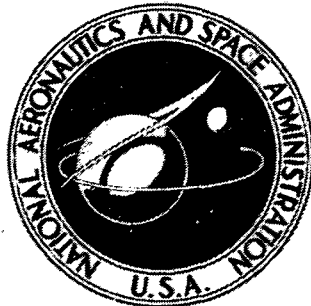


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**AN ANNOTATED BIBLIOGRAPHY
OF PYRRONE AND BBB PUBLICATIONS**

by Harold D. Burks

Langley Research Center

Hampton, Va. 23365

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16. Abstract <p style="text-align: center;">This annotated bibliography covers the research and development of two closely related classes of high-temperature polymers, polyimidazopyrrolones (Pyrrone) and bis-benzimidazo-benzophenanthrolines (BBB), from their inception in 1965 through 1971. This compilation of available reference information is not inclusive, but it is sufficiently complete to aid the polymer chemist and materials engineer in the research and development of these two high-temperature stable polymeric systems.</p>			
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AN ANNOTATED BIBLIOGRAPHY OF PYRRONE
AND BBB PUBLICATIONS

By Harold D. Burks
Langley Research Center

SUMMARY

An annotated bibliography was assembled which covers the research and development of two closely related classes of high-temperature polymers, polyimidazopyrrolones (Pyrrone) and bis-benzimidazo-benzophenanthrolines (BBB), from their inception in 1965 through 1971. The compilation of available reference information is not inclusive, but it is sufficiently complete to aid the polymer chemist and materials engineer in the research and development of these two high-temperature stable polymeric systems.

INTRODUCTION

During the past decade the requirements for high-temperature, lightweight materials for aerospace applications have far exceeded the capabilities of existing materials systems. The polymer chemist has found it necessary to develop advanced polymeric systems to meet these new requirements, and the materials engineer has had the responsibility for the proper design and application of these systems. Unfortunately, the polymer chemist generally is not familiar with the technical reports and publications of interest to the materials engineer, and conversely, the materials engineer generally is not familiar with the reports and publications of interest to the polymer chemist.

The intent of this publication is to minimize this problem as it applies to two closely related polymer systems – the polyimidazopyrrolones (Pyrrone) developed by the NASA Langley Research Center, and the bis-benzimidazo-benzophenanthrolines (BBB) developed by the USAF Materials Laboratory. Pyrrone is the generic term for poly(imidazopyrrolone). It is also referred to as poly(benzoylenebenzimidazole), poly(benzimidazopyrrolone), and poly(isoindolobenzimidazole).

The Pyrrone and BBB abstracts have been separated into two sections – the Pyrrones in a 100-series, and the BBB's in a 200-series. These abstracts were separated because of differences in the synthesis and chemical structure of these two polymer systems. Within each section the abstracts are listed alphabetically according to first author.

Not all available publications are listed. In a few instances where two or more articles contained the same basic information, the one with the most extensive coverage is listed. Also, several Air Force Materials Laboratory Technical Reports are excluded because of their "Controlled Distribution" status. To have included this information would have restricted the distribution of this publication. The following generally available abstract publications were searched: Chemical Abstracts (including Post P and Post J), International Aerospace Abstracts, and Scientific and Technical Aerospace Reports (STAR).

Temperatures are recorded in °C unless otherwise noted.

