polyisobutylene; its enthalpy exceeds that of polyethylene by 2.36 kcal/mol, as do also the (hypothetical) α,β-disubstituted polyolefin structures 8 and 12 by about 7 and 10 kcal/mol, respectively. Tatevskii's scheme does not indicate steric hindrance in any of these branched polymers with respect to polyethylene, primarily because it lacks the necessary steric parameters capable of discriminating subtle steric differences in alkanes larger than eight carbon atoms.

Comparing the experimental ΔH_f°(g)'s of the isotactic polypropylene[14,15] and the isotactic poly(1-butene)[14] with the corresponding values predicted from the SZ scheme, a steric hindrance of about 0.4 kcal for the polypropylene and about 0.8 kcal for the poly(1-butene) is observed. Since the SZ scheme does not consider steric interactions beyond 1–3 carbons, it is reasonable to assume that the enthalpies of formation calculated by this scheme would be closer to syndiotactic polymer where the higher order steric hindrance arising from a sandwiched segment of a polymer would be the least. The above energy differences for the isotactic polymers are then reconcilable. More experimental enthalpy of formation data on well-characterized polyolefins, including such totally syndiotactic polymers as polypropylene, are under way and will be useful in understanding higher order interactions which in turn should help to improve the existing bond-energy schemes for predicting properties of polymers.

Acknowledgment. The authors wish to express their sincere thanks to Dr. A. P. Kudchadker for his assistance and advice in the numerous calculations. This work was supported through the Robert A. Welch Foundation and the Texas A&M Thermodynamics Research Center.

Thermally Stable Ladder Polyquinoxalines

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Received November 20, 1967

ABSTRACT: Five thermally stable quinoxaline polymers have been prepared by the condensation of the aromatic tetramines 1,2,4,5-tetraminobenzene and 2,3,6,7-tetraminodibenzo-*p*-dioxin with 2,5-dihydroxy-*p*-benzoquinone or the tetraketones 1,2,6,7-tetraketopyrene and 1,2,5,6-tetraketoanthracene. All of the polymers obtained were completely soluble in 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane. The polymers prepared from the condensation of 1,2,4,5-tetraminobenzene with the tetraketones 1,2,6,7-tetraketopyrene and 1,2,5,6-tetraketoanthracene had molecular weights of 7000 and 12,000, respectively. All of the polymers obtained had good thermal stability in air, although the ladder polymers were not significantly more stable than the single-strand polyquinoxalines. The thermal stability of the ladder polymers in a nitrogen atmosphere was considerably greater than that of the corresponding single-strand polymer.

The concept of new, high-performance polymers which are capable of demonstrating enhanced thermal stability has attracted much interest. One class of polymers that possess potentially useful thermal properties is the polyquinoxalines.[1–7] The thermal stability of these polymers has been attributed to their totally aromatic structure. The single-strand polyquinoxalines are yellow-brown to black in color, moderately soluble in hexamethylphosphoramide, and stable in air and nitrogen atmospheres to 500–550°.

The quinoxaline ring-forming reaction, a condensation of an *o*-diamine with a 1,2-dicarbonyl, has proven to be an efficient one for the synthesis of polymers. This reaction should be adaptable to the formation of ladder polymers and the efficiency of this reaction should ensure a perfect ladder structure. The incorporation of the quinoxaline nucleus into ladder or double-strand polymers should enhance the thermal stability of the polymer and allow an investigation of the ladder polymer concept as applied to heterocyclic polymers.

Discussion

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 will be totally aromatic. When 2,5-dihydroxy-*p*-benzoquinones and aromatic tetramines were polymerized, dihydroquinoxaline polymers were obtained.

The polymerization of 2,5-dihydroxy-*p*-benzoquinone (I) with 1,2,4,5-tetraminobenzene (II) or its hydrochloride salt in hexamethylphosphoramide or 116% polyphosphoric acid gave VIII.[8] The degree of polym-

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(1) J. K. Stille and J. R. Williamson, *J. Polymer Sci.*, **B2**, 209 (1964).

(2) J. K. Stille and J. R. Williamson, *ibid.*, **A2**, 3867 (1964).

(3) J. K. Stille, J. R. Williamson, and F. E. Arnold, *ibid.*, **A3**, 1013 (1965).

(4) J. K. Stille and F. E. Arnold, *ibid.*, **A4**, 551 (1966).

(5) G. DeGaudemaris and B. Sillion, *ibid.*, **B2**, 203 (1964).

(6) G. DeGaudermaris, B. Sillion, and J. Preve, *Bull. Soc. Chim. France*, 1793 (1964).

(7) P. M. Hergenrother and H. H. Levine, *J. Polymer Sci.*, **A1**, **5**, 1453 (1967).

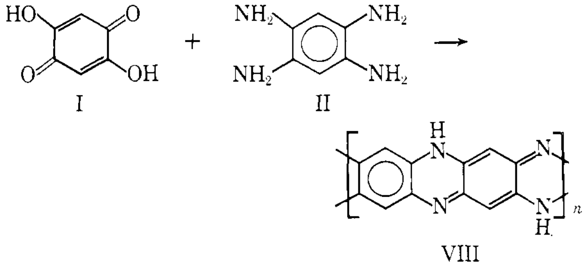
(8) The names of the polymers appear in the Experimental Section. We wish to thank the Chemical Abstracts Service for suggesting these names.

