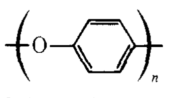
$-(OCH_2)_n-$

polyformaldehyde
poly(oxymethylene)



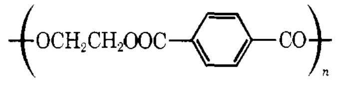
poly(phenylene oxide)
poly(oxy-1,4-phenylene)

$-(NH(CH_2)_6NHCO(CH_2)_4CO)_n-$

poly(hexamethylene adipamide)
poly(iminohexamethyleneiminoadipoyl)

$-(OCH_2CH_2)_n-$

poly(ethylene oxide)
poly(oxyethylene)



poly(ethylene terephthalate)
poly(oxyethyleneoxyterephthaloyl)

$-(NHCO(CH_2)_5)_n-$

poly(ϵ-caprolactam)
poly[imino(1-oxohexamethylene)]

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Synthesis and Properties of Thermally Stable Ladder Polymers Containing the 1,4-Pyrazine Ring Obtained from Polyheterocyclizations of Tetramines and Tetraketones in Poly(phosphoric acid) and *m*-Cresol

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ABSTRACT: The synthesis of ladder polyquinoxalines in *m*-cresol and poly(phosphoric acid) from reactions of the tetramines 1,2,4,5-tetraminobenzene, 1,2,5,6-tetraminonaphthalene, and 1,2,5,6-tetraminoanthraquinone with the tetraketones pyrene-4,5,9,10-tetrone and anthracene-1,2,5,6-tetrone generally give higher molecular weight polymers than the reaction carried out in other reaction solvents. Polyquinoxalines prepared from 1,2,5,6-tetraminoanthraquinone have good solubility in acid solvents such as methanesulfonic acid, and can be solubilized in basic dimethyl sulfoxide by their reduction with dithionate. Black films with a metallic luster can be cast from solution. Polymers prepared from pyrene-4,5,9,10-tetrone had better thermal stability than the other ladder polymers.

Research directed toward the synthesis and characterization of polymers containing the quinoxaline ring has shown that the utilization of the reaction of a 1,2-dicarbonyl with an aromatic *o*-diamine as the polymer forming reaction has produced high molecular weight materials.[1-3] The reaction is quantitative, and provides nearly perfect quinoxaline ring formation; these features have made it valuable as a polymerization reaction both from the vantages of achievement of high molecular weights and thermal stability gained through the complete ring closure to give this aromatic nucleus. The reaction solvent, *m*-cresol, has been shown to be particularly valuable in the synthesis of high molecular weight linear polyquinoxalines from the reaction of aromatic tetramines with bisglyoxals or bisbenzils. These polymers have excellent thermal stability and mechanical properties; especially attractive is their outstanding adhesive strength.

Ladder polymers containing the phenazine, or in general the 1,4-pyrazine ring fuzed to other aromatic ring systems, should exhibit better thermal stability than their linear counterparts. Theoretical studies by application of a Monte Carlo model on ladder polymers containing six-membered rings indicate that the double-stranded polymers are more stable than the single-stranded model.[4] This has been confirmed in studies of thermal stabilities of ladder polymers containing a variety of structural units.[5,6]

Earlier studies[7] on ladder polymers containing the 1,4-pyrazine unit, obtained from the reaction of aromatic tetramines with suitable aromatic tetraketones, revealed that they had about the same thermal stability in air as the single-stranded polyquinoxalines, as shown by thermal gravimetric analysis (TGA), but had much better stability in an inert atmosphere. The polymerization reactions carried out in hexamethylphosohoramide were slow, however, requiring a week to produce material having intrinsic viscosities greater than one. In addition, the resulting polymers had poor solubility in most solvents. The present study was undertaken to discover better reaction solvents and ways of improving the solubility of the resulting ladder polymer.

Results and Discussion

Two aromatic tetraketones, pyrene-4,5,9,10-tetrone (**1**), and anthracene-1,2,5,6-tetrone (**2**) and three tetramines, 1,2,4,5-tetraminobenzene (**3**), 1,2,5,6-tetraminonaphthalene (**4**), and 1,2,5,6-tetraminoanthraquinone (**5**) (see Chart I) were employed in the polymerization reactions. Tetramine **4** was specifically synthesized for the preparation of ladder polymers to provide angular irregularities in the chain in anticipation of imparting improved

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(1) J. K. Stille, *Encycl. Polym. Sci. Technol.*, **11**, 389 (1969).

(2) A. M. Berlin, *Usp. Khim.*, **39**, 158 (1970).

