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Aromatic Polymers: Single- and Double-Stranded Chains

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SUMMARY

The work directed toward the syntheses of thermally stable organic polymers which has been carried out in this laboratory over the past few years is reviewed. The syntheses of polyaromatic five-membered heterocycles obtained from the 1,3 dipolar addition reactions of disyndones and dinitrilimines, obtained from both hydrazide chloride and tetrazole precursors, show that the tetrazole monomer produces the highest-molecular-weight polypyrazole. All the polypyrazoles have good thermal stability. The 1,4 cyclo-addition reactions of bis-tetracyclones with diacetylenes afford high-molecular-weight phenylated polyphenylenes which are colorless, amorphous, and soluble in common organic solvents and have excellent thermal stability. Dipyrone are not as suitable double dienes as the bis-tetracyclones, since high-molecular-weight polyphenylenes are not obtained. The syntheses of high-molecular-weight linear polyquinoxalines by the reaction of some bis-glyoxals with aromatic bis-o-diamines lead to thermally stable materials. By the condensation of suitable tetraketones connected by aromatic rings with the appropriate aromatic tetraamines, ladder polyquinoxalines with extremely good thermal stability can be obtained.

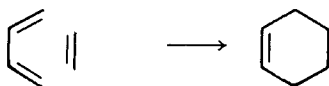
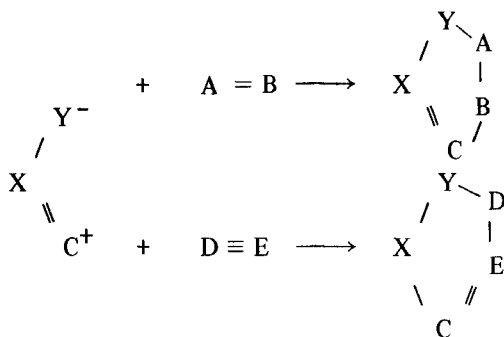
INTRODUCTION

Polymers which contain only aromatic structures either directly linked together, or linked by certain connecting groups which are not readily degraded thermally, should achieve the highest degree of thermal stability of any organic polymer. During the past few years, we have been engaged in the synthesis and partial evaluation of organic polymers structurally designed to show good thermal stability. Several approaches have been explored, all of which have relied on the formation of an aromatic ring as the synthesis employed for the polymer-forming reaction. Exploration of aromatic polymers in which the aromatic units were both singly and doubly connected was carried out.

SINGLE-STRANDED CHAINS

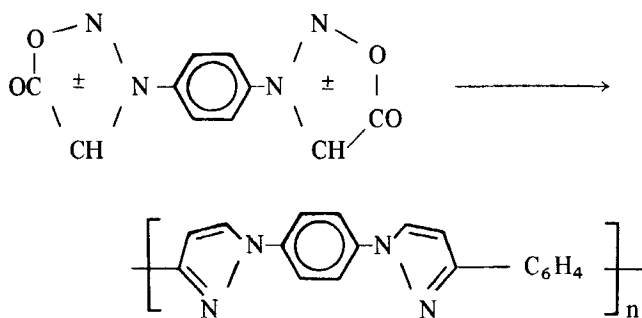
1,3 Dipolar Cyclo-Additions

The cyclo-addition reaction can be employed in theory as a mode of propagation in the synthesis of macromolecules; the 1,2, 1,3, and 1,4 cyclo-additions are well-known organic reactions. Many of the 1,3 dipolar addition reactions are suitable for use as polymer-forming reactions, since



the difunctional monomers are synthesized readily and many of the dipolar additions are nearly quantitative. Especially suited to the production of a stable polymer is the fact that certain products of the 1,3 dipolar addition are five-membered aromatic heterocycles. Thus, when the dipolarophile is a triple-bonded species such as an acetylene or a nitrile, and the dipole contains an atom, Y, which retains a lone pair of electrons in the product, the ring contains the requisite 6- π electrons. Three types of dipoles, the sydrones, the nitrilimines, and the nitrile oxides, seemed especially suited in this respect; both the sydnone dipole and the nitrilimine dipole, generated from two different precursors—the hydrazide chloride and the tetrazole—were investigated.

The addition of acetylenes to sydrones produces pyrazoles, presumably through a Diels-Alder intermediate which loses carbon dioxide. Consequently, several disydnone and diethynyl monomers of the appropriate structure were synthesized and polymerized [1, 2]. The reaction of p-phenylene-3,3'-disydnone (**I**) with m- and p-diethynylbenzene (**IIa,b**) gave good conversions to polymer (**IIIa,b**). Although these polymers had the good thermal stability that could be expected of such an aromatic polymer (TGA break, 420-500°C), the inherent viscosities were usually in the range 0.3-0.5; viscosities higher than 0.6 could not be obtained.



(I)



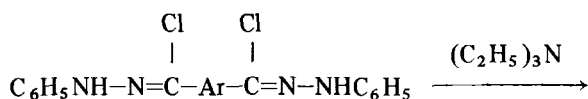
(II)

a. m- C_6H_4 b. p- C_6H_4

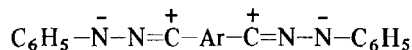
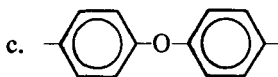
(III)

a. m- C_6H_4 b. p- C_6H_4

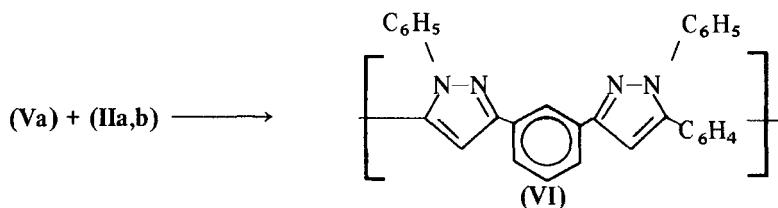
Nitrilimines, which may be generated by the action of base on acid hydrazide chlorides, react rapidly with alkynes and alkenes to form pyrazoles and pyrazolines, respectively. The acid hydrazide chlorides, isophthaloylphenylhydrazide chloride (**IVa**), terephthaloylphenylhydrazide chloride (**IVb**), and 4,4'-oxdibenzoylphenylhydrazide chloride (**IVc**), were synthesized for polymerization with bis-dipolarophiles [3, 4]. Generation of the bisnitrilimine (**V**) in situ by the action of a tertiary amine base in the presence of *m*- and *p*-diethynylbenzene afforded the polypyrazoles (**VI**)-(VIII). When *m*-divinyl benzene was the available dipolarophile the polymer (**IX**) containing the pyrazoline ring was formed.