TABLE I
THE SYNTHESIS OF POLYMER VIII IN VARIOUS SOLVENTS

Solvent	Reaction time,[a] hr	Solubility[b]	$[\eta]^c$
N,N-Dimethylacetamide	36	50	0.57
Hexamethylphosphoramide	120[d]	100	0.58
	72[d]	100	0.49
	24[d]	100	0.45
	120	100	0.55
	72	100	0.61
	24	100	0.48
116% polyphosphoric acid	6[d]	30	1.45

[a] These reactions were carried out in flasks under dry nitrogen atmospheres at 180°. [b] Weight per cent of the polymer which would dissolve in excess hexamethylphosphoramide, after precipitation. [c] Inherent viscosities were obtained in hexamethylphosphoramide at concentrations of 0.25 g/dl. [d] These data correspond to polymer synthesized with 1,2,4,5-tetraminobenzene tetrahydrochloride. All other data were obtained from polymers synthesized using the corresponding free amine.

erization of VIII was markedly dependent on the polymerization solvent (Table I). The low degree of polymerization in the hexamethylphosphoramide solvent is possibly due to the formation of a complex of the solvent with the growing polymer. The fact that the tetramine and the dihydroxy diketone could be recovered from solution free of bound solvent indicated that a monomer solvent complex was not the source of the difficulty. The polymer, however, retained a constant weight of solvent per recurring unit even after continuous extraction with benzene. The complex decomposed at 210–225° with the liberation of hexamethylphosphoramide. The polymer obtained from such a thermal treatment was shown to have the identical ultraviolet and infrared spectra as the polymer obtained from the condensation of the monomers in 116% polyphosphoric acid. High-temperature dehydrogenation of the dihydro polymers to obtain the potentially more stable totally aromatic polymer apparently could not be effected. Work in this laboratory and elsewhere[9] indicated that the desired dehydrogenation could not be effected on the appropriate model compound. A summary of the thermal gravimetric analyses of this polymer appears in Table II.



When polymer VIII was pyrolyzed in a nitrogen atmosphere and the effluent products were analyzed, the only volatile products observed were hydrogen cyanide and ammonia. One possible route of decomposition which could conceivably give rise to such products is an unzipping of the polymer backbone to yield cyanogen as one primary intermediate. At the elevated temperatures, cyanogen could therefore account for the formation of hydrogen cyanide.

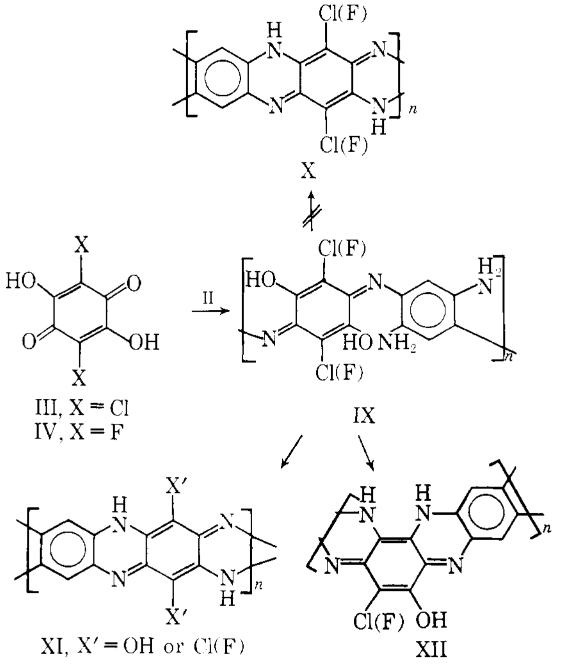
TABLE II

Polymer	TGA decomposition point,[a] °C Air	Nitrogen
VIII	525	535
XI (XII)	235	235
XIII	520	600
XIV	550	~700
XV	550	~700
XVI	550	~700
XIX	550	600
XX	500	550

[a] The temperatures of decomposition reported are those corresponding to the intersection of the slopes of the two lines, but at a weight loss of less than 5% at a 5°/min rate of heating.

When 3,6-dichloro-2,5-dihydroxy-*p*-benzoquinone (III) or 3,6-difluoro-2,5-dihydroxy-*p*-benzoquinone (IV) were employed in place of 2,5-dihydroxy-*p*-benzoquinone (I) as monomers, the dihydroquinoxaline polymer X containing only chlorine or fluorine substituents was not obtained as indicated both by elemental analysis of the polymers and the fact that both water and hydrogen halide were evolved during polymerization. Instead, polymers XI and/or XII which contain both halide and hydroxyl substituents were formed (Scheme I). Apparently, after the intermediate Schiff's base IX is formed, several possible reaction routes are available. The ring closure can occur with the loss of water or hydrogen halide. The presence of the hydroxyl groups, which was confirmed by infrared spectroscopy, severely decreases the thermal stability of the polymers which decomposed at 200–225°. A similar ring-closure reaction has been reported.[10]

SCHEME I



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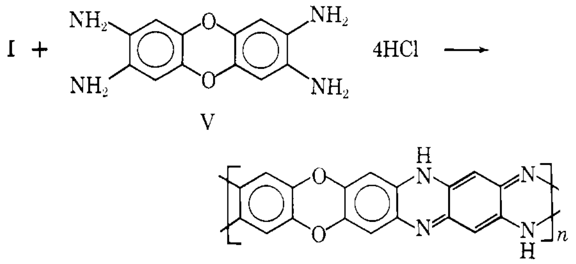
(9) G. Badger and R. Pettit, *J. Chem. Soc.*, 3211 (1951).