(3) P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C6**, 1 (1971).

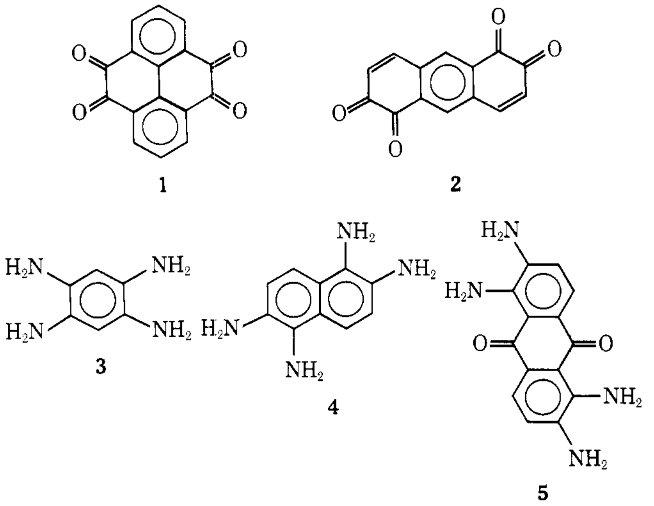
(4) M. M. Tessler, *J. Polym. Sci., Part A-1*, **4**, 2521 (1966).

(5) C. G. Overberger and J. A. Moore, *Fortschr. Hochpolym. Forsch.*, **7**, 113 (1970).

(6) W. DeWinter, *Ind. Chim. Belge*, **35**, 1097 (1970).

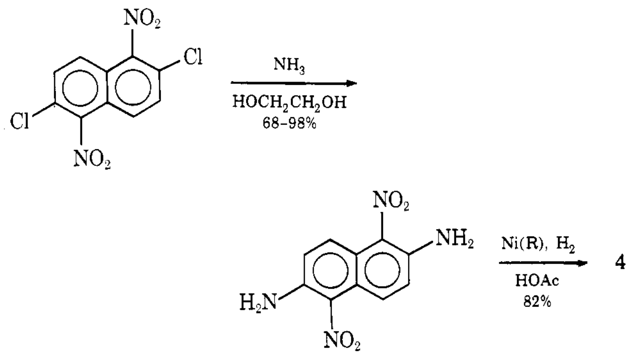
(7) J. K. Stille and E. L. Mainen, *Macromolecules*, **1**, 36 (1968).

Chart I

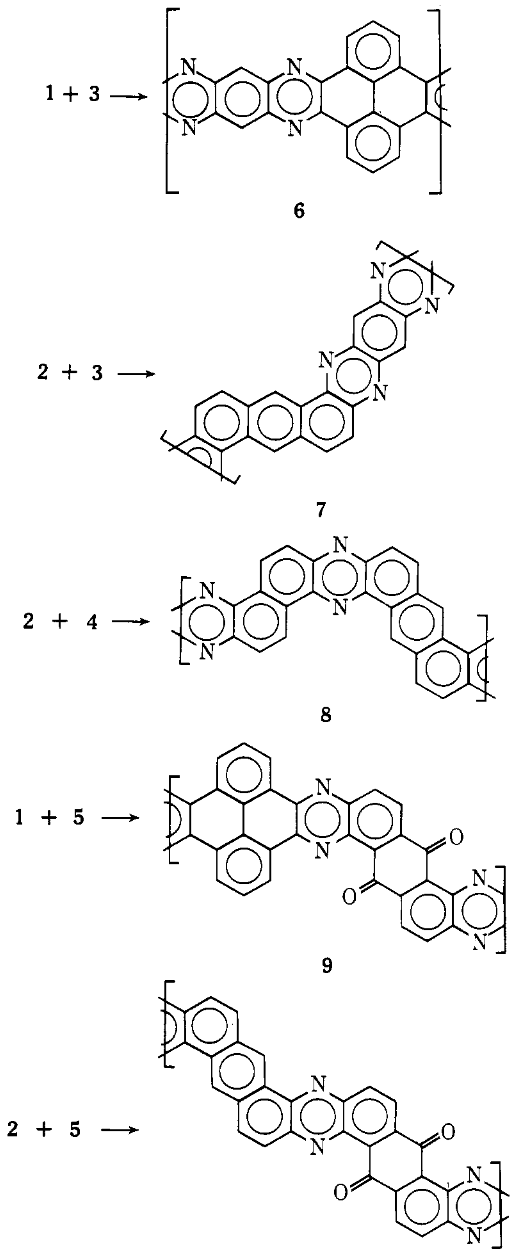


solubility *(vide infra)*. This amine was synthesized in good yields from 2,6-dichloro-1,5-dinitronaphthalene by nucleophilic displacement of chlorine by ammonia followed by reduction of the nitro groups (Scheme I). The free amine is not easily purified and is somewhat unstable; consequently it was used only as the tetrahydrochloride salt.