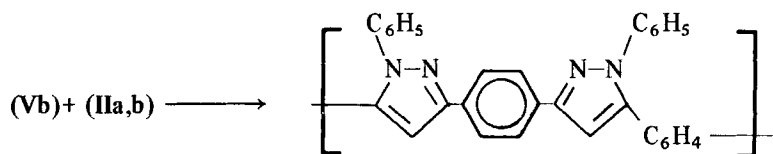


(IV)

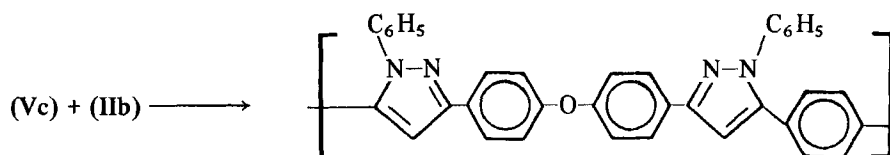
Ar = a. *m*-C₆H₄b. *p*-C₆H₄

(V a,b,c)

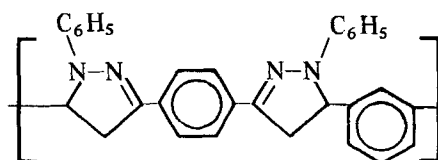
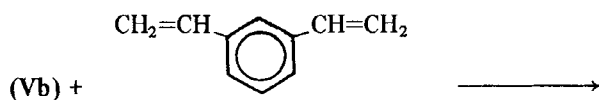
a. *m*-C₆H₄b. *p*-C₆H₄



(VII)

a. m-C₆H₄b. p-C₆H₄

(VIII)



(IX)

These totally aromatic polymers (VI)-(VIII) also showed good thermal stability (TGA break, air 460-500°C), but high-molecular-weight materials could not be obtained (best $\eta_{inh} = 0.32$). The question of whether the aromaticity associated with the pyrazole ring is necessary to the thermal stability of these polymers can be answered by comparing the thermal decomposition of the polypyrazole (VIIa) and its hydrogenated derivative, the polypyrazoline (IX). An initial break in the TGA curve of (IX) in air (Fig. 1) is obtained at 360°C, and, after approximately a 15% weight loss, the remainder of the curve follows that of the polypyrazole and shows a break at 520°C. In nitrogen, the thermogravimetric analysis of the polypyrazoline shows a break followed by complete decomposition at 360°C. This greater ultimate stability in air rather than nitrogen can be explained on the basis of the oxidation or dehydrogenation of the pyrazoline moieties to pyrazole units. The 15% weight loss is of course greater than that calculated for the loss of hydrogen only, so evidently some pyrazoline groups are degrading before their oxidation takes place. This conversion of pyrazoline to pyrazole was supported by comparing the infrared spectrum of the polymer taken just following the 360°C break, but prior to the 520°C break, to the spectra of the untreated polypyrazoline and corresponding polypyrazole.

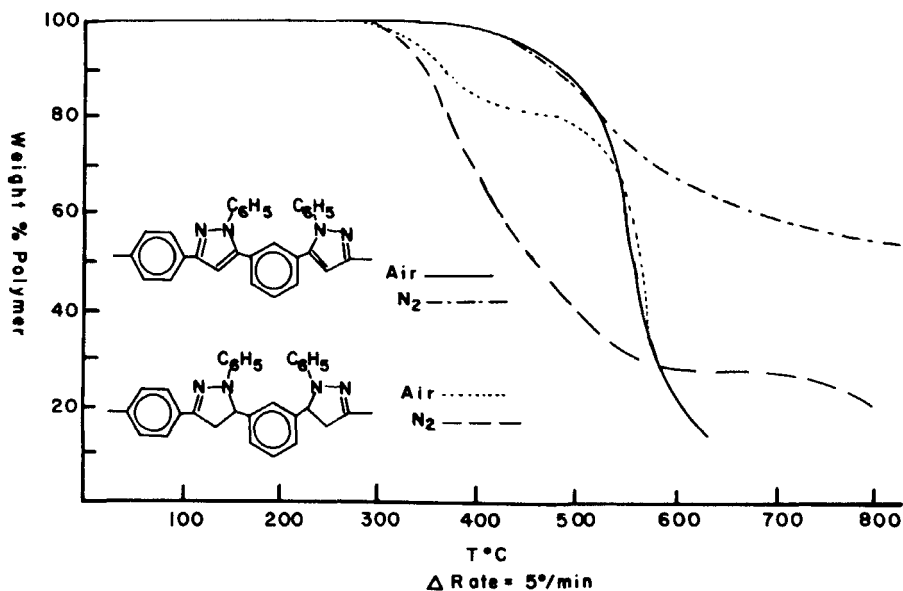
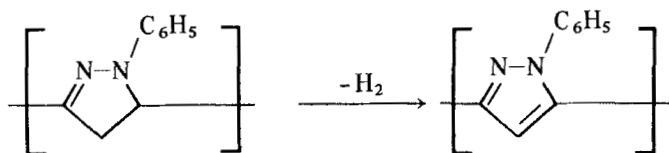
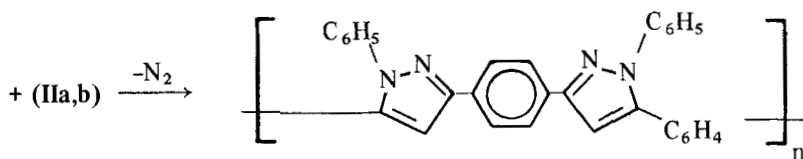