(10) (a) J. K. Stille, E. L. Mainen, M. E. Freeburger, and F. W. Harris, *Polymer Preprints*, **8**, No. 1 (1967); (b) J. K. Stille and M. E. Freeburger, *J. Polymer Sci.*, in press.

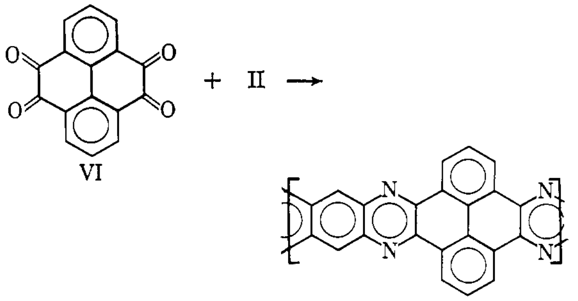
The free amine corresponding to 2,3,6,7-tetraminodibenzo-*p*-dioxin tetrahydrochloride (V) could not be isolated by conventional neutralization techniques. Treatment of the tetrahydrochloride with base led only to decomposition products; therefore only the amine hydrochloride could be polymerized to give polymer XIII. The physical characteristics and thermal stability of polymer XIII were generally similar to those of polymer VIII.



V

XIII

When tetraketones were polymerized with aromatic tetramines, quinoxaline ladder polymers were obtained. The polymerization of 1,2,6,7-tetraketopyrene (VI) with tetraminobenzene (II) gave polymer XIV. Reactions of tetraketone VI with the tetramine tetrahydrochlorides, II·4HCl or V, in either hexamethylphosphoramide or phosphoric acid failed to give polymer.



VI

XIV

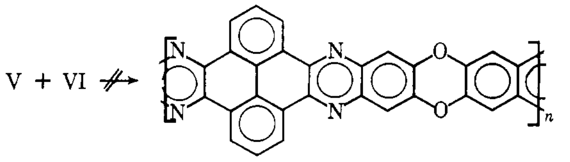
A study of the polymerization (Table III) revealed that a portion of the polymer formed precipitated from solution during the reaction. An inspection of the weight per cent of the precipitated fraction or the viscosity of the precipitated fraction at various times showed that the reaction proceeded more rapidly up to about 72 hr reaction time and then became slower. These results would be expected from a typical condensation polymerization, but they also indicated that during the reaction, as condensation occurred, the molecular weight increased to a point that the polymer was no longer soluble and precipitation occurred. Once the polymer precipitated from solution, the buildup of molecular weight was dependent on the slow reaction between soluble fragments and the precipitated fraction. That this polymer actually precipitated from solution and did not precipitate on cooling to room temperature was demonstrated by the fact that only 30% of the precipitated fraction of a sample which polymerized for 120 hr was soluble after 48 hr of continuous extraction in hexamethylphosphoramide at 190°. The formation of the precipitated fraction could not be attributed to cross-linking since the polymers obtained were entirely soluble in concentrated sulfuric acid and 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane. The inherent viscosity of a precipitated fraction of 1.76 g/dl in the hydrated tetrafluoroacetone solvent prior to extraction with the hot hexamethylphosphoramide increased to 1.89 g/dl after extraction. The slight increase in viscosity was probably due to the extraction of a low molecular weight fraction which had been occluded in the polymer.

TABLE III
POLYMERIZATIONS TO YIELD POLYMERS XIV AND XV

Polymer	Reaction time,[a] hr	% precipitated[b]	Solubility in HMP[c]	[η][d]	[η][e]
XIV	14	0	...	...	...
XIV	24	12	61	0.31	...
XIV	72	36	35	1.69	...
XIV	120	45	30	1.89	2.11
XV	24	36	85	1.02	...
XV	72	75	68	1.45	...
XV	120	91	58	1.90	2.02

[a] The polymerizations were carried out at 180° in sealed glass ampoules using deoxygenated hexamethylphosphoramide. [b] The per cent of polymer precipitated from the cooled reaction mixture. The remainder of the polymer was soluble at the conclusion of the reaction. [c] Per cent of the precipitated fraction which would redissolve in excess hexamethylphosphoramide. All of the polymers were 100% soluble in 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane. [d] The inherent viscosities of the portion of the precipitated fractions which could be redissolved in hexamethylphosphoramide at concentrations of 0.25 g/dl. [e] Inherent viscosity of the precipitated fraction in the 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane at concentrations of 0.25 g/dl.

Since the free amine corresponding to V could not be isolated, the *in situ* neutralization of the amine hydrochloride under polymerization conditions was carried out. This attempt yielded the tetraketone starting material and a black unidentifiable product as the only isolable materials. This result was disappointing since polymer XIV could be obtained from the *in situ* neutralization of the amine hydrochloride corresponding to II under identical conditions.