Scheme I



Scheme II



Polymerization reactions (Scheme II), carried out in *m*-cresol and poly(phosphoric acid), gave black polymers. Polymerizations of the tetraketones with tetraminobenzene **3** in *m*-cresol carried out over a period of about 3 days during which time the temperature was raised from ambient to 202° produced polymers with inherent viscosities greater than one (Table I). Polymerization of these tetraketones with the other tetramines (**4** and **5**) in *m*-cresol did not produce high molecular weight materials. This can be attributed to the lower reactivity of 1,2,5,6-tetraminoanthraquinone, especially of the amino groups adjacent to the carbonyl functions, and the fact that the 1,2,5,6-tetraminonapthalene (**4**), as the free amine, could not be highly purified. After precipitation from *m*-cresol, polymers **6** and **7** (powder) were heated to 350°. During the course of this heat treatment, *m*-cresol, the last traces of which are difficult to remove, was evolved from the polymer at 300° under reduced pressure. Just prior to and during the elimination of the *m*-cresol, the polymer sintered into larger particles. When the polymer was exhaustively extracted with benzene prior to this thermal treatment, no *m*-cresol was evolved during the heating, and the sintering was not observed. Furthermore, the polymer heated in the presence of some *m*-cresol had greater thermal stability than that which did not contain *m*-cresol (TGA, air 545° *vs.* 500°, respectively). These results suggest that *m*-cresol is acting as a plasticizer to allow complete cyclization and/or molecular weight increase through end group reactions. Heat-treated polymer was no longer soluble.

Polymerization in poly(phosphoric acid) gave polymers with intrinsic viscosities greater than one in a day's time at temperatures from ambient to 200°. In several cases very high inherent viscosities could be obtained. This powerful heterocyclization solvent[8] was efficient in driving the condensation of tetraminoanthraquinone **5**; in addition, it afforded the convenience of using the hydrochlorides of **3** and **4**. Copolymerizations utilizing appropriate combinations of tetraketones **1** and **2** with tetramines **3** and **5** were also carried out in poly(phosphoric acid).

Several structural features in the polymers were included to improve the solubility of these rigid ladders. Tetraketone **2** as well as tetramines **4** and **5** do not possess C_2 axes of symmetry, and this can lead to syn-anti isomerism in the polymer chain, presumedly at random. For example, polymer **7**, obtained from tetraketone **2** and tetrami-

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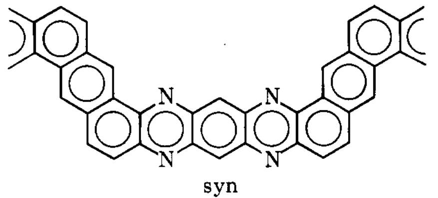
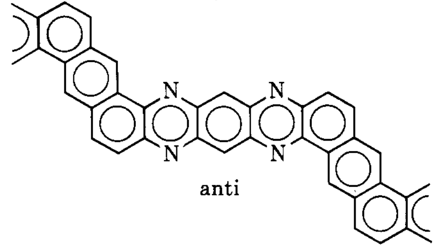
[8] N. Yoda and M. Kurihara, *J. Polym. Sci., Part D, Macromol. Rev.*, **5**, 109 (1971).

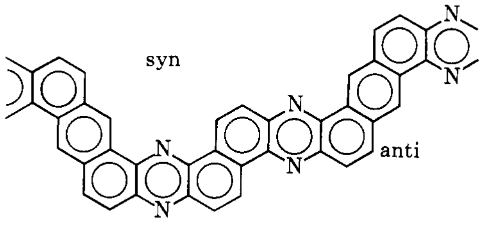
Table I
Ladder Polyquinoxalines

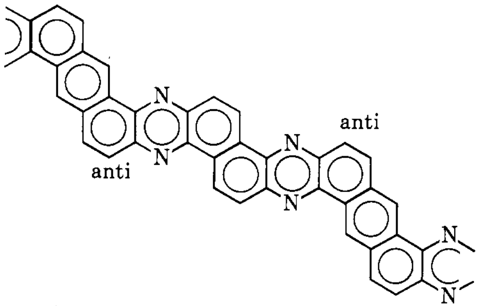
Monomers		Polymer Solvent	Polymer[a]	η_{inh}	Concn (g/dl)[b]	TGA[d]	
Ketone	Amine					Air Break (°C)	N, % Wt Loss 800°
1	3	C[e]	**6**	1.27	0.25	540	18
			6A			545	12
1	3[c]	PPA[e]	**6**	2.2	0.10	530	14
2	3	C	**7**	2.2	0.015	440	44
2	3[c]	PPA	**7**	0.43	0.25	460	33
2	4	C	**8**	0.66	0.06	455	38
			8A			455	37
2	4[c]	PPA	**8**	1.0	0.06	450	29
1	5	C	**9**	0.3	0.25	510	41
			9A			510	25
1	5	PPA	**9**	1.3	0.25	545	18
2	5	C	**10**	0.3	0.25	460	39
			10A			485	27
2	5	PPA	**10**	2.13	0.25	470	26
1	3[c] and 5	PPA	**11**	3.60	0.25	530	17
1 and 2	3[c] and 5	PPA	**12**	0.85	0.25	480	38

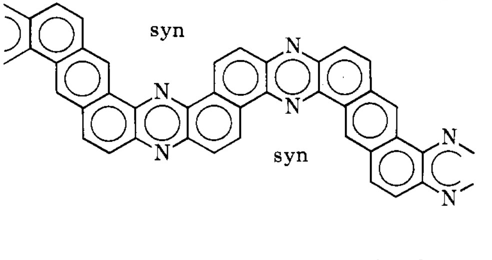
[a] A designates polymer which was treated after isolation by heating a precipitated sample at 350–400° for 1 hr. The resulting polymer was essentially insoluble. [b] In methanesulfonic acid. [c] Used as the tetrahydrochloride. [d] Thermal gravimetric analyses both in air and nitrogen were obtained at a heating rate of 5°/min. In a nitrogen atmosphere, the numbers give the per cent weight loss when the TGA reached 800°. [e] C = *m*-cresol; PPA = poly(phosphoric acid).











nobenzene, should have syn and anti catenation sequences. The combination of a tetraketone and a tetramine, both of which lack C_2 symmetry should extend the number of isomeric catenation sequences; the reaction of **2** and **5** gives rise to such isomerism in **10**.

Tetraminoanthraquinone has an additional structural feature, the carbonyl group, which could also improve the solubility of the polymer in strong acid. Further, the quinoid group can be reduced to the hydroquinone ring which is soluble in strong base.[9] Air effectively reoxidizes the hydroquinone to the quinone structure. Greater solubility could also be expected to be provided by copolymers.

The most effective solubilization was provided by the introduction of the anthraquinone moiety. No increased solubilization which could be ascribed directly to syn–anti isomerization exclusively (polymer **7**) was observed. Copolymers **11** and **12**, as well as polymers **9** and **10**, all of which contained the anthraquinone group, were readily soluble in sulfuric acid, methanesulfonic acid and trifluoromethanesulfonic acid. Somewhat brittle films of polymers **9–12** were cast from methanesulfonic acid; a black film of copolymer **10** which could be peeled from the glass casting plate had a metallic luster. Brittle fibers were extruded from methanesulfonic acid solutions. When polymers **9–12** were reduced by dithionate in aqueous dimethyl sulfoxide containing sodium hydroxide at 80°, a viscous polymer solution was obtained. Extrusion of these solutions into various nonsolvents afforded only brittle fibers.

The thermal stability of the ladder polymers containing the 1,4-pyrazine rings was good. TGA breaks in air occurred at about the same temperature as for single-stranded polyquinoxalines. The stability in an inert atmosphere was generally better than that exhibited by the single-stranded polyquinoxalines.[7] The greatest difference

[9] J. Szita, L. H. Brainnizan, and C. S. Marvel, *J. Polym. Sci., Part A-1*, **9**, 691 (1971).

in thermal stability in the ladder polymers both in air and in an inert atmosphere was between those ladders containing the pyrene nucleus and those which did not. Polymers **6**, **9**, and **11** in which the tetraketone was **1** only, showed consistently higher breaks in the TGA curves, as well as a lower weight loss in nitrogen at 800°. This difference in stability may be accounted for by the linear annellation principle,[10] although the magnitude of the effect of the heterocyclic rings in place of carbocyclic rings in thermal stability is unknown. While 1,2,6,7-dibenzopyrene containing four aromatic sextets is colorless, thermally stable, and quite unreactive, tetracene with one sextet is orange and more highly reactive; pentacene decomposes at temperatures over 300°.

Experimental Section

Monomers. Pyrene-4,5,9,10-tetrone (1). The synthesis of this tetraketone from pyrene was carried out as described.[7,11] The monomer was purified by two recrystalizations from nitrobenzene and then sublimed at 225° (50 μ), mp 396° (lit.[11] mp 365°).

Anthracene-1,2,5,6-tetrone (2). The synthesis of tetraketone **2** from 2,6-dihydroxy-9,10-anthraquinone was carried out as described.[12,13] The monomer was recrystallized twice from dioxane, mp 310° (lit.[13] mp 320°). Thin-layer chromatography on silica gel with a benzene–dimethylformamide (30:1) solvent revealed no detectable impurities.

1,2,4,5-Tetraminobenzene (3). This tetramine monomer was obtained from Burdick and Jackson as the tetrahydrochloride. The tetrahydrochloride was purified under nitrogen by recrystallization from degassed hydrochloric acid followed by recrystallization from a degassed ethanol-water mixture. The free amine was obtained as described[14] and was purified by sublimation at 160° (0.3 μ), mp 279-281 dec (lit.[14] mp 274-276°).

1,2,5,6-Tetraminonaphthalene (4). 2,6-Dichloronaphthalene, obtained from the reaction of sodium 2-hydroxynaphthalene-6-sulfonate with phosphorus pentachloride,[15,16] was nitrated to obtain 2,6-dichloro-1,5-dinitronaphthalene[17] which was converted to **4** as described in the following steps.

1. 2,6-Diamino-1,5-dinitronaphthalene. Ammonia was passed into 240 ml of stirred reagent grade ethylene glycol at 25° until 28 g (1.64 mol) of the gas was dissolved. To this solution 11.6 g (0.041 mol) of 2,6-dichloro-1,5-dinitronaphthalene was added, and the solution was sealed in a 1-l. Hastaloy C stirred autoclave and heated to 155-160° for 20 hr. Approximately 200 psi was registered on the pressure gauge. After 20 hr the bomb was allowed to cool and the pressure was released. The product which crystallized as red-brown crystals was collected by suction filtration. The product was washed with water and dried under reduced pressure at 150° to give 6.80 g (76%) yield of product, mp 284-285°. A yield of crude material as high as 98% could be obtained in smaller runs; ir (KBr) 2.87 and 2.97 (NH_2) 6.69, 7.37, and 7.62 μ (NO_2).

An analytical sample was prepared by two recrystallizations from glacial acetic acid. *Anal.* Calcd for $C_{10}H_8N_4O_4$: C, 48.37; H, 3.28; N, 22.57. Found: C, 48.17; H, 3.20; N, 22.38.

2. 1,2,5,6-Tetraminonaphthalene Tetrahydrochloride. A suspension of 4.02 g (0.0162 mol) of 2,6-diamino-1,5-dinitronaphthalene was dissolved in 180 ml of glacial acetic acid by heating it to the reflux temperature for 15 min and allowing it to cool to 60°. Approximately 0.5 g of Raney nickel was added to the suspension and the entire mixture was assembled on a low-pressure Parr shaker with a heating base set to maintain 45-50° in the hydrogenation bottle. The bottle was flushed by filling it with hydrogen and emptying it four times. It was then filled to 60 psi and the uptake of hydrogen was recorded. When the uptake of hydrogen was completed, the brown suspension was gravity filtered to remove the Raney nickel. The residue was rinsed with 30 ml of hot glacial acetic acid which was added to the filtrate, and the dark brown filtrate was added to 500 ml of cold concentrated hydrochloric acid. The precipitated gray tetramine tetrahydrochloride was collected by suction filtration and washed with 30 ml of cold concentrated hydrochloric acid to yield 3.80 g (70%) of a cream colored salt, mp > 300°.

Approximately 3.0 g of the tetrahydrochloride was dissolved in 350 ml of degassed, distilled water and approximately 2.0 g of activated charcoal was added. The mixture was mechanically shaken for 1 min, allowed to stand for 10 min, and then filtered through a Celite 545 (concentrated HCl washed) filled medium porosity sintered funnel. After pouring the filtrate into a stirred concentrated HCl solution, the white salt crystallized from solution on cooling with a 79% recovery after filtration. The salt was dried under reduced pressure at room temperature; ir (KBr) 3.25-3.45, 3.90, 6.45 and 6.67 μ ($NH_2 \cdot HCl$). *Anal.* Calcd for $C_{10}H_{16}Cl_4N_4$: C, 35.93; H, 4.88; N, 16.76. Found: C, 36.09; H, 4.97; N, 16.11.

A solution of 1 g of the tetrahydrochloride in 40 ml of degassed water was added to 20 ml of a degassed 5% sodium hydroxide solution in a nitrogen-filled dry box. The precipitated free amine was filtered, washed with degassed distilled water, and transferred to a vacuum sublimator. The crude product was dried under reduced pressure at 25° and then sublimed at 170° (3 μ) to produce an off-white free amine, mp 234° dec; ir 3.00, 3.10, 6.10–6.30 μ (NH_2).

1,2,5,6-Tetraminoanthraquinone (5). This monomer was prepared as described,[18] recrystallized three times from acetophenone, and dried under reduced pressure.

Polymerizations

All polymerizations were carried out under a nitrogen atmosphere. Solvents and monomers were charged in a nitrogen-filled dry box. The *m*-cresol solvent was freshly distilled under nitrogen prior to use, poly(phosphoric acid) was freshly prepared from 85% phosphoric acid and phosphorus pentoxide. Nearly quantitative yields of polymers were obtained from all polymerizations. Table I gives some of the properties of the polymers. Thermal gravimetric analyses were obtained on a Du Pont 950 thermal gravimetric analyzer.

Poly(dibenzo[*a*,*c*]pyrazino[2,3-*i*]phenazine-4,5:12,13-tetrayl) (6). *1. m-Cresol.* To a slurry of 0.4181 g (3.023 mmol) of 1,2,4,5-tetraminobenzene (**3**) in 10 ml of *m*-cresol was added with stirring 0.7939 g (3.027 mmol) of pyrene-4,5,9,10-tetrone (**1**) in 18 ml of *m*-cresol at 25°, to give a reaction mixture containing 4% solids. The mixture was stirred for 18 hr at 25° and for 24 hr at 65°, and then the temperature was increased over an 8-hr period to 200° at which temperature it was maintained for 32 hr. The polymer was precipitated by addition of the reaction mixture to 150 ml of chloroform, and the polymer was removed by centrifugation. The crude polymer was dried at 25° under reduced pressure. A portion of the polymer was continuously extracted with benzene for 24 hr and then dried under reduced pressure. The polymer was thermally advanced under reduced pressure by slowly heating it to 350° and then holding that temperature for 1 hr.

2. Poly(phosphoric acid). Poly(phosphoric acid) (84%) was prepared by the slow addition of 16.4 g of phosphorus pentoxide with stirring to 11.95 g of 85.6% phosphoric acid in an ice bath under nitrogen. After the addition, the mixture was heated for 3 hr at 80°, at which time the mixture was homogeneous and colorless. The poly(phosphoric acid) was cooled to 65° and 0.8521 g (3.000 mmol) of 1,2,4,5-tetraminobenzene tetrahydrochloride (**3**·4HCl) and 0.7867 g (3.000 mmol) of pyrene-4,5,9,10-tetrone (**1**) was added to give a solution containing 4% solids. The mixture was stirred at 80° for 12 hr and was then heated as follows: 80-110°, 0.5 hr; 110°, 0.5 hr; 110-140°, 1.0 hr; 140-150°, 3 hr; 150-190°, 0.5 hr; 190-200°, 0.5 hr. The resulting viscous, rubbery black mass which had balled up on the stirrer was agitated in water overnight, filtered, extracted with water in a Soxhlet for 48 hr, extracted with methanol for 2 hr, and then dried under reduced pressure to afford **6**; λ_{max} (H_2SO_4) 613 nm (ϵ 8 × 10^2/recurring unit). Fibers obtained by extrusion of a sulfuric acid solution into 50, 60, and 70% aqueous sulfuric acid were brittle.

Poly(benzo[*a*,*c*]pyrazino[2,3-*i*]phenazine-10,11:2,3-tetrayl-2-vinylene) (7). *1. m-Cresol.* The reaction was carried out as described for the preparation of **6** in *m*-cresol except that 1.3000 g

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(10) E. Clar, "Polycyclic Hydrocarbons," Academic Press, New York, N. Y., 1964.

(11) H. Vollman, H. Becker, M. Corell, and H. Streeck. *Ann.*, **531**, 1 (1937).

(12) M. V. Gorelik, *Zh. Obshch. Khim.*, **34**, 2003 (1964); *J. Org. Chem. USSR*, **1**, 584 (1965).

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

(14) H. A. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961).

(15) A. Weissberger and R. Sargenwald, *Z. Phys. Chem. (Leipzig)*, **20**, 145 (1939).

(16) A. Claus and O. Zimmerman, *Chem. Ber.*, **14**, 1477 (1881).

(17) H. A. Piggott and F. H. Slinger, *J. Chem. Soc.*, 259 (1952).

(18) W. Bracke and C. S. Marvel, *J. Polym. Sci., Part A-1*, **8**, 3177 (1970).

(5.456 mmol) of anthracene-1,2,5,6-tetrone (**2**) and 0.7541 g (5.452 mmol) of 1,2,4,5-tetraminobenzene (**3**) in a total of 50 ml of *m*-cresol was used to give a solution containing 3.4% solids. The mixture was heated as follows: 25°, 22 hr; 70°, 24 hr; 70–105°, 1.5 hr; 105°, 0.5 hr; 105–148°, 1.5 hr; 148°, 0.5 hr; 148–200°, 3.5 hr; 200°, 40 hr. The polymer was isolated and dried as described for **6**. This polymer was soluble in methanesulfonic acid to the extent of 15 mg/100 ml, but could not be dissolved in sulfuric acid. The polymer was thermally advanced as described for **6**.

2. Poly(phosphoric acid). To 84% poly(phosphoric acid) prepared from 33.8 g of 85% phosphoric acid and 49.6 g of phosphorus pentoxide was added 0.9528 g (4.000 mmol) of anthracene-1,2,5,6-tetrone (**2**) and 1.1352 g (3.995 mmol) of 1,2,4,5-tetraminobenzene tetrahydrochloride (**3**·4HCl) to give a solution containing 2.5% monomer. The mixture was heated as follows: 80–105°, 1 hr; 105–140°, 2 hr; 140–160°, 15 hr; 160–210°, 1 hr. The polymer was isolated by agitating the reaction mixture in water for 12 hr, filtering, washing with 5% aqueous sodium carbonate for 12 hr, washing with water, and continuously extracting with water in a Soxhlet extraction for 72 hr and then with methanol for 24 hr. The black powder was dried under reduced pressure. It was soluble in methanesulfonic acid but only very slightly soluble in sulfuric acid.

Poly(pyrazine[2′,3′:5,6]naphtho[2,3-*a*]phenazine-2,3:9,10-tetrayl-9-vinylene) (8). *1. m-Cresol.* The reaction was carried out as described for the preparation of **6** in *m*-cresol except that 0.4100 g (2.176 mmol) of 1,2,5,6-tetraminonaphthalene (**4**) and 0.5188 g (2.177 mmol) of anthracene-1,2,5,6-tetrone (**2**) in 30 ml of *m*-cresol was used to give a solution containing 3% solids. The mixture was heated as follows: 25°, 3 hr; 65°, 17 hr; 96°, 4.5 hr; 120°, 18 hr; 120–200°, 4 hr; 200°, 45 hr. The polymer was isolated and purified as described for **6**.

2. Poly(phosphoric acid). To 84% poly(phosphoric acid) prepared from 13.0 g of 85% phosphoric acid and 17.9 g of phosphorus pentoxide was added 0.6908 g (2.899 mmol) of anthracene-1,2,5,6-tetrone (**2**) and 0.9688 g (2.898 mmol) of 1,2,5,6-tetraminonaphthalene tetrahydrochloride (**4**·4HCl) to give a solution containing 4% monomers. The solution was heated at 80° for 12 hr and then exactly as described for the preparation of **6** in poly(phosphoric acid). The polymer was isolated and purified as described for **6**. It was only slightly soluble in sulfuric acid, but was eventually soluble in methanesulfonic acid.

Poly(12,19-dihydro-12,19-dioxodibenzo[*a,c*]pyrazino-[2′,3′:5,6]naphtho[2,3-*h*]phenazine-4,5:14,15-tetrayl) (9). *1. m-Cresol.* This polymerization was carried out as described for the preparation of **6** in *m*-cresol except that 0.7342 g (2.799 mmol) of pyrene-1,2,6,7-tetrone (**1**) and 0.7511 g (2.800 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) in 38 ml of *m*-cresol were used to give a solution containing 2.3% solids. The mixture was heated exactly as that described for the preparation of **8**. Isolution, purification, and thermal advancement were carried out as described for **8**.

A 0.2-g portion of the purified polymer which had not been thermally advanced was suspended in a mixture of 1 ml of dimethyl sulfoxide (Me_2SO), 0.2 g of finely ground sodium hydroxide, 0.29 g of sodium dithionate, and 1 ml of water. The mixture was stirred under a nitrogen atmosphere at 25° for 2 hr, and then heated to 80–90° for 2 hr. The polymer dissolved, and the mixture became so viscous that it could not be stirred, even at 100°. An additional 1 ml of the Me_2SO–water mixture was added, and heating was continued for 1 hr at 100°. Extrusion of this cooled solution from 18- and 22-gauge needles into a 0.1 N hydrochloric acid solution in 1:1 Me_2SO–water produced only brittle fibers.

2. Poly(phosphoric acid). To 85% poly(phosphoric acid) prepared from 10.7 g of 85% phosphoric acid and 14.7 g of phosphorus pentoxide was added 0.5365 g (2.000 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) and 0.5244 g (2.000 mmol) of pyrene-1,2,6,7-tetrone (**1**) to give a solution containing 4% monomer. The solution was heated exactly as described for the preparation of **6**. Isolation and purification were carried out as described for **6**. The polymer was completely soluble in concentrated sulfuric acid and methanesulfuric acid, λ_{max} (H_2SO_4) 480 (ϵ 3.1×10^2/recurring unit). Extrusion of solutions of this polymer in methanesulfonic acid or from the Me_2SO–sodium hydroxide–sodium dithionate mixture as described for this polymer prepared in *m*-cresol gave only brittle fibers.

Poly(benzo[1,2-*a*:4,5-*a*′]diphenazine-1,2:10,11-tetrayl-10,11-dicarbonyl) (10). *1. m-Cresol.* This polymerization was carried out as described for the preparation of **6** in *m*-cresol except that 0.8048 g (2.998 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) and 0.7146 g (2.999 mmol) of anthracene-1,2,5,6-tetrone (**2**) in 30 ml of *m*-cresol were used to give a solution containing 5% solids. The mixture was heated exactly as that described for the preparation of **8**. Isolation and purification was carried out as described for **8**.

2. Poly(phosphoric acid). To 85% poly(phosphoric acid) prepared from 33.8 g of 85% phosphoric acid and 49.6 g of phosphorus pentoxide was added 0.9528 g (4.000 mmol) of anthracene-1,2,5,6-tetrone (**2**) and 1.072 g (3.994 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) to give a solution containing 2.4% monomers. The mixture was heated as follows: 80–100°, 1 hr; 135–145°, 5 hr; 145–180°, 0.5 hr; 180–200°, 0.5 hr. The polymer was isolated and purified exactly as described for **7** prepared in poly(phosphoric acid).

Polymerization of 1, 3, and 5. Copolymer 11. To 84% poly(phosphoric acid) prepared from 33.8 g of 84% phosphoric acid and 49.6 g of phosphorus pentoxide was added 1.2100 g (4.613 mmol) of pyrene-4,5,9,10-tetrone (**1**), 0.7095 g (2.500 mmol) of 1,2,4,5-tetraminobenzene tetrahydrochloride (**3**·4HCl), and 0.6700 g (2.496 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) to give a solution containing 3.1% monomers. The resulting solution was heated as follows: 80–90°, 2 hr; 90–135°, 0.5 hr; 135–150°, 2 hr; 150–170°, 6 hr; 170–175°, 11 hr; 170–200°, 0.5 hr. The polymer was isolated and purified exactly as described for **7** prepared in poly(phosphoric acid). This polymer was soluble in methanesulfonic acid and sulfuric acid. A film was cast from a 5% solution of methanesulfonic acid, and the solvent was removed by heating at 160° for 3 hr under reduced pressure. Brittle fibers of the polymer were obtained both by extrusion of methanesulfonic acid solutions or Me_2SO–sodium hydroxide–sodium dithionate solutions prepared as described for **9**.

Polymerization of 1, 2, 3, and 5. Copolymer 12. To 84% poly(phosphoric acid) prepared from 33.8 g of 85% phosphoric acid and 49.6 g of phosphorus pentoxide was added 0.6050 g (2.307 mmol) of pyrene-4,5,7,10-tetrone (**1**), 0.5955 g (2.499 mmol) of anthracene-1,2,5,6-tetrone (**2**), 0.7095 (2.500 mmol) of 1,2,4,5-tetraminobenzene tetrahydrochloride (**3**·4HCl), and 0.6700 g (2.496 mmol) of 1,2,5,6-tetraminoanthraquinone (**5**) to give a solution containing 3.1% of monomers. The mixture was heated as follows: 85–100°, 2 hr; 100–120°, 0.5 hr; 120–145°, 7 hr; 145–155°, 12 hr; 155–170°, 0.5 hr; 170–200°, 0.5 hr. The polymer was isolated and purified exactly as described for **7** prepared in poly(phosphoric acid). It was soluble in sulfuric and methanesulfonic acids.

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