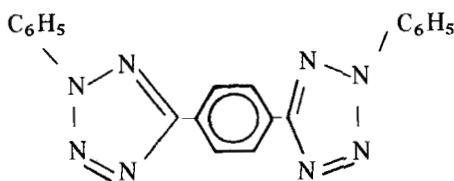
Fig. 1. TGA of a polypyrazole and a polypyrazoline.



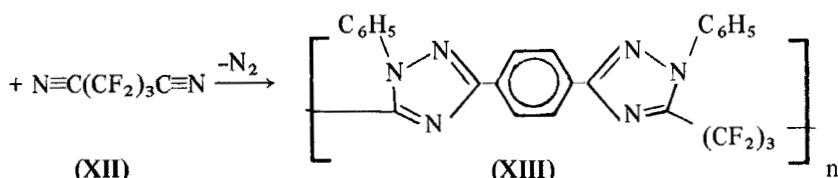
The reactions of bis-nitrilimine dipoles generated from bis-tetrazoles are much more suitable for the formation of high-molecular-weight polymers. The tetrazole monomer, 2,2'-diphenyl-5,5'-p-phenyleneditetrazole (X), reacts with *m*- and *p*-diethynylbenzene (IIa,b) in tetralin at 200°C in a bomb to give high yields of polymer (XI) with inherent viscosities as high as 1.67 [5]. Although neither sydnone nor nitrilimine generated from hydrazide chlorides react readily with nitriles, nitrilimines generated from tetrazoles give excellent yields of triazoles. Thus, the polymerization of (X) with perfluoroglutaronitrile (XII) afforded polymer (XIII) ($\eta_{inh} = 0.18$).



(XI)

a. *m*-C₆H₄b. *p*-C₆H₄

(X)



(XII)

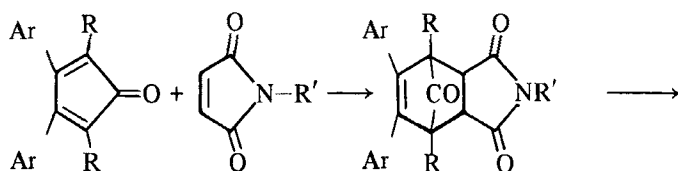
(XIII)

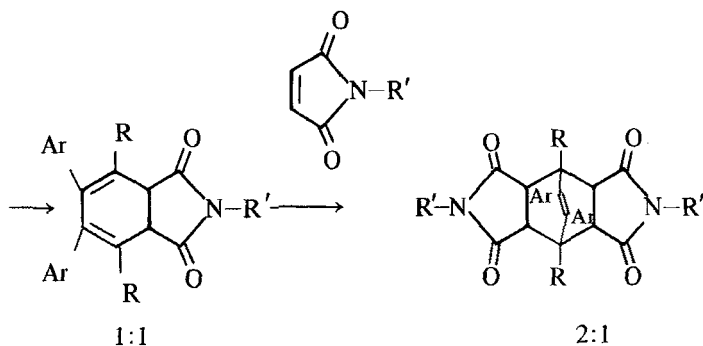
The thermal gravimetric analyses of the polypyrazoles showed a stability characteristic of the aromatic nitrogen-containing heterocyclic ring, although less stable than some other polymers containing the aromatic nitrogen heterocycle fused to a benzene ring.

1,4 Cyclo-Addition

The well-known 1,4 cyclo-addition reaction of a 1,3 diene to a dienophile, commonly known as the Diels-Alder reaction, or diene synthesis, has been established as a useful synthetic organic reaction. Although this reaction provides a high yield of six-membered ring adduct in certain cases, there are few reported syntheses of polymers which employ it as a step-growth reaction [6,7]. In theory, this polymerization reaction should be successful if a monomer which contains both the diene and dienophilic portions were subjected to the polymerization conditions. Alternatively, high-molecular-weight polymer should be obtained from the reaction of equal molar amounts of a bis-diene with a bis-dienophile.

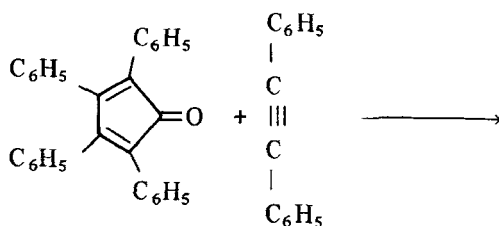
Cyclopentadienones can undergo a variety of Diels-Alder reactions depending on the substitution on the cyclopentadienone ring, the dienophile, and the reaction conditions. Tetraaryl-substituted cyclopentadienones react with olefinic dienophiles with the loss of carbon monoxide to give a 1:1 adduct. Reaction of the newly formed diene with another molecule is prevented by the high degree of aryl substitution, whereas cyclopentadienones substituted by smaller (alkyl) groups in the 2 and 5 positions will react further to give the 2:1 adduct. It was the 1:1 stoichiometry that was of particular interest to us in these reactions.