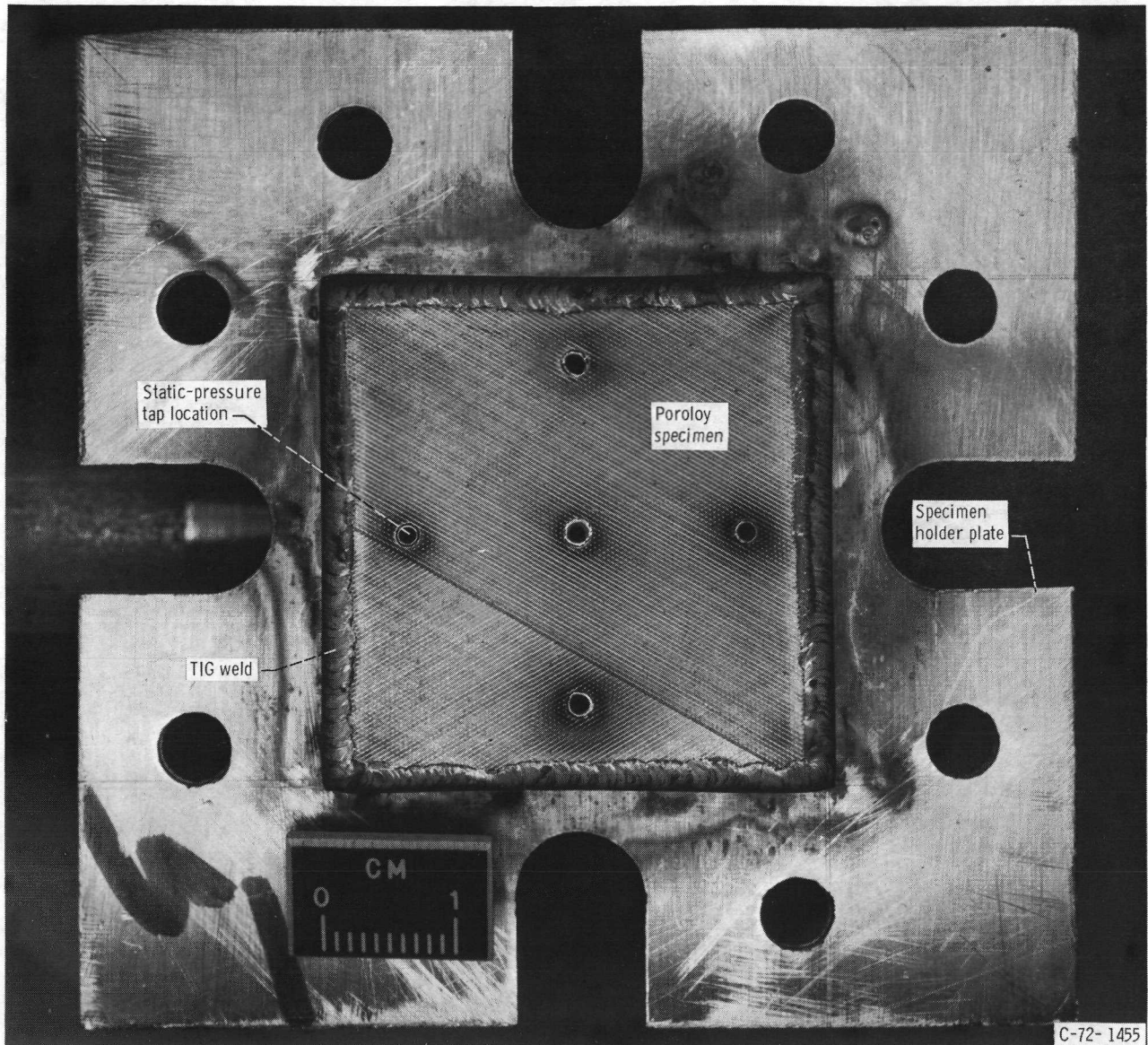


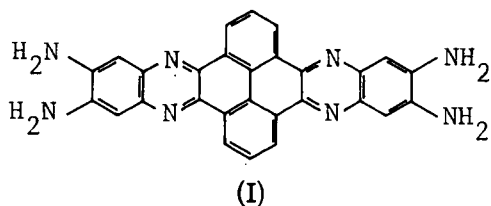
Figure 1. - Poroloy test specimen.

transpiration-cooling studies reported in references 1 and 2. The Poroloy was fabricated from Driver-Harris 242 wire to a thickness of 0.061 cm (0.024 in.) and to a nominal specific flow rate of 0.352 g/sec-cm^2 ($5.0 \times 10^{-3} \text{ lb/sec-in.}^2$) based on standard conditions of 17.0 N/cm^2 (24.7 psia) upstream pressure, 10.1 N/cm^2 (14.7 psia) downstream pressure, and airflow at 294 K (70° F). A detailed description of the Poroloy fabrication process is presented in reference 5. A 3.56- by 3.56-cm (1.4- by 1.4-in.) specimen was cut from a Poroloy sheet and TIG welded to the test fixture. Five holes of 0.203 centimeter (0.080 in.) diameter were drilled in the specimen, as shown in figure 1, for pressure taps. The actual flow size of this specimen was reduced to about

SECTION I - PYRRONE
(Bibliography With Abstracts)

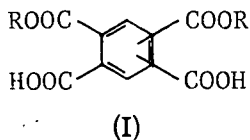
100.00 Arnold, Fred E.: Ladder Polymers Containing Heterocyclic Units of Different Structure. *J. Polym. Sci., Pt. B*, vol. 7, no. 10, 1966, pp. 749-753.

Ladder polymers, consisting of two different aromatic heterocyclic structures occurring in an alternating order sequence along the polymer backbone, were prepared. 2,3,11,12-Tetraaminodiquinoxalino[2,3-e,2',3'-l]pyrene (I) was obtained by the condensation of 1,2-diamino-4,5-bis(p-tolylsulfonamido)benzene with 1,2,6,7-tetraketopyrene yielding 2,3,11,12-tetrakis(p-tolylsulfonamido) diquinoxalino[2,3-e,2',3'-l]pyrene (II), which was detosylated in acid media to give the free amine I. I was polymerized with 1,4,5,8-naphthalenetetracarboxylic acid in polyphosphoric acid to produce a ladder polymer (III) made up of alternating bisquinoxalinopyrene and bisimidazo naphthalimide structures. Polycondensation of I or II with pyromellitic anhydride yielded ladder polymer (IV) containing alternating bisquinoxalinopyrene and bisimidazopyromellitide structures. Both III and IV could be cast into films from methanesulfonic acid.



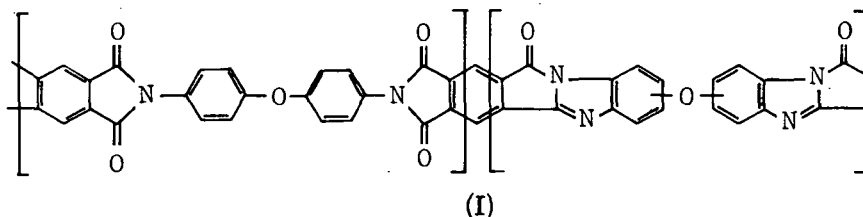
101.00 Bell, Vernon L.: Heteroaromatic Polymers Via Salt Intermediates. *J. Polym. Sci., Pt. B*, vol. 5, 1967, pp. 941-946.

Crystalline salts were synthesized from equimolar amounts of aromatic diester diacids (I) and aromatic di- and tetraamines. These salts were used to prepare several classes of heteroaromatic polymers, including polyimidazopyrrolones and polyimides, through the normal polyamide stage. It was pointed out that, in addition to the advantages gained by using an intermediate salt with exact balance of the monomers, the melting characteristics of the salts can be altered by varying the ester groups on the diacid half.



102.00 Bell, Vernon L.: Imidazopyrrolone/Imide Copolymers. *Stability of Plastics*, Soc. Plast. Eng., Sept. 1967, pp. B-1 – B-12.

A series of copolymers containing imidazopyrrolone and imide groups (I) was prepared by the solution polymerization of pyromellitic dianhydride with mixtures of 3,3',4,4'-tetraaminodiphenyl ether and p,p'-oxydianiline, respectively. Tensile properties of thin films of the copolymers were measured, and a general increase in tensile modulus and a decrease in elongation with increasing imidazopyrrolone content were noted. The copolymers were more resistant to degradation by strong acids and bases than the corresponding polyimide. Thermal stabilities of the copolymers in air increased with increasing imide content, while in vacuum the thermal stabilities were greater for imide-rich copolymers below 600^o C but greater for imidazopyrrolone-rich copolymers above 625^o C.



103.00 Bell, Vernon Lee: Polyimidazopyrrolones. *Encycl. Polym. Sci. & Technol.*, vol. 11, 1969, pp. 240-246.

The preparation, characterization, properties, and applications of poly(imidazopyrrolone) heteroaromatic polymers derived from aromatic o-tetraamines and dianhydrides were reviewed with 13 references. The preparation of ladder and stepladder polymers by solution polymerization and melt condensation was described and the thermal stability and radiation stability of the polymers were discussed.