In an effort to obtain greater solubility for these rigid molecules,[11] a series of polymers was prepared in which the degree of structural uniformity was changed from a rod to a less regular polymer. The rodlike polymer XIV, a "kinked" polymer XV (Table III), and a copolymer XVI containing both the recurring units of XIV and XV were employed in the study. It is interesting (Table IV) that after 120 hr the amount of precipitate obtained from polymer XV was greater than that from XIV, but the solubility of the precipitate from XIV was greater. The copolymer is intermediate in these respects. A sample of polymer XIV with

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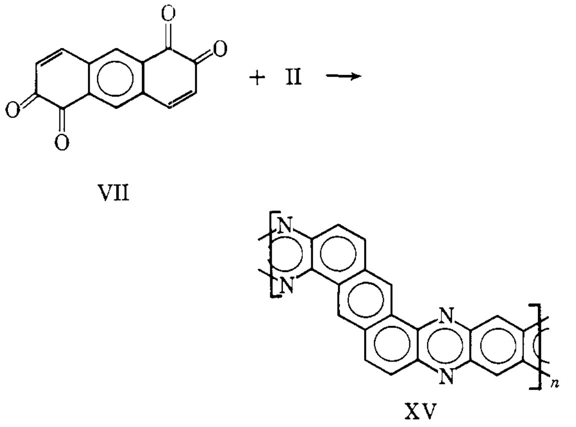
[11] C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 4.

TABLE IV
SOLUBILITY OF LADDER POLYMERS IN HMP

Polymer[a]	Moles of VI	Moles of VII	% Precipitated[b]	Solubility[c]	$[\eta]$[d]
XIV	1	0	45	30	1.89
XVI	1	1	68	50	1.81
XV	0	1	91	58	1.90

[a] See Table III, footnote *a*. [b] See Table III, footnote *b*. [c] See Table III, footnote *c*. [d] See Table III, footnote *d*.

an inherent viscosity of 1.60 g/dl had a molecular weight of 7000 while a sample of polymer XV with an inherent viscosity of 1.90 had a molecular weight of 12,000.



VII

XV

The complete solubility of polymers XIV, XV, and XVI in various solvents demonstrates that they are not cross-linked to any degree, but are apparently perfect ladders. Several factors may be operating to prevent cross-linking and give only intramolecular ring closure. Once the initial Schiff's base has been formed, there is a high probability that ring closure will occur as a result of the high dilution of the reactants in the solvent (3–5% by weight). In addition, the bulk of the aromatic nucleus bearing the ketone function probably prevents the approach of a second bulky molecule to form a cross-link. Further, completeness of the ring-closure reaction is aided by the fact that the second condensation in any ring completes an aromatic ring.

The ladder polyquinoxalines were not significantly more stable in air than the single-strand quinoxalines (Table II) and decomposed at about 550°. 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°.

In an effort to relate the effect of the ladder structure to thermal stability, the partial ladder polymer XIX was synthesized from 3,3-diaminobenzidene (XVIII) and 1,2,6,7-tetraketopyrene (VI). By a comparison of polymers XIV, XIX, and poly[2,2′-(1,4-phenylene)-6,6′-diquinoxaline][2] (XX), it was found that the polymer containing single links in the backbone had lower stability than the ladders (Figure 1).

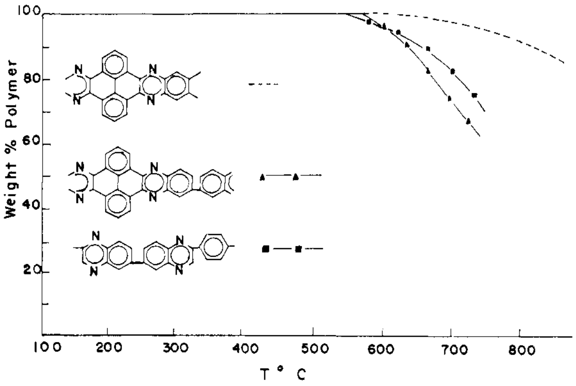
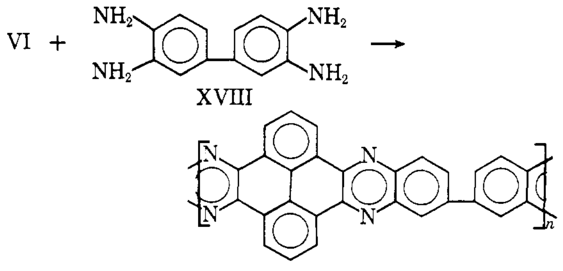


Figure 1. Comparison of the thermogravimetric analyses of polymers XIV, XIX, and XX; heating rate, 5°/min

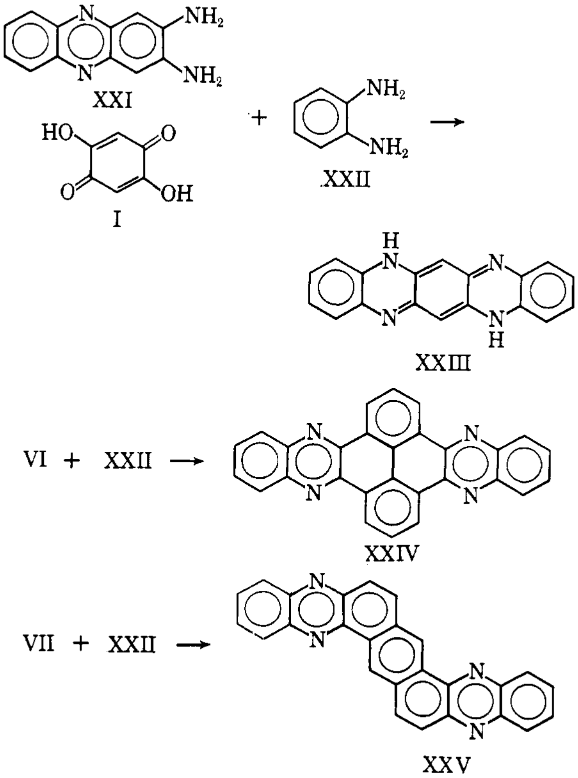
A series of model compounds was prepared for the purpose of comparison of spectral properties with those of the polymers. An authentic sample of XXIII was prepared by the reaction of 2,3-diaminophenazine (XXI) and *o*-phenylenediamine (XXII) in refluxing benzyl alcohol.[9] Compound XXIII was also prepared by the condensation of 2,5-dihydroxy-*p*-benzoquinone and *o*-phenylenediamine using hexamethylphosphoramide or polyphosphoric acid as solvents. It was demonstrated that the compounds were identical, independent of the method of preparation. The model compounds XXIV and XXV were prepared