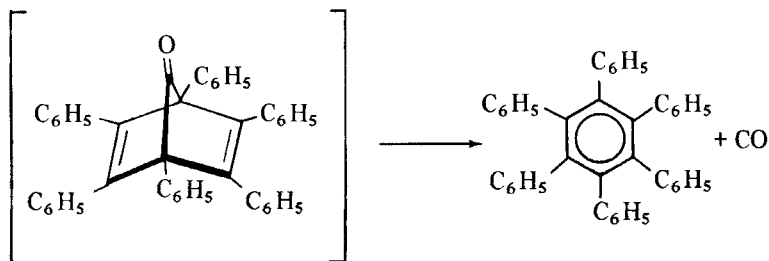




The reaction of 3,3'-(oxydi-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) (XIV) with *N,N'*-*o*- or *p*-phenylene-bis-maleimide (XVa,b) in refluxing 1,2,4-trichlorobenzene (213°C) or *o*-chloronaphthalene (263°C) yields the polyimides (XVIa,b). Polymer (XVIb) reaches an intrinsic viscosity of 1.06 in 4 hr in refluxing 1,2,4-trichlorobenzene, while (XVIa) attains an intrinsic viscosity of only 0.33 after 25 hr. At 25°C, both polymers are soluble in dimethylformamide, from which clear, slightly yellow films can be cast. The polymers dehydrogenate slowly at elevated temperatures or more rapidly with chemical dehydrogenation reagents (refluxing nitrobenzene) to form the aromatic polyimide. (See page 1053.)

Another means of carrying the cyclopentadienone Diels-Alder reaction to the monoadduct stage is to employ an acetylenic dienophile and obtain a product which is no longer a diene, but is aromatic. The reaction of tetraphenylcyclopentadienone with diphenylacetylene affords hexaphenylbenzene by loss of carbon monoxide from the intermediate adduct.





The reaction of bis-tetracyclones (XVII)-(XIX) with *m*- and *p*-diethynylbenzene (IIa,b) in toluene at 225°C for 24 hr afforded the phenylated polyphenylenes (XX) and (XXI) in quantitative conversions [8, 9].

Molecular weights of 30,000-60,000 could be obtained. The polymers showed outstanding thermal stability (TGA break, 550°C in air or nitrogen, Fig. 2), are all soluble in common organic solvents (up to 15 wt%), form clear films, and are colorless and amorphous. The thermal decomposition of these polymers has been shown to take place by the loss of pendent phenyl groups as phenyl radicals. Thus, the thermal treatment of a film

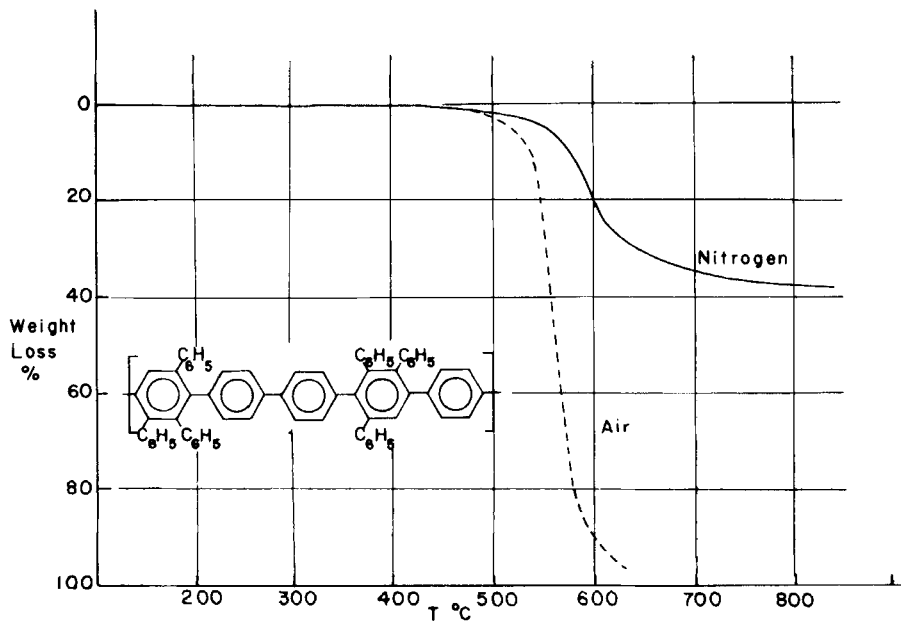
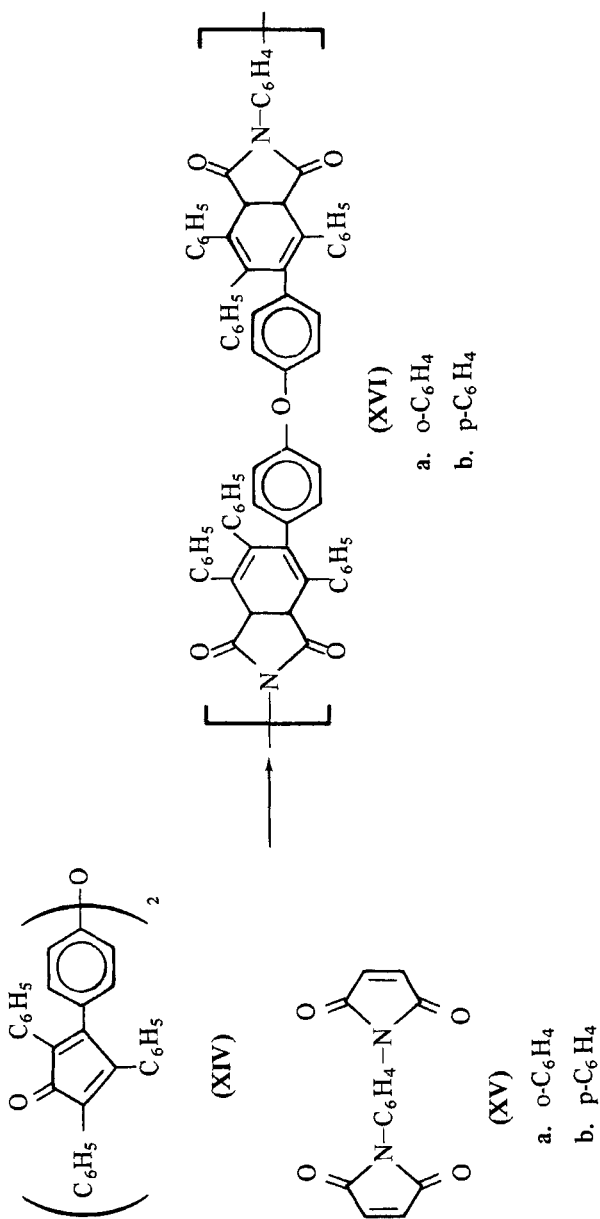
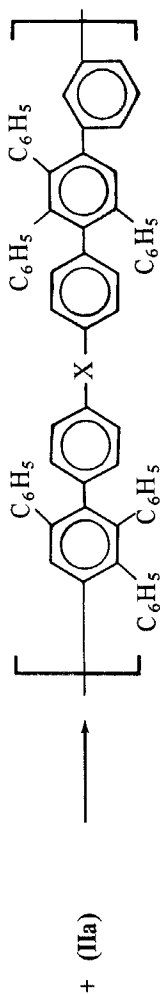


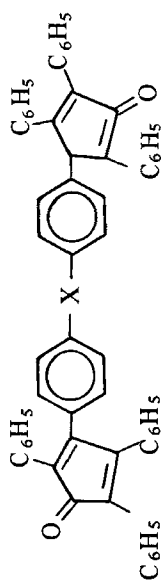
Fig. 2. TGA of a polyphenylene.





(XX)

- a. X = nil
 b. X = O
 c. X = S



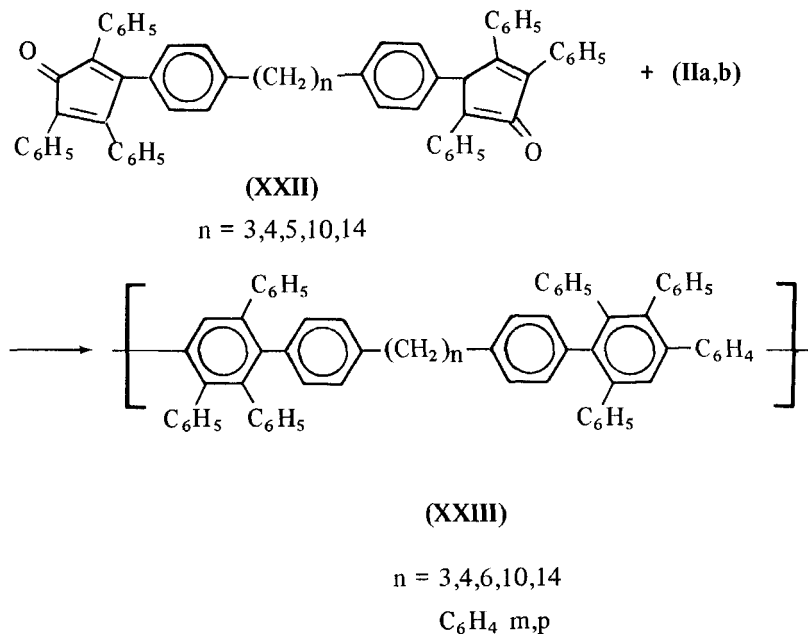
- (XVII) X = nil
 (XVIII) X = O
 (XIX) X = S

(XXI)

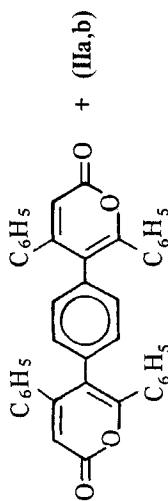
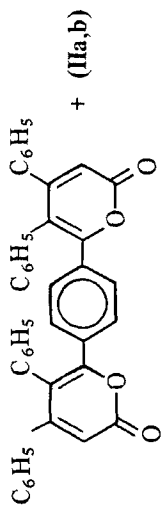
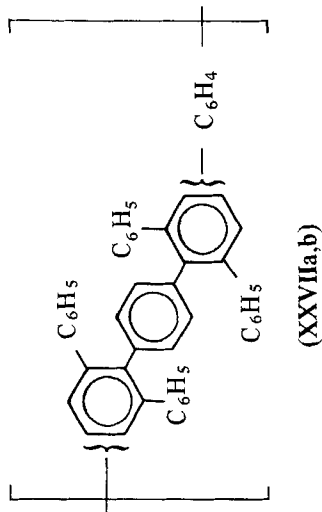
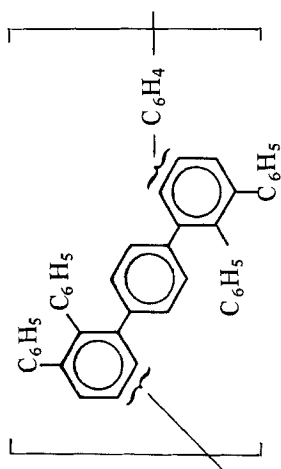
- a. X = nil
 b. X = O
 c. X = S

under nitrogen produces a cross-linked film which is still amorphous but insoluble. The polymers show no weight loss on isothermal aging in air at 350°C for 100 hr, but they become insoluble during this treatment.

In addition, several bis-tetracyclones linked by methylene units have been synthesized. The polymerization reactions of these tetracyclones (XXII) with *m*- and *p*-diethynylbenzene (IIa,b) produced a series of polymers (XXIII) containing short blocks of phenylene units connected by methylene chains [8, 10]. High-molecular-weight polymers ($\bar{M}_n = 31,000-59,000$) with a range of properties were obtained. Most surprising was the good thermal stability (TGA break, 460-520°C in air and nitrogen) shown by these polymers containing alkylene connecting groups.



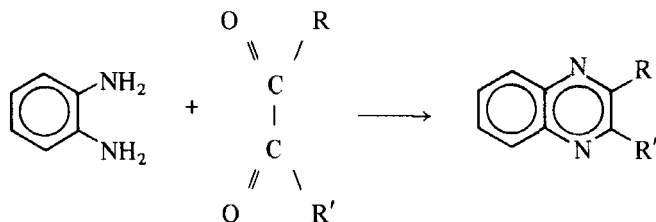
Since the thermal degradation of the phenylated polyphenyls of the types (XX) and (XXI) is evidenced by the loss of the pendent phenyl groups, and since the reported properties of *p*-polyphenylene are quite different than those of (XXIa), the synthesis of an unphenylated polyphenylene was of particular interest. Monophenyl-substituted 2-pyrones also react with acetylenes at elevated temperatures to form phenyl-substituted benzenes. Monosubstituted 2-pyrones are stable at room



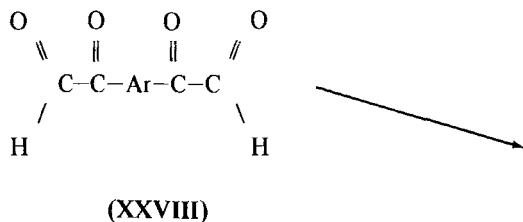
temperature whereas monosubstituted cyclopentadienones dimerize even below room temperature with the loss of carbon monoxide. The polymerization reactions of several substituted bis-pyrones have been carried out in a preliminary investigation of this reaction [11]. The polymerizations of (XXIV) and (XXV) with *m*- and *p*-diethynylbenzene in toluene at 225°C for 20-48 hr yielded both soluble and insoluble fractions of polymers (XXVI) and (XXVII). Although the soluble fractions of the polymer were of low molecular weight ($\eta = 0.1$), they showed the same thermal stability as polyphenyls (XX) and (XXI).

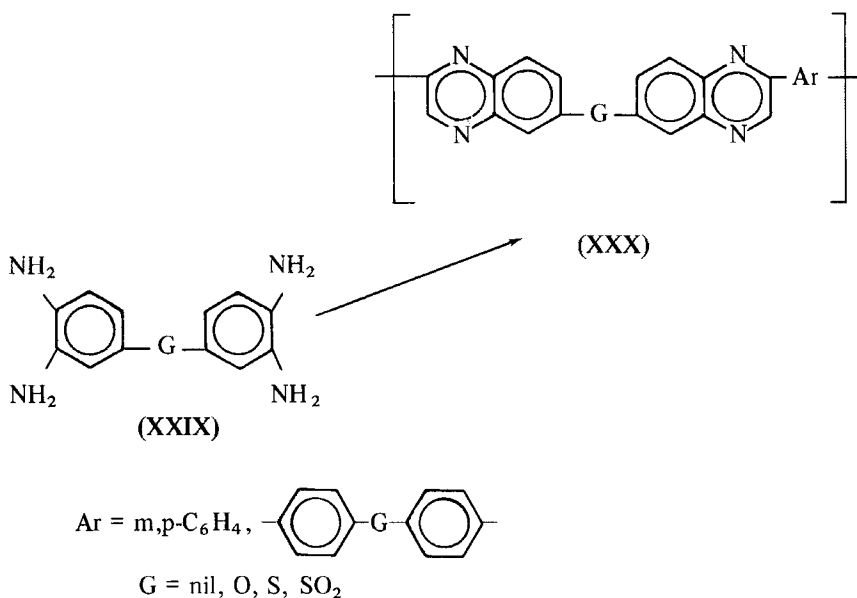
Linear Polyquinoxalines

The reaction of an aromatic *o*-diamine with a 1,2-dicarbonyl compound forms a quinoxaline. This reaction is especially suited for the formation of thermally stable polymers since it is rapid and nearly quantitative (with minimal side reactions), gives complete intramolecular cyclization, and produces an aromatic nucleus which is π -isoelectronic with naphthalene.



Thermally stable polyquinoxalines (XXX) have been obtained from the reactions of tetraamines (XXIX) with bisglyoxals (XXVIII) [12-15]. These polymers containing the quinoxaline moiety connected by combinations of the single oxygen, sulfur, and sulfone atom links with diphenyl ether, diphenyl sulfide, and diphenyl sulfone connections have been prepared by a two-stage polymerization.





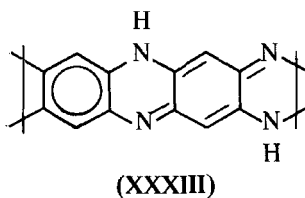
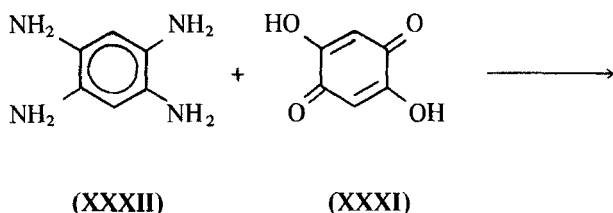
A solution polymerization under 200°C followed by a solid-state polymerization at 375°C affords high-molecular-weight quinoxaline polymers ($\eta_{\text{inh}} = 1.0$) that have excellent thermal stability. Typical polymer samples in an atmosphere of air show breaks in the thermal gravimetric analysis curve at 500°C , while under a nitrogen atmosphere the degradation is less rapid. Most of the polymer samples have moderate solubility after the solution polymerization but only limited solubility after the second-stage polymerization. The solubilities are greater, however, than those of quinoxaline polymers that do not contain the somewhat flexible oxygen, sulfur, and sulfone links.

DOUBLE-STRANDED CHAINS

The quinoxaline-forming reaction of an aromatic o-diamine with a 1,2-dicarbonyl has been adapted for the synthesis of ladder structure by the use of the appropriate tetraamines and tetraketones. In order to utilize the quinoxaline-forming reaction for the synthesis of ladder polymers, amine monomers containing two sets of aromatic o-diamine functions doubly joined and ketone monomers containing two sets of 1,2-dicarbonyls doubly

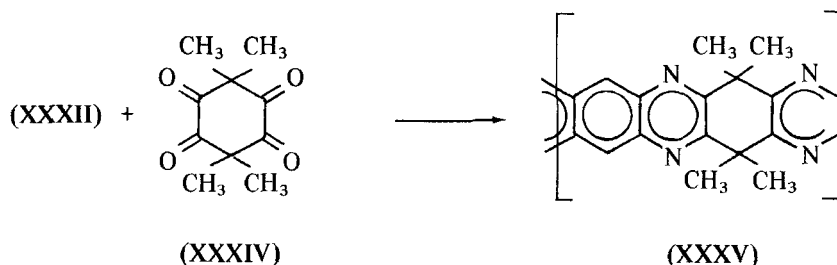
linked are required. Ideally, the attachment of the sets of functions is such that the resulting polymer is totally aromatic.

The polymerization of 2,5-dihydroxy-p-benzoquinone (XXXI) with 1,2,4,5-tetraaminobenzene (XXXII) affords the dihydroquinoxaline polymer (XXXIII) [16, 17]; the highest molecular weights ($\eta_{inh} = 1.45$) were obtained in polyphosphoric acid. It was hoped that (XXXIII) would undergo facile thermal dehydrogenation to the completely aromatic system, but apparently this does not occur since this polymer did not show any better thermal stability than the single-stranded polyquinoxalines. Whether or not this instability is due to incomplete ring formation and occasional singly linked units, or is inherent in the dihydropyrazino-quinoxaline system, is not clear; however, the analogous phenoxazine ring system in a polymer which is presumably a completely ladder structure also has relatively poor thermal stability [18].



In order to help determine the extent to which the thermal stability might be a reflection of incomplete ring closure, as a result of the lower reactivity of the hydroxyl group compared with a carbonyl group, the tetraketocyclohexane, 3,3,6,6-tetramethylcyclohexan-1,2,4,5-tetraone (XXXIV), which cannot enolize to the hydroxyketone, was synthesized [19]. When (XXXIV) was polymerized with 1,2,4,5-tetraaminobenzene (XXXII), ladder polyquinoxaline (XXXV) was obtained ($\eta_{inh} = 1.06$), which showed very poor thermal stability. The break in the TGA at 400°C probably can be attributed to the facile cracking of the isopropylidene fragment.

Ultimately, tetraketones containing aromatic connecting units were



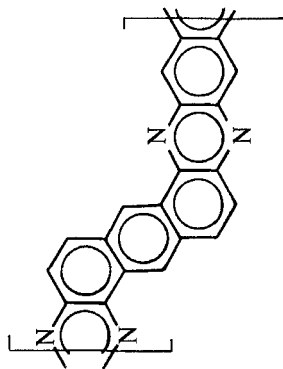
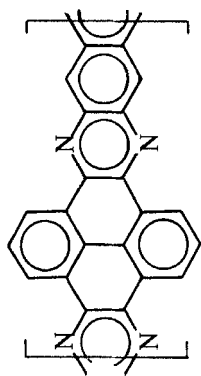
synthesized in order to obtain a ladder polyquinoxaline that was truly aromatic [17, 20]. The polymerization of 1,2,6,7-tetraketopyrene (XXXVI) or 1,2,6,7-tetraketoanthracene (XXXVII) with tetraaminobenzene (XXXII) in hexamethylphosphoramide at 180°C for 120 hr yielded the fully aromatic ladder polyquinoxalines (XXXVIII) and (XXXIX), respectively. The polymers were insoluble in cold hexamethylphosphoramide but were completely soluble in tetrafluorodichloroacetone hydrate, and inherent viscosities of 2.1 could be obtained. These polymers probably have molecular weights of 7000-15,000.

The ladder polyquinoxalines were not significantly more stable in air than the single-stranded quinoxalines, and they decomposed at about 550°C. In a nitrogen atmosphere, however, the stability of the totally aromatic ladder polymers was greatly enhanced, and in general there was no appreciable weight loss up to 700°C.

In an effort to relate the effect of ladder structure to thermal stability, a comparison was made between a single-stranded polyquinoxaline of the type (XXX), the ladder polyquinoxalines (XXXVIII) and (XXXIX) and a partially ladder polymer containing occasional single links prepared from the reaction of tetraketone (XXXVI) and 3,3'-diaminobenzidine. It is evident that there is little difference in the thermal stability of these polymers in air, except perhaps the rate of weight loss (Fig. 3). The noticeable difference is in the stability in nitrogen. The single-stranded and partially ladder polymers show breaks at 575°C, while the ladder polyquinoxalines do not show appreciable weight loss at 700°C.

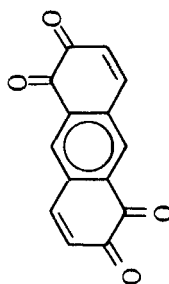
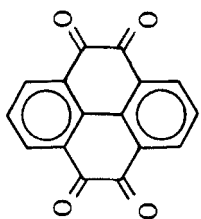
CONCLUSIONS

From these studies, certain valuable conclusions can be made concerning the synthesis, structure, and thermal stability of the variety of aromatic polymers described.



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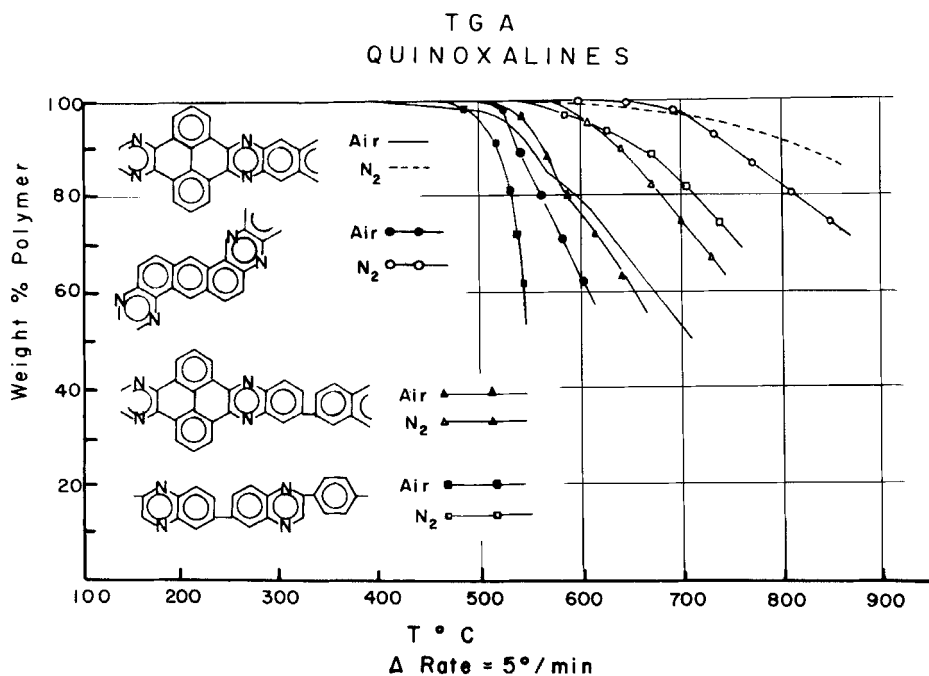


Fig. 3. TGA of polyquinoxalines.

Certain cyclo-addition reactions can be valuable synthetic pathways to aromatic polymers. Of the 1,3 cyclo-addition reactions studied, the 1,3 dipolar addition reaction of the nitrilimine as generated from the tetrazole precursor appears to be the most satisfactory in that it affords the highest-molecular-weight materials. The Diels-Alder 1,4 addition reaction can be made to yield high-molecular-weight polymers provided the particular addition reaction and monomers are carefully chosen.

The quinoxaline-forming reaction of a 1,2 dicarbonyl compound with an aromatic *o*-diamine meets all the requirements for a step-growth polymerization reaction since it is quantitative, rapid, and provides complete closure. Perfect or nearly perfect ladder polyquinoxalines are not insoluble, but moderate-molecular-weight materials are soluble in hydrogen-bonding solvents.

Most single-stranded aromatic polymers show breaks in the TGA in air and nitrogen near 500°C. Polypyrazoles, which contain an aromatic five-membered nitrogen heterocyclic ring, are thermally more stable than the

nonaromatic hydrogenated analogs, the polypyrazolines. Phenylated polyphenylenes have very good thermal stability, as shown by the TGA break at 525°C, but have especially good isothermal aging stability.

Totally aromatic linear polyquinoxalines have excellent thermal stability (TGA break, 500-550°C). Ladder polyquinoxalines, which contain totally aromatic units, have about the same stability in air but superior stability under nitrogen (TGA break ~700°C). Certain other quinoxaline ladders which have nonaromatic links display poor thermal stability; in some cases the stabilities are inferior to those of the single-stranded aromatic quinoxalines.

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Discussion of Paper by J. K. Stille

Aromatic Polymers: Single- and Double-Stranded Polymer Chains

- J. Heller: I am surprised to see such low molecular weights of your ladder polymers for relatively high viscosities. For our spiropolymers we find, for a viscosity of 1.7, light-scattering molecular weights of about 60,000. Could it be that you are dealing with a highly poly-disperse system? Perhaps you should try light scattering.
- J. K. Stille: Our molecular weights are number average molecular weights taken on a vapor pressure osmometer with tetrafluorodichloroacetone hydrate as a solvent. We did not use membrane osmometry because the solvent dissolves the membrane; we did not attempt light scattering because the solutions are intensely colored. Our molecular weights are perhaps not very reliable because of the method and the problems encountered. Also, we probably had a large number of low-molecular-weight species, but I would not be surprised if such a rigid system of relatively low molecular weight displayed this high solution viscosity.
- D. Magay: Are not you comparing weight average to number average molecular weights since, with light scattering, weight average, and with osmometry, number average is being measured?
- J. K. Stille: Yes, our molecular weights are number average.
- H. Levine: Perhaps one must consider that light-scattering data on rigid backbones must be interpreted carefully. The structures are far different from the usual, more flexible polymers.

- J. K. Stille: Perhaps Dr. Berry would like to comment on this.
- C. G. Berry: The determination of the molecular weight from the light-scattering data on the polymers described here should not be too difficult. The shape of the reciprocal scattering curve is known for rod-like polymers in any case, but one does not expect appreciable difficulty in the extrapolation to zero scattering angle for the chain lengths of interest. Another problem involving depolarization of the scattered light could be handled if it is encountered.
- T. B. Lefferdink: Is dehydrogenation of the ladder polymers best accomplished by direct pyrolysis or is an oxidation reaction preferred?
- J. K. Stille: Dehydrogenation of the polyimides or dihydropyrazoles under pyrolysis conditions (e.g., refluxing in a very high-boiling solvent or heating in the dry powder form) resulted in a reduction of molecular weight or cross-linking, respectively, depending on the conditions. Refluxing in mild oxidizing solvents such as nitrobenzene did not result in the molecular weight reductions; dehydrogenation proceeds relatively rapidly.