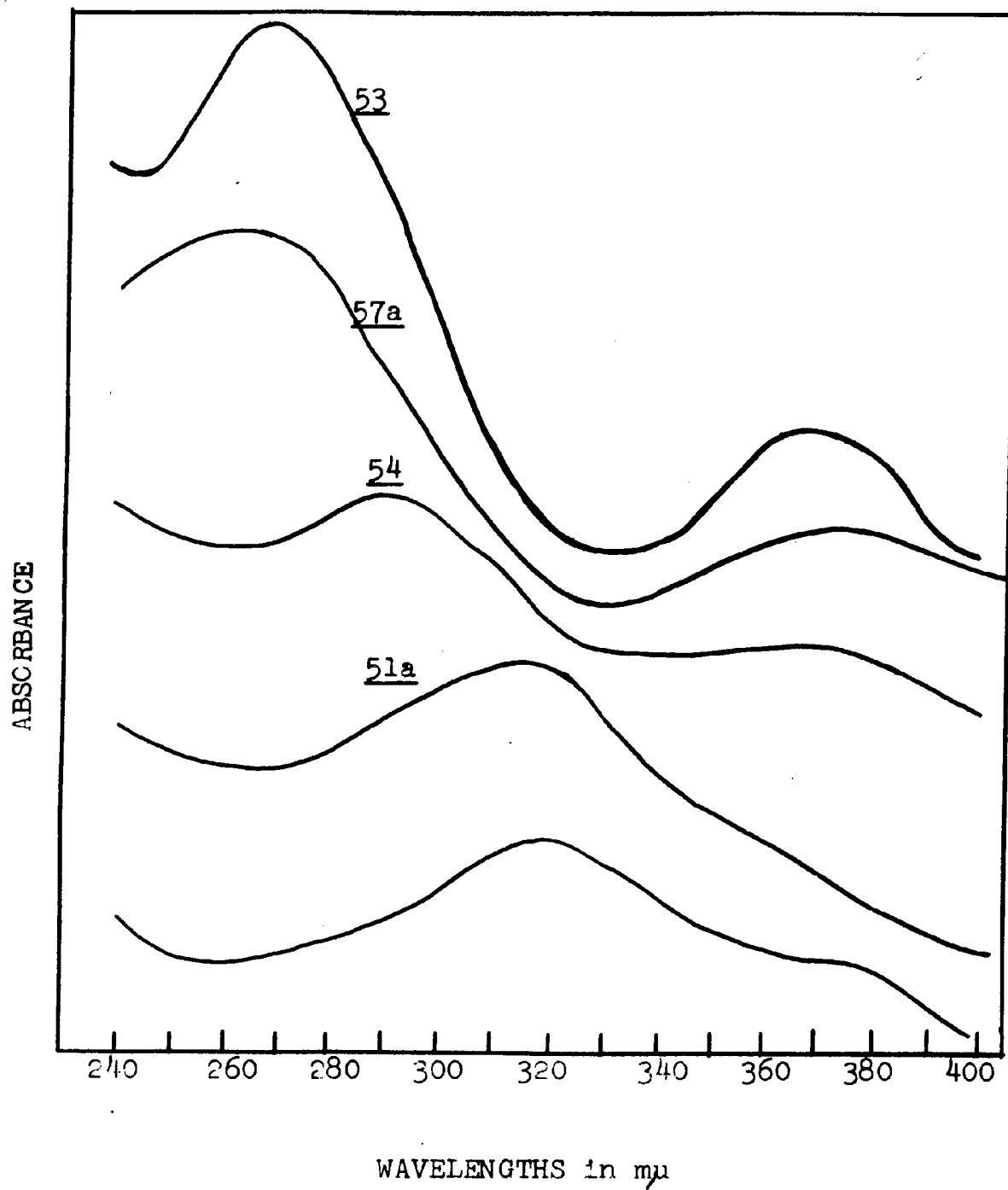
FIGURE 9.



ULTRAVIOLET SPECTRA OF SOME 2,2'-BITHIAZOLES

Absorbance Values Not Quantitative

FIGURE 10.



ULTRAVIOLET SPECTRA OF SOME POLYBITHIAZOLES

Absorbance Values not Quantitative

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