104.00 Bell, Vernon L.: Preparation and Properties of Imide-Pyrone Copolymers. *J. Appl. Polym. Sci.*, vol. 14, no. 9, 1970, pp. 2385-2398. (Also published as NASA TN D-5559, 1969.)

Two series of copolymers containing imidazopyrrolone (Pyrone) and imide groups were prepared by solution polymerization. Thin films of the copolymers showed a general increase in the tangent modulus and a decrease in elongation with increasing Pyrrone content. The copolymers were more resistant to degradation by strong acids and bases

than the corresponding polyimides. The thermal stabilities of the copolymers in air improved with increasing imide content, while the thermal stabilities in a vacuum improved with increasing Pyrrone content. These copolymers represent a way to combine the desirable properties of both classes of homopolymers.

105.00 Bell, Vernon L., Jr.: Process for Interfacial Polymerization of Pyromellitic Dianhydride and 1,2,4,5-Tetraamino-Benzene. U.S. Pat. 3,518,232, June 30, 1970.

This invention relates to a process of producing an interfacial polymerization product of pyromellitic dianhydride and 1,2,4,5-tetraaminobenzene. A poly(amide acid amine) was formed which was thermally cyclodehydrated to a Pyrrone ladder polymer.

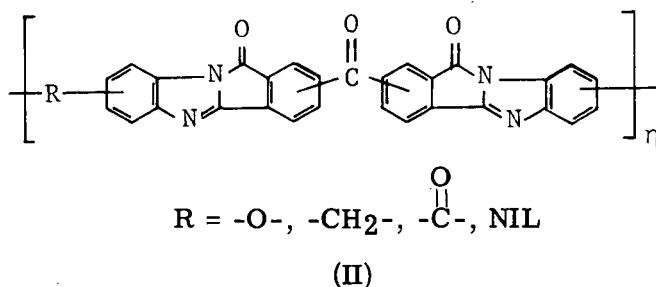
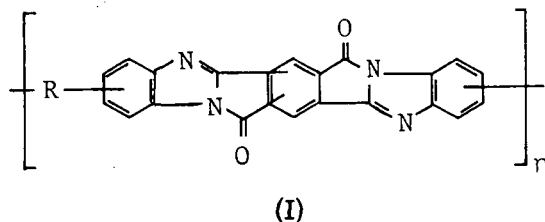
106.00 Bell, Vernon L.; and Jewell, Robert A.: Properties of Polyimidazopyrrolones. Amer. Chem. Soc. Polym. Preprints, vol. 8, no. 1, Apr. 1967, pp. 235-243. (Also available as NASA TM X-59873.)

Polyimidazopyrrolone (Pyrrone) synthesis procedures were described, their theoretical structures were depicted, and the solution properties of polyimide precursors of the Pyrrones were listed. The typical tensile properties of poly(imidazopyrrolone) films were assessed, and it was found that the film properties were quite independent of the curing atmosphere. However, ultimate curing temperature was noted to exert a marked influence on the mechanical properties. The data indicated a general increase in strength and modulus, together with a corresponding decrease in elongation, as the ultimate curing temperature was increased. Experiments on the resistance of polymer films to degradative effects of ionizing radiation both in air and in vacuum indicated that, although some degradation may have begun after 21 000 megarads of 3 MeV electrons, the tensile properties of the films after the extreme dose of 28 000 megarads were still nearly equivalent to the initial values.

107.00 Bell, Vernon L.; and Jewell, Robert A.: Synthesis and Properties of Polyimidazopyrrolones. J. Polym. Sci., Pt. A-1, vol. 5, no. 12, Dec. 1967, pp. 3043-3060.

The preparation of polyimidazopyrrolones (I, II) by three general synthetic methods was presented. The effects of structure, conversion temperature, and conversion environment were determined. The polyimidazopyrrolones were shown to retain useful mechani-

cal properties at elevated temperatures, after severe chemical treatment and after unusually high exposure to ionizing radiation. Thermogravimetric analysis of the polymers indicated the effect of structure on oxidative stability was relatively minor; furthermore, the relative stabilities of a series of eight polymers in air were not directly comparable to the order of stability in a vacuum environment.



108.00 Bell, Vernon L., Jr.; and Pezdirtz, George F.: Imidazopyrrolone/Imide Copolymers. U.S. Pat. 3,532,673, Oct. 6, 1970.

This invention relates to novel copolymer compositions, composed of imide and imidazopyrrolone groups as integral units in the polymer chains, which have unusual levels of stability to strong acids and bases. The polymers were made by the solution polymerization of aromatic dianhydrides with mixtures of aromatic di- and tetraamines.

109.00 Bell, Vernon L.; and Pezdirtz, George F.: Poly(imidazopyrrolones): A New Class of Radiation Resistant Polymers. Amer. Chem. Soc. Polym. Preprints, vol. 6, no. 2, Sept. 1965, pp. 747-756. (Also available as NASA TM X-57034.)

Experimental procedures were presented for the preparation of polymers, which are called stepladder (partial ladder) and ladder polyimidazopyrrolones or "Pyrrones," from the reaction of a dianhydride with a tetraamine in highly-polar solvents such as

dimethylformamide, dimethylacetamide, and dimethylsulfoxide. A method was also given for the synthesis of the polymers using the tetrahydrochloride salts of tetraamides. Evidence for the existence of the all-ladder structure of the polymers was deduced from the infrared spectra of thin films. Radiation effect data were obtained on 1 mil (2.54×10^{-5} m) films from a PMDA-TADPO polymer. Preliminary results indicated that the imidazopyrrolones appeared to be one of the most radiation resistant polymers to be developed to date. The results of thermal stability studies were also summarized.

110.00 Bell, Vernon L.; and Pezdirtz, George F.: Polyimidazopyrrolones: A New Route to Ladder Polymers. *J. Polym. Sci., Pt. B*, vol. 3, no. 12, Dec. 1965, pp. 977-984.