XVIII

XIX

SCHEME II



XXI

I

XXII

XXIII

XXIV

XXV

Table V

Model compd	λ, mμ	$\epsilon \times 10^{-3}$	Polymer	λ, mμ	$\epsilon \times 10^{-3}$
XXIII	312	4.0	VIII	334	1.0
	270	2.8		304	3.3
				274	1.6
XXIV	409	3.0	XIII	333	1.1
	356	7.6		306	3.3
	295	6.3		268	1.5
XXV	519	1.2	XIV	355	2.9
	431	9.8		322	5.9
	331	3.0		273	5.8
	246	3.2			
			XV	505	14
				454	29
				320	18
				274	53

by the condensation of *o*-phenylenediamine and the tetraketones VI and VII, respectively (Scheme II). Comparison of the ultraviolet and visible spectra and especially the infrared spectra of the model compounds and polymers confirmed the assigned structures. A summary of the ultraviolet and visible absorption maxima appear in Table V.

Experimental Section

Monomers. 1,2,4,5-Tetraminobenzene (II) was prepared as previously described.[12,13] Nitration of 1,3-dichlorobenzene in fuming nitric acid, followed by nucleophilic amination, hydrogenation, and precipitation in hydrochloric acid, led to the amine hydrochloride. The free amine, obtained from the neutralization of the hydrochloride salt, was purified by sublimation at 150–160° (0.1 mm), mp 272–273° (lit.[12] mp 274–276°).

2,3,6,7-Tetraminodibenzo-*p*-dioxin Tetrahydrochloride (V). The tetranitro precursor of this compound was synthesized as previously described.[14] The hydrogenation of 2,3,6,7-tetranitrodibenzo-*p*-dioxin catalyzed by Raney nickel in acetic acid followed by precipitation of the hydrochloride salt in hydrochloric acid yielded the amine hydrochloride in a 8.0% yield over-all. All attempts to neutralize the hydrochloride salt did not yield the free amine.

Anal. Calcd for $C_{12}H_{16}N_4O_2Cl_4$: C, 37.31; H, 4.15; N, 13.99. Found: C, 37.18; H, 4.37; N, 13.63.

2,5-Dihydroxy-*p*-benzoquinone (I) was purchased from Eastman Chemical Co. It was purified by sublimation at 100° (0.1 mm), subl pt 214–216° (lit.,[15] subl pt 215–220°).

3,6-Dichloro-2,5-dihydroxy-*p*-benzoquinone (III) was purchased from Fisher Chemical Co. in analytical grade purity, mp 282.5–283° (lit.[15] mp 283–284°).

3,6-Difluoro-2,5-dihydroxy-*p*-benzoquinone (IV) was prepared as previously described.[16] The hydrolysis of fluoranil under basic conditions followed by acidification gave the fluoranilic acid product. The material was purified by sublimation at 100° (0.01 mm), mp 228–230° dec (lit.[16] mp 230° dec).

1,2,6,7-Tetraketopyrene (VI) was prepared as previously described.[17] The ozonation of pyrene to form 4-formyl-5-phenanthroic acid,[18] a ring-closure reaction with phenylhydrazine, followed by reduction gave 1-amino-2-hydroxypyrene. The α-hydroxyamine was oxidized by chromium trioxide in water to give 1,2-diketopyrene. The crucial step of this synthesis is the oxidation of 1,2-diketopyrene to the tetraketone. It is essential that all of the diketone be in solution prior to the addition of the oxidizing agent, chromium trioxide in water, which converts it into 1,2,6,7-tetraketopyrene. The over-all yield of this synthesis was 15%. The monomer was recrystallized from nitrobenzene and washed with methanol to remove the last traces of solvent, mp 370–371° (lit.[17] mp 365°).

1,2,5,6-Tetraketoanthracene (VII)[19,20] was prepared as previously described.[19] Treatment of 2,6-dihydroxyanthracene with a zinc chloride–sodium nitrite solution followed by the reduction of the resulting α,α′-dioxime diketone with sodium hydrosulfite gave 1,5-diamino-2,6-dihydroxyanthracene. Oxidation of the dihydroxydiamine with sodium dichromate in dilute sulfuric acid gave 1,2,5,6-tetraketoanthracene. Recrystallization from dioxane gave a 3% over-all yield of product, mp 305–306° (lit.[20] mp 320°).

3,3′-Diaminobenzidene (XVIII).—A sample of the 3,3′-diaminobenzidene tetrahydrochloride was neutralized and purified by sublimation at 170°, mp 180–180.8° (lit.[21] mp 179–179.5°).

Polymers. The polymerizations were carried out in flasks under dry nitrogen atmospheres or in ampoules sealed under reduced pressure. All solvents were deoxygenated prior to use in both techniques. The polymers were treated to a second-stage heating cycle at 250° (0.1 mm) which removed some occluded solvent and in some cases caused solid phase polymerization.

Poly(1,6-dihydropyrazino[2,3-*g*]quinoxaline-2,3,8-triyl-7-(2H)-ylidene-7,8-dimethylidene) (VIII) (Table I). Method 1. The reaction of 0.2843 g (2.058 mmoles) of 1,2,4,5-tetraminobenzene and 0.2804 (2.001 mmoles) of 2,5-dihydroxy-*p*-benzoquinone in hexamethylphosphoramide solvent at 180° followed by precipitation in chloroform gave 0.3481 g of a shiny black polymer. The polymer was extracted for 12 hr with benzene and dried under reduced pressure (0.1 mm) over phosphorus pentoxide.

In the second-stage thermal treatment, 0.100 g of polymer was heated to 250° for 1 hr in a rotating flask under reduced pressure (0.1 mm). After a few minutes of heating, the polymer became a dull black powder. The weight loss corresponded to 0.024 g. This indicated an approximate yield of 0.2677 g (64%) free of hexamethylphosphoramide.

Anal. Calcd for $(C_{12}H_6N_4)_n$: C, 70.55. Found: C, 65.49.

This polymer was extremely difficult to analyze due to the adherence of an inorganic residue.

Method 2. To a polyphosphoric acid solution prepared from 31 g of phosphorus pentoxide and 35 g of phosphoric acid was added 0.5776 g (2.038 mmoles) of 1,2,4,5-tetraminobenzene tetrahydrochloride dissolved in 5 g of phosphoric acid. The temperature of the mixture was raised to 140° to allow the complete displacement of hydrogen chloride. When the evolution of gas ceased 0.2803 g (2.001 mmoles) of 2,5-dihydroxy-*p*-benzoquinone dissolved in 5 g of phosphoric acid was added to the reaction mixture. The temperature of the reaction mixture was raised to 180° and the reaction allowed to proceed for 6 hr. At the conclusion of the reaction, the cooled reaction mixture was added slowly

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(13) R. Nietzki and A. Schadler, *Ber.*, **30**, 1666 (1892).

(14) H. Gilman and J. Dietrich, *J. Am. Chem. Soc.*, **80**, 366 (1958).

(15) "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961.

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(20) P. Boldt, *Naturwissenschaften*, **51**, 137 (1964); *Chem. Ber.*, **99**, 2322 (1966).

(21) F. Dawans and C. S. Marvel, *J. Polymer Sci.*, **A3**, 3549 (1965).

to 500 ml of water. The finely divided, black precipitate was washed twice with 50 ml of water, three times with 50 ml of a 15% ammonium carbonate solution, and finally twice with 50 ml of water. The polymer was dried at 180° (0.1 mm) over phosphorus pentoxide. The yield of polymer was 0.462 g (96%).

Anal. Calcd for $(C_{12}H_6N_4)_n$: C, 70.55; H, 2.90. Found: C, 70.05; H, 2.81.

Poly(1,6-dihydropyrazino[2,3-*g*]quinoxaline-2,3,8-triyl-2,7-dichloro(hydroxy)ylidene-7,8-dimethylidene) (XI or XII). This procedure is typical of the method used to carry out this polymerization. To a glass ampoule was added 0.4134 g (1.456 mmoles) of 1,2,4,5-tetraminobenzene tetrahydrochloride, 0.3042 g (1.456 mmoles) of 3,6-dichloro-2,5-dihydroxy-*p*-benzoquinone, and 25 ml of hexamethylphosphoramide. The ampoule was sealed with a rubber septum and subjected to three freeze–evacuate–thaw deoxygenation cycles. The ampoule was sealed with an internal pressure of 1 mm and placed in a closed metal reactor with 10 ml of water. The reaction was effected by heating the metal bomb to 180° for 72 hr. At the conclusion of the reaction, the ampoule was cooled and opened and the polymer was precipitated by the dropwise addition of the solution to chloroform. The polymer was collected by suction filtration and extracted overnight with benzene.

It was not possible to carry out the normal second-stage thermal treatment because the material decomposed at 235°. The carbon–hydrogen analysis indicated the structure XI or XII.

Anal. Calcd for $(C_{12}H_4N_4Cl_2)_n$: C, 53.32; H, 1.48. Calcd for $(C_{12}H_6N_4O_2)_n$: C, 60.98; H, 2.51. Found: C, 56.32; H, 1.82.

Poly(1,6-dihydropyrazino[2,3-*g*]quinoxaline-2,3,8-triyl-2,7-difluoro(hydroxy)ylidene-7,8-dimethylidene) (XI or XII). The reaction of 0.3052 g (1.718 mmoles) of 2,5-difluoro-3,6-dihydroxy-*p*-benzoquinone with 0.5010 g (1.764 mmoles) of 1,2,4,5-tetraminobenzene was carried out exactly as that described for the 2,5-dichloro analog. Both water and hydrogen fluoride were evolved in the synthesis of this polymer. Suitable elementary analyses on the basis of either the fluoro- or the hydroxy-containing recurring unit could not be obtained.

Poly(1,6-dihydropyrazino[2,3-*g*]dibenzo-*p*-dioxinoquinalino-2,3,8-triyl-7(2H)-ylidene-7,8-dimethylidene) (XIII). The following procedure is typical of the method used to carry out this polymerization. To a polyphosphoric acid solution prepared from 31 g of phosphorus pentoxide and 35 g of phosphoric acid was added 0.7945 g (1.999 mmoles) of 2,3,6,7-tetraminodibenzo-*p*-dioxin dissolved in 5 g of phosphoric acid.

The polymerization was carried out and the polymer was isolated exactly as described for polymer VIII, method 2. The yield of the polymer was 0.5702 g (92%).

Anal. Calcd for $(C_{18}H_8N_4O_2)_n$: C, 69.68; H, 2.60. Found: C, 70.95; H, 2.40.

Poly(dibenzo[*a,c*]pyrazino[2,3-*i*]phenazine-4,5,12,13-tetrayl) (XIV) (Table III). To a glass ampoule was added 0.2630 g (1.003 mmoles) of 1,2,6,7-tetraketopyrene and 0.1370 g (0.9915 mmole) of 1,2,4,5-tetraminobenzene in a drybox. The ampoule was subjected to three freeze–evacuate–thaw cycles. The ampoule was sealed with an internal pressure of 1 mm and placed in a sealed metal bomb with 10 ml of water. The reaction was effected by heating the bomb to 180° for 120 hr. The reaction yielded two fractions. The fraction which had precipitated at the conclusion of the reaction was collected and washed with 10 ml of hot benzene. The material which remained in solution was precipitated by dropwise addition of the solution to chloroform. Both fractions were continuously extracted for 12 hr. After drying, the solution fraction weighed 0.1880 g and the precipitated fraction weighed 0.1453 g.

In the second-stage thermal treatment, 0.100 g of the soluble fraction lost 0.002 g while 0.100 g of the precipitated fraction lost 0.001 g. These weight losses indicated an approximate yield of 0.1439 g (43%) for the precipitated fraction and 0.1853 g (55%) for the soluble fraction. The total conversion for the reaction was 98%.

Anal. Calcd for $(C_{22}H_8N_4)_n$: C, 80.48; H, 2.45. Found: C, 80.76; H, 1.85.

Poly(benzo[*a,c*]pyrazino[2,3-*i*]phenazine-10,11:2,3-tetrayl-2-vinylene) (XV) (Table III). To a glass ampoule was added 0.1549 g (0.6507 mmole) of 1,2,5,6-tetraketoanthracene, 0.0911 g (0.6593 mmole) of 1,2,4,5-tetraminobenzene, and 25 ml of hexamethylphosphoramide.

The polymerization was carried out as described for XIV. The reaction yielded two fractions. The polymer which had precipitated at the conclusion of the reaction was collected and washed with 10 ml of hexamethylphosphoramide. The material in solution was precipitated by the dropwise addition of the solution to chloroform. Both fractions were continuously extracted with hot benzene for 12 hr. After drying, the soluble portion weighed 0.0178 g while the precipitated fraction weighed 0.1796 g. In the second-stage treatment, 0.100 g of the precipitated fraction lost 0.001 g while the solution fraction lost 0.008 g. These weight losses indicated a yield of 0.1778 g (89%) for the precipitated fraction and 0.0098 g (4%) for the soluble portion.

Anal. Calcd for $(C_{20}H_8N_4)_n$: C, 79.14; H, 2.63. Found: C, 79.06; H, 2.43.

Preparation of the Copolymer XVI (Table IV). The procedure used to prepare a copolymer from 0.0404 g (0.169 mmole) of 1,2,5,6-tetraketoanthracene, 0.0441 g (0.168 mmole) of 1,2,6,7-tetraketopyrene, and 0.0463 g (0.334 mmole) of 1,2,4,5-tetraminobenzene was identical with those which were used to prepare the homopolymers. The yield of the precipitated fraction was 0.0681 g.

Poly(4,11-dibenzo[*hi,uv*]5,9,14,18-tetraazahexacene) (XIX). To a glass ampoule was added 0.1035 g (0.4929 mmole) of 3,3′-diaminobenzidene, 0.1297 g (0.4947 mmole) of 1,2,6,7-tetraketopyrene, and 25 ml of hexamethylphosphoramide. The ampoule was sealed and heated in the conventional manner for 72 hr. The yield of the precipitated fraction after extraction and the second-stage heat treatment was 0.09421 g (46%).

Anal. Calcd for $(C_{28}H_{12}N_4)_n$: C, 83.16; H, 2.97. Found: C, 83.40; H, 2.65.

Attempted Preparation of Poly(1,6-dihydropyrazino[2,3-*g*]dibenzo-*p*-dioxinoquinoxalino-2,3,8-triyl-7(2H)-ylidene-7,8-dimethylidene). To a glass ampoule was added 0.3526 g (0.9038 mmole) of 1,2,5,6-tetraminodibenzo-*p*-dioxin tetrahydrochloride, 0.2369 g (0.9036 mmole) of 1,2,6,7-tetraketopyrene, and 25 ml of hexamethylphosphoramide. The ampoule was sealed in the conventional manner and heated to 180° for 120 hr. At the conclusion of the reaction the ampoule contained a deep orange solution and a black precipitate. The solution contained unreacted starting tetraketone and no other readily identifiable products. The precipitate, presumably amine decomposition products, was not identified.

The Pyrolysis of Poly(1,6-dihydropyrazino[2,3-*g*]quinoxalino-2,3,8-triyl-7(2H)-ylidene-7,8-dimethylidene) (VIII). The Du Pont 950 thermal gravimetric analyzer was modified with a pyrolysis bucket capable of holding approximately 0.5 g of sample. The effluent gases were trapped at liquid nitrogen temperature. The trap was fitted with a stopcock so that at the conclusion of the experiment the contents could be transferred without fear of loss. The instrument was programmed for a normal heating cycle of 800° in a nitrogen atmosphere. At the conclusion of the pyrolysis, the contents of the trap were transferred to a gas infrared cell. The products were identified by means of their infrared spectra to be ammonia and hydrogen cyanide.

Model Compounds. 5,12-Dihydro-5,7,12,14-tetraazopentacene (XXIII). Method 1.[9] A mixture of 8.00 g (38.0 mmoles) of 2,3-diaminophenazine and 6.00 g (55.5 mmoles) of *o*-phenylenediamine was dissolved in 60 ml of benzyl alcohol. The reaction mixture was heated for 14 hr. The dark green precipitate from the reaction mixture was collected, extracted with boiling, dilute sulfuric acid, and neutralized with an alcohol solution saturated with ammonia. This procedure afforded 3.52 g (33%) of product. For analytical purposes, the deep purple compound was purified by sublimation. Owing to the difficulty in observing the melting point of the material, carbon and hydrogen analyses were used as the criteria of purity.

Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.01; H, 4.24. Found: C, 76.14; H, 4.43.

Method 2. A mixture of 1.31 g (9.35 mmoles) of 2,5-dihydroxy-*p*-benzoquinone and 1.06 g (9.81 mmoles) of *o*-phenylenediamine was dissolved in 50 ml of hexamethylphosphoramide and stirred for 12 hr at 150°. At the conclusion of the reaction the solution was added dropwise to chloroform to yield a purple precipitate. This compound was shown by comparison of infrared spectra to be identical with the sample prepared by method 1. This procedure afforded 1.62 g (61%) of product.

Method 3. A mixture of 1.31 g (9.35 mmoles) of 2,5-dihydroxy-*p*-benzoquinone and 1.00 g (9.25 mmoles) of *o*-phenylenediamine was dissolved in 50 ml of 116% polyphosphoric acid and heated for 12 hr at 150°. The cooled reaction mixture was added to 500 ml of water and washed with 100 ml of a 15% ammonium carbonate solution. This afforded 2.61 g (98%) of a compound shown by comparison of infrared spectra to be identical with the known sample prepared by method 1.

Diquinoxal[2,3-*e*,2′,3′-*l*]pyrene (XXIV). To a solution of 0.412 g (3.83 mmoles) of *o*-phenylenediamine in 50 ml of acetic acid was added 0.500 g (1.90 mmoles) of 1,2,6,7-tetraketopyrene. The solution was stirred at 60° for 1 hr. The yellow precipitate was collected, washed with a 15% ammonium carbonate solution, and recrystallized from nitrobenzene to afford 0.610 g (97%) of the product, mp >420° (lit.[17] >420°).

Diquinoxalo[2,3-*a*,2′,3′-*h*]anthracene (XXV). To 0.200 g (0.830 mmole) of 1,2,5,6-tetraketoanthracene in 50 ml of dioxane was added 0.181 g (1.68 mmoles) of *o*-phenylenediamine. The mixture was stirred for 1 hr at the reflux temperature and cooled. The yellow precipitate was recrystallized from nitrobenzene to afford 0.224 g (71%) of product, mp >450° (lit.[19] >450°).

Structural and Physical Characterization. Infrared spectra of both model compounds and polymers were obtained as potassium bromide pellets on a Perkin-Elmer Model 21 infrared spectrometer.

Ultraviolet and visible spectra of both model compounds and polymers were obtained in sulfuric acid solutions on a Cary Model 14 recording spectrophotometer. A compilation of these appears in Table V.

Thermal gravimetric analyses were obtained using a Du Pont 950 thermal gravimetric analyzer. The compilation of these studies both in air and nitrogen atmospheres appears in Table II.

Number-Average Molecular Weight. The molecular weights were obtained on a Mechrolab 301A vapor pressure osmometer.

Viscosities (inherent) of all polymer samples were obtained in hexamethylphosphoramide or 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-dihydroxypropane solutions of 0.250 g/100 ml at 25°. The inherent viscosities are listed in Tables I, III, and IV.

Solubilities. The solubility determinations were carried out by stirring a known quantity of the polymer (0.1–0.3 g) in 25 ml of hexamethylphosphoramide for a period of 12–24 hr. At the conclusion of the stirring the solutions were filtered through medium-porosity glass funnels. Aliquots of 2 or 5 ml of the solutions were pipetted into preweighed aluminum dishes. The solvent was removed by placing the dishes in a hot-air circulating oven. The aluminum dishes were heated to constant weight and the solubility was calculated on the basis of the residue in the pan.

Acknowledgment. The authors are grateful to the United States Army Office of Ordnance Research, Durham, N. C., for its support of this research. The Du Pont 950 thermal gravimetric analyzer used in this study was obtained, in part, through a gift from Dunlop Research Centre, Ontario, Canada.