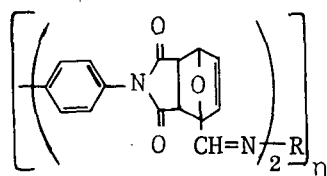
The article describes the preparation and properties of a new class of ladder and stepladder polymers, the polyimidazopyrrolones. The polymers resulted from the reaction of aromatic dianhydrides and aromatic tetraamines. The general preparatory procedure was as follows: 4.20 g (0.0192 M) of pyromellitic dianhydride was dissolved in 40 ml of dimethylformamide and added to a stirred solution of 4.60 g (0.20 M) of 3,3',4,4' tetraaminodiphenyl ether in 35 ml of dimethylformamide. Within 15 to 20 seconds the solution exhibited a mild exotherm. Stirring was continued for 5 to 10 minutes after which a portion of a solution of 0.30 g (0.0014 M) of pyromellitic dianhydride in 5 ml of dimethylformamide was added to the stirred solution until the desired viscosity was obtained. The tensile strength, elongation, and Young's modulus for Pyrrone polymer films were given.

111.00 Berlin, A. A.; Liogon'kii, B. I.; and Shamraev, G. M.: Thermostable Polymers From Dianhydrides of Aromatic Tetracarboxylic Acids and Tetraamines. *Russ. Chem. Rev.*, vol. 40, no. 3, 1971, pp. 284-300. (Translated from *Usp. Khim.*, vol. 40, no. 3, 1971, p. 513.)

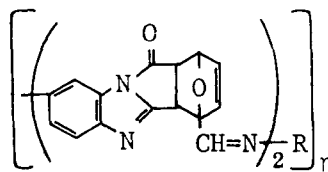
The preparation, properties, and structure of polymers based on dianhydrides of aromatic tetracarboxylic acids and tetraamines were surveyed through 1970. Compounds of this type possess excellent thermal stability, resistance to radiation and chemicals, catalytic activity, and semiconductor properties. The fields of practical application of the polymers were examined. A list of 77 references was included.

112.00 Berlin, A. A.; Liogon'kii, B. I.; and Zapadinski, B. I.: Heat-Stable Polymers Based on Furan Adducts. *Vysokomol. Soedin., Ser. B*, vol. 10, no. 5, 1968, pp. 315-316.

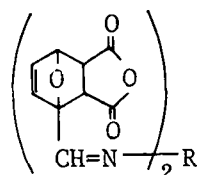
Polyimides (I) and polyimidazoles (II) [$R = 4,4'$ -biphenylene (a), 3,3'-dimethyl-4,4'-biphenylene (b), and 4,4'-oxydiphenylene (c)] were prepared from Diels-Alder adduct (III) and benzidine or 3,3'-diaminobenzidine, either by the reaction in HCONMe_2 at 20° followed by bulk polymerization at $200^\circ/10^{-5}$ mm, or in one step in polyphosphoric acid at 200° for 8 hr. IVa, IVb, and the unreported IVc, m 124-125 $^\circ$ (cyclohexane), were prepared according to R. Erhardt (1897). IVa and IVb were purified on Al_2O_3 m 234-235 $^\circ$ and 190-191 $^\circ$, respectively. The Diels-Alder reaction of IV with maleic anhydride in boiling C_6H_6 for 36 hr gave the corresponding III. Ir spectra were in accord with the proposed structures. The polymers were stable up to 350-450 $^\circ$ in air.



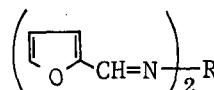
(I)



(II)



(III)

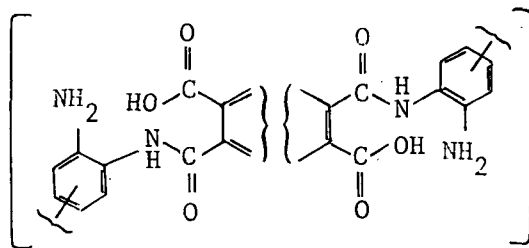


(IV)

113.00 Berry, G. C.; and Rumon, K. A.: Dilute Solution Studies of Pyrroline Prepolymers. *J. Polym. Sci., Pt. A-2*, vol. 8, 1970, pp. 2089-2094.

Data on dilute solutions of a Pyrroline "prepolymer" (I) from pyromellitic dianhydride and 3,3'-diaminobenzidine were presented and the tendency of this polymer to aggregate in certain solvents commonly used in dilute solution studies was discussed. It

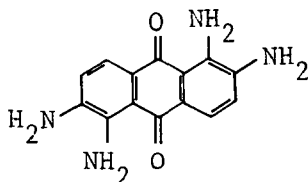
was concluded that reliable molecular weights can be determined if solvents that interact with the prepolymer through hydrogen bonding were used.



(I)

114.00 Bracke, William; and Marvel, C. S.: Polymers Containing Anthraquinone Units: Polymers From 1,2,5,6-Tetraaminoanthraquinone. *J. Polym. Sci., Pt. A-1*, vol. 8, 1970, pp. 3177-3187.

A preparation for 1,2,5,6-tetraaminoanthraquinone (I) was worked out. The reactivity of this compound in nucleophilic substitutions and nucleophilic additions was studied. Polymers were made by condensation with pyromellitic anhydride, terephthaloyl chloride, and isophthaloyl chloride. The synthesis and properties of the corresponding model compounds were also reported. After reduction with sodium dithionite, the polymers were soluble in dimethylformamide-water mixtures.



(I)

115.00 Bradbury, E. J.; and Dunnivant, W. R.: Feasibility Study on Isostatic Pressing of Pyrrones. Contract No. NAS 1-8245, Battelle Memorial Inst., [1969]. (Available as NASA CR-66858.)

Studies were conducted on the fabricability of Pyrrone systems (BTDA-DAB and PMDA-DAB made in DMAc and BTDA-DAB made in ethylene glycol) by room-temperature isostatic and conventional compression molding techniques. Although uncured polymer powders could be isostatically compacted, completely cyclized polymers were not com-

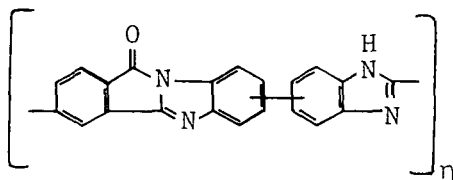
packed at 100 000 psi (6.895×10^8 Pa) even with liquid slip agents added. The low bulk density and noncompacting character of finely ground cured and partially cured Pyrrone powder prevented successful metal encapsulation for hot isostatic compaction. However, the capability of the Pyrrones to be compression molded at elevated temperatures by dead-cure procedures was demonstrated and this fabrication method was emphasized. Correlations or conditions required to successfully mold Pyrrone pellets to various density and hardness values were developed. It was shown that the molding procedure was complicated by an unfavorable thermal expansion relationship between the polymer and the mold. Compressive stresses appear to be generated in mold restrained polymer during cooling such that serious cracking may occur.

116.00 Colson, J. G.; Michel, R. H.; and Paufler, R. M.: Polybenzoylenebenzimidazoles. *J. Polym. Sci., Pt. A-1*, vol. 4, no. 1, Jan. 1966, pp. 59-70; Errata, p. 2349.

A polyamide amino acid was prepared by the solution condensation of 3,3'-diaminobenzidine and pyromellitic dianhydride. This polymer was cast as a film and converted to a polybenzoylenebenzimidazole. The gross conversion path was elucidated by spectroscopy and was substantiated by model compound studies. A novel ladder polymer was prepared from 1,2,4,5-tetraaminobenzene and pyromellitic dianhydride.

117.00 Culbertson, B. M.; and Murphy, R.: Polymers With Alternating Benzimidazole—1,2-Benzoylenebenzimidazole Nuclei. *J. Polym. Sci., Pt. B*, vol. 6, no. 3, 1968, pp. 241-245.

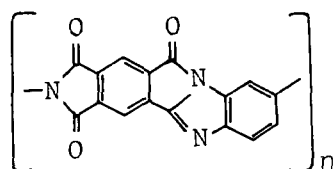
Polycondensation of trimellitic anhydride (I) with 3,3'-diaminobenzidine (II) yielded the title polymers (III), which had thermal stability in N and air to $\sim 550^\circ$. Polycondensation of I and II was accomplished by three separate processes: (a) heating at 300° for 1 hour in N, and in vacuo for 0.5 hour at 300° and 2 hours at $300-400^\circ$; (b) combining in acetone at room temperature to form an intermediate product which was polycondensed at 300° for 1 hour under N; (c) solution polycondensation for 2 hours in 115 percent polyphosphoric acid under N at $200-210^\circ$. Inherent viscosities (0.5%, concentrated H_2SO_4 , 25°) of III prepared by the three methods were 0.30, 0.20, and 0.22, respectively.



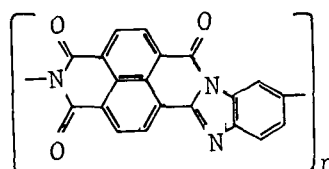
(III)

118.00 D'Alelio, Gaetano F.; and Kieffer, H. E.: Polymers Containing Imidazopyrrolone-imide or -imidazole Structures. *J. Macromol. Sci. - Chem., Pt. A*, vol. 2, no. 6, Oct. 1968, pp. 1275-1280.

Polymers containing alternating imidazopyrrolone and imide or imidazole structures were prepared. 1,2,4-Triaminobenzene (I) was condensed with pyromellitic anhydride or 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, giving the polymers II and III, respectively. I and 3,3'-diaminobenzidine were also condensed with trimellitic anhydride and chloride, but gave only low-molecular-weight products. III was the most thermally stable of the polymers prepared.



(II)



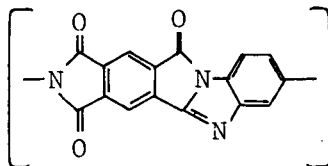
(III)

119.00 Dawans, F.; and Marvel, C. S.: Polymers From Ortho Aromatic Tetraamines and Aromatic Dianhydrides. *J. Polym. Sci., Pt. A*, vol. 3, no. 10, Oct. 1965, pp. 3549-3571.

Aromatic heteropolymers were synthesized from aromatic tetraamines and dianhydrides; some of the polymers had a ladder-type structure. The properties and thermal stability of the polymer were studied. The experimental conditions yielding the imidazopyrrolone structure were determined on model compounds. Polymers containing mixed aromatic units in the chain were prepared from pyromellitic anhydride or 3,3',4,4'-benzophenone tetracarboxylic dianhydride, and 3,3'-diaminobenzidine, 3,3',4,4'-tetraaminodiphenyl ether, 1,4,5,8-tetraaminonaphthalene, or 1,2,4,5-tetraaminobenzene. The polycondensations were carried out in melt and in solution (in melted phenol, pyridine, dimethylacetamide, 116% polyphosphoric acid). The inherent viscosities of a number of polymers synthesized by melt condensation were in the range of approximately 0.2-0.7; the higher polymers were obtained by carrying out the polycondensations in solution in 116% polyphosphoric acid; in this case, the intrinsic viscosities ranged from 1.1 to 1.8. Most of the polymers did not melt at 350° C and were soluble in the usual organic solvents, but the ladder-type structure polymers were soluble only in concentrated sulfuric acid.

120.00 Dunnavant, W. R.: Imide-Imidazopyrrolone Copolymers From Aromatic Dianhydrides and Aromatic Triamines. *J. Polym. Sci., Pt. B*, vol. 6, no. 1, 1968, pp. 49-52.

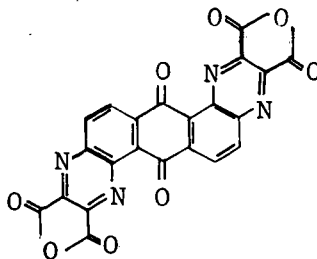
Condensation of pyromellitic dianhydride with 1,2,4-triaminobenzene gave a soluble polyamide-acid-amine prepolymer, which underwent cyclodehydration in air at 300° to yield the title copolymers. The triamine may enter the chain in either head-to-head or tail-to-tail fashion, but its lack of symmetry requires that the imide and imidazopyrrolone structures alternate at each amine nucleus, and that at least half of the repeating units are of structure I. Films prepared from these copolymers did not burn in a direct flame, and had a tensile strength of 26 000 psi (1.793×10^8 Pa), Young's modulus of 10^6 psi (6.895×10^9 Pa), thermostability at temperatures $>400^\circ$, and original flexibility after 22 hours at 350°.



(I)

121.00 Dutt, Prabir K.; and Marvel, Carl S.: Polymers Containing Anthraquinone and Quinoxaline Units: Polypyrrolones. *J. Polym. Sci., Pt. A-1*, vol. 8, no. 11, 1970, pp. 3225-3234.

Thermally stable ladder or partial ladder polypyrrolones containing anthraquinone units were prepared by condensation of 1,2,5,6-bis(alpha,beta-dicarboxypyrazino)anthraquinone dianhydride (I) with 1,2,4,5-tetraaminobenzene tetrahydrochloride, 3,3',4,4'-tetraaminobiphenyl 3,3',4,4'-tetraaminodiphenyl ether, or 1,2,5,6-tetraaminoanthraquinone in dimethylacetamide or tetramethylene sulfone. The polymers were colored, powdery, insoluble in organic solvents, slightly soluble in concentrated sulfuric acid, and could be solubilized in alkali by reduction with sodium dithionite.



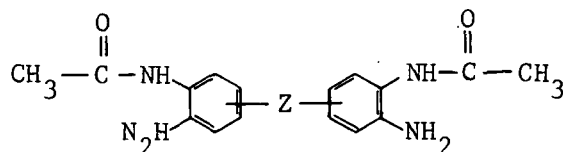
(I)

122.00 Fokin, E. P.; Gershkokhen, S. L.; and Kol'chenko, T. L.: Heat-Resistant Poly(benzimidazolepyrrolidones). U.S.S.R. Pat. 202,518, Sept. 14, 1967. (From Izobret., Prom. Obraztsy, Tovarnye Znaki, vol. 44, no. 19, 1967, pp. 131-132.)

The title compounds were prepared by polycondensation of o-tetraamines and dianhydrides of tetracarboxylic acids in a polar solvent at 20-50° followed by cyclization at 200-300°.

123.00 Frost, L. W.; and Bower, G. M.: Polyimidazopyrrolones and Related Polymers. I. Dianhydrides and o-Acetamidodiamines. J. Polym. Sci., Pt. A-1, vol. 9, 1971, pp. 1045-1070.

Solutions of polyimidazopyrrolone precursors prepared by reaction of tetraamines and dianhydrides in polar solvents tend to crosslink and gel very easily. Substitution of o-acetamidodiamines (e.g., I) for the tetraamines gave stable solutions. A study of cure mechanisms by TGA, infrared, and pyrolysis experiments with polymers and model compounds indicated that the acetylated materials were converted cleanly to imides at 150° C. At temperatures above 350° C, structural changes and further polymerization occurred, with little imidazopyrrolone formation. Polymers derived from tetraamines cured by multiple mechanisms but finally yielded the imidazopyrrolone structure. The acetylated polymers and copolymers gave acceptable laminates but poor films.



Z = 0, NIL

(I)

124.00 Frost, L. W.; and Bower, G. M.: Synthesis of Pyrroline Polymers. NASA CR-1556, 1970.

Several methods were found to control the gelation problem encountered in preparing pyrrolones from dianhydrides and tetraamines in polar solvents. Addition of a tertiary amine increased shelf life and attainable solids. Similar improvement was found when orthochloro groups were used for steric deactivation of two amine groups. Complete

elimination of the gel problem was achieved by blocking two amine groups with acetyl or carbethoxy groups. Low molecular weight "salt" intermediates made from diester diacids and tetraamines were also relatively free from gelation problems. A two-solution system for preparing Pyrrone-imide copolymers provided another way to avoid gelation. Infrared and TGA studies showed that thermal curing gave good conversion to Pyrrone only from dianhydride-tetraamine polymers. Both blocked amine and salt types gave other structures, some of which were probably crosslinked.

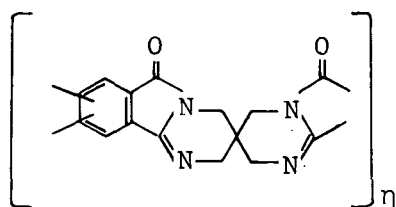
- 125.00 Frost, L. W.; and Bower, G. M.: Synthesis of Pyrrone Polymers. Contract No. NAS 1-7354, Westinghouse Res. Labs., June 1968. (Available as NASA CR-66693.)

When Pyrrone prepolymers are prepared by the reaction of a dianhydride and a tetraamine in a polar aprotic solvent, some chain branching occurs, and gelation is difficult to avoid. In this study stable solutions of linear prepolymers were prepared by substituting various diacetamido diamines for the tetraamines. Satisfactory laminates were prepared from one of these polymers, although film casting attempts failed. Infrared and TGA studies showed that a 150° C cure converted the prepolymer to a polyimide, which was quite stable at 300° C. Some conversion to the Pyrrone occurred at 350-400° C, although it was far less complete than for polymers derived from tetraamines. When prepolymer was prepared from a dianhydride and a tetraamine, it was found that addition of triethylamine or other bases reduced the gelation tendency and permitted an increase of polymer concentration from 10 to 16%. Acids accelerated gelation. Poor laminates were obtained from these solutions. Solutions of low molecular weight polymers up to 30% solids were obtained by the reaction of tetraamines with diester diacids.

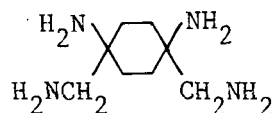
- 126.00 Heller, Jorge; Hodgkin, J. H.; and Martinelli, F. J.: The Synthesis of Spiropolyimides. J. Polym. Sci., Pt. B, vol. 6, no. 3, 1968, pp. 153-157.

Spiropolyimides were prepared which had a spiro linkage in their backbone and thus were intermediate between ladder and linear polymers. Attempts to polymerize $(H_2NCH_2)_4C$ with pyromellitic dianhydride (I) by solution polymerization or melt polymerization gave only intractable black tars, but interfacial polycondensation in water and MeCOEt, containing the amine and anhydride, respectively, gave a white polymer (II). II had a low molecular weight, was colorless, soluble in H_2SO_4 , HCl, and HCO_2H , and insoluble in other organic or fluorinated solvents, and was dissolved and hydrolyzed in dilute base. Polymerization of 1,4-diamino-1,4-bis(aminomethyl)cyclohexane (III) with I in poly-

phosphoric acid at 250° gave dark, intractable, low molecular weight polymers, but similar polymerizations of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride with III gave light green polymers (IV) of moderate molecular weight which were soluble in H₂SO₄ and HCO₂H. As polymerization times and temperatures increased, the molecular weight of the IV also increased, but they contained strongly bonded organic impurities which could be removed only by prolonged washing with hot dilute NaOH. Prolonged heating at 250° also gave IV bonded through all 4 amino groups of III rather than through only the 2 aminomethyl groups, and, when heated at 300°, IV became insoluble, indicating that cross-linking had occurred. The spiropolyimides had a slightly lower thermal stability than aromatic ladder polymers of similar structure. Conversions of <75% were obtained in the various polymerizations.



(II)



(III)

127.00 Hodgkin, J. H.; and Heller, J.: Thermally Stable Spiropolymers. *J. Macromol. Sci. - Chem.*, vol. A3, no. 6, Oct. 1969, pp. 1067-1086.

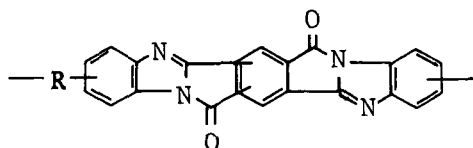
The condensation of the aliphatic spiro-tetraamine 2,2-bis(aminomethyl)-1,3-diaminopropane (I) or 1,4-bis(aminomethyl)-1,4-diaminocyclohexane (II) with pyromellitic dianhydride (III) or 1,4,5,8-naphthalenetetracarboxylic dianhydride (IV) was studied. It was found that in polyphosphoric acid at temperatures greater than 200° C and after long reaction times, either tetraamine produced the desired spiropolymer with the dianhydride (IV), but only tars could be isolated when the dianhydride (III) was used. Although these condensations proceed through a polyimide precursor which then cyclizes by elimination of water, condensations of (II) with (IV) only yielded the fully cyclized material and all attempts to isolate the imide precursor failed. Strong evidence for total cyclization was obtained by comparing the infrared and ultraviolet spectra of the polymer and of model compounds that were representative of the fully cyclized and imide forms. Condensations of (I) and (IV) yielded polymers that were only 50% cyclized. The polymer based on spiro-tetraamine (I) started to lose weight at 300° C in both air and vacuum, while the polymer based on amine (II) showed no weight loss until 500° C in vacuum and 400° C in air.

128.00 Hughes, C. T.: Preparation and Characterization of Low DP End-Capped Pyrrone Moldings. NASA CR-1633, 1970.

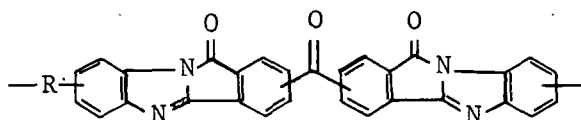
Pyrrone polymers (BTDA-DAB) were studied to determine their utility as structural molding resins. Because of the problems previously associated with the molding of these resins, a major portion of the work was in a novel synthesis route. This route was based on the idea of making short chain fully cyclized precursor molecules which were then chain extended. The newly formed bonds were cyclized during the mold cycle. The molding process was studied in considerable detail with over 175 moldings made for physical, mechanical and/or thermal characterization. The mechanical properties of the best moldings were exceptional in high temperature properties. Filled moldings were made with particulate fillers including colloidal silica, carbon, graphite, MoS₂ powder, and industrial diamonds. Flexural tests were obtained on some of these composites.

129.00 Jewell, Robert A.: Relative Thermophysical Properties of Some Polyimidazopyrrolones. J. Macromol. Sci. - Chem., Pt. A, vol. 3, no. 6, Oct. 1969, pp. 1147-1159.

A comparative thermogravimetric study of eight polyimidazopyrrolone films of varying composition (see below) revealed that the thermal stability of the polymers increased with increasing theoretical percentages of carbonyl groups within the polymer repeat unit. The films degraded more rapidly in air than in vacuo, but the order of stability was the same in the two environments. Dynamic heating of the film in vacuo developed three distinct temperature regions in which maximum rates of weight loss occurred at characteristic temperatures, and each temperature region was associated with the evolution of a particular gaseous species.

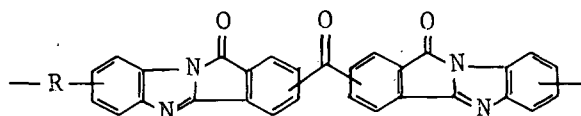


R = -O-, -CH₂-, -CO-, NIL

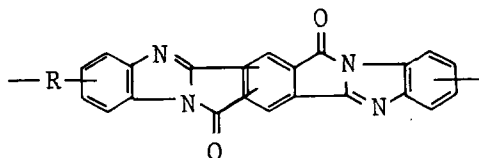


130.00 Jewell, Robert A.: Thermal Degradation Studies of Several Pyrrone Films. J. Appl. Polym. Sci., vol. 12, no. 5, May 1968, pp. 1137-1145.

An investigation of the thermal degradation of several polyimidazopyrrolone films (formulas below) in air and in vacuum over the 100 to 1000° C range was made by thermogravimetric analysis using both isothermal heating and programmed heating rates of 2, 3, 5, and 7.5° C/min. At pressures of 10⁻⁶ torr (1.3 × 10⁻⁴ Pa) or less, maximum weight losses averaged 30% at 800° C. Rates of volatilization and activation energies were derived to provide comparisons between the various structures.



R = -O-, NIL



131.00 Johnson, C. L.; Bagley, E. B.; and Tolbert, T. L.: High-Temperature Molding of Pyrrones. Polym. Eng. & Sci., vol. 10, no. 6, Nov. 1970, pp. 340-344.

Due to their crosslinked, ladderlike structure, cured Pyrrones do not melt and thus are difficult to form at the customary temperatures and pressures of thermoplastics. At unusually high processing temperatures of the order of 500°, these materials underwent transient flow sufficient to allow molding of the materials. This observation, supported by analytical information, suggested that flow occurred because of breakage of covalent organic bonds and subsequent structural rearrangement of the crosslinked polymer network. Polymers made from the reaction of pyromellitic dianhydride with 3,3'-diaminobenzidine in dimethylacetamide were used.

132.00 Jones, William R., Jr.; Hady, William F.; and Johnson, Robert L.: Friction and Wear of Poly(amide-imide), Polyimide, and Pyrrone Polymers at 260° C (500° F) in Dry Air. NASA TN D-6353, 1971.

A pin-on-disk sliding friction apparatus was used to determine the friction and wear of (1) a poly(amide-imide), (2) a polyimide, and (3) a Pyrrone in dry air at 260° C (500° F). Low wear was obtained with a Pyrrone, intermediate wear with a polyimide, and very high wear with a poly(amide-imide). All three polymers exhibited low (<0.20) coefficients of friction. The poly(amide-imide) exhibited thermal degradation at 260° C (500° F). Experiments were conducted using a hemispherically tipped rider (pure polymer) sliding on a rotating steel disk. Other conditions included a sliding speed of 10 m/min (390 in./min), a 1.5-kg load, and a mineral oil lubricant.

133.00 Karre, L. E.; Keller, L. B.; and Miller, L. J.: Development and Processing of Pyrrone Polymers. NASA CR-1310, 1969.

This report describes the development and processing of polymers formed from the condensation reaction of aromatic dianhydrides with aromatic tetraamines in various solvents. In Phase I, the primary efforts involved the synthesis and characterization of the polymer formed from the condensation of pyromellitic dianhydride (PMDA) with diamino-benzidine (DAB) in polar solvents and the subsequent preparation and testing of fabricated articles. In Phase II, primary efforts included the synthesis, characterization, and subsequent fabrication of the polymer formed from the condensation of benzophenone tetracarboxylic dianhydride (BTDA) with diaminobenzidine (DAB) in the esterifying solvent ethylene glycol.

Phase III of the program was directed toward glass cloth laminates fabricated from the polymer formed from the condensation of BTDA with DAB in the esterifying solvent ethanol. The laminates had flexural strengths above 70 000 psi (4.826×10^8 Pa) and moduli above 3×10^6 psi (2.068×10^{10} Pa), but more important, the thermal stability was greatly improved over the PMDA-DAB articles. The most promising resin system of the three investigated, from the standpoint of both mechanical strength and thermal stability, was the polymer formed from BTDA and DAB in ethanol.

- 134.00 Karre, Lowell E.; and Kelliher, Warren C.: Processing of Pyrrone Foams. Materials '71, SAMPE Vol. 16, Soc. Aerosp. Mater. Process Eng., c.1971, pp. 231-243.

Processing parameters were established for successful molding of Pyrrone foams. Chemically blown foams and syntactic foams with densities ranging from 20 to 60 pounds per cubic foot ($3.2 \times 10^2 \text{ kg/m}^3$ to $9.6 \times 10^2 \text{ kg/m}^3$) were obtained. The mechanical properties of these materials were determined at -100° F (-74° C), room temperature, and 700° F (374° C). The resins were formed by the condensation of benzophenone tetracarboxylic acid dianhydride (BTDA) with diaminobenzidine (DAB) under a variety of different conditions.

- 135.00 Kelliher, Warren C.: Properties and Potential Applications of a New High-Temperature Polymer, Pyrrones. Aerospace Related Technology for Industry, NASA SP-5075, 1969, pp. 165-169.

The Pyrrones, a new class of heteroaromatic polymers, were developed at the NASA Langley Research Center for use in high-temperature environments. In this paper, details are given on the chemistry involved and different forms available of the intermediate or prepolymer stage of these resins. Films, coatings, laminates, foams, and moldings were discussed. The more significant strength properties of these fabricated forms were given and the general properties of the polymers were listed.

- 136.00 Kimmel, Boyce G.: Formulation and Processing of Advanced Plastics Composites. Materials '71, SAMPE Vol. 16, Soc. Aerosp. Mater. Process Eng., c.1971, pp. 266-271.15.

Processing techniques were developed for the fabrication of advanced plastics composites from novel resins, reinforcements, and fillers. In many cases, resins were nearly intractable, and little or no information was available on their processing. Many reinforcements were fragile and did not respond to conventional impregnating techniques. Composites of the desired composition and reinforcement configuration were fabricated by the use of precise processing techniques. Formulation, molding, and post-curing conditions were varied as necessary to produce test specimens of high quality from each combination of resin, reinforcement, and filler. Composite specimens fabricated included those based on novel heat resistant resins such as branched, crosslinked polyphenylene, polyimidazopyrrolone (Pyrrone), modified polyphenylene oxide, polyferrocenylene, polyphenylene sulfide, and polyaryloxysilane. Novel reinforcements used included boron

nitride fibers, graphite cloth coated with pyrolytic graphite, high modulus graphite fabric, and zirconia fabric. Fillers used included vanadium pentoxide, polyaminoborane, and poly(perfluorophenylene).

A novel molding technique was described which permits the fabrication of huge reinforced plastics structures under high pressure without the use of a molding press. This process, designated DIFTEX, utilizes the differential thermal expansion of different metals to provide molding pressure. High density phenolic composites reinforced with glass and carbon fibers were molded in thicknesses to 7 inches (0.18 m).

137.00 Kimmel, B. G.; and Karre, L. E.: Preparation and Characterization of the Pyrrones as Thermal Structural Materials. NASA CR-1791, 1971.

This report describes the development of techniques for preparing foams of various densities from the Pyrrone polymers formed by the condensation reaction of aromatic dianhydrides with aromatic tetraamines.

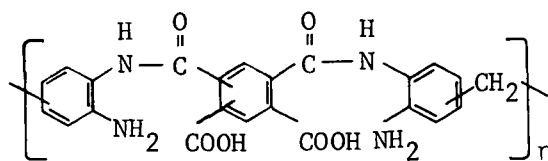
The work was divided into two principal phases: feasibility studies and the preparation and characterization of Pyrrone foams.

In the first phase, the feasibility of preparing foams from polymers formed by the condensation of 3,3'-diaminobenzidine (DAB) with either pyromellitic dianhydride (PMDA) or 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) was investigated. Approaches used to prepare foams included the controlled heating of Pyrrone solutions, the use of volatile fillers, the addition of thermally activated chemical blowing agents, and the incorporation of lightweight fillers. From the results of the feasibility studies, the last two approaches, blowing agents and lightweight fillers, were chosen for further study and optimization. Although good foams were produced by the first two methods, heating of Pyrrone solutions and the use of volatile fillers, these methods were not felt to be adaptable to the fabrication of large foam sections. Also as a result of the feasibility studies, no further effort was expended on the nearly intractable PMDA-DAB polymers.

In the second phase, two types of Pyrrone foam were developed and characterized: a chemically blown foam and a syntactic foam. The initial goal of this effort was to produce foams of 30 (4.8×10^2 kg/m³) and 60 pounds per cubic foot (9.6×10^2 kg/m³) densities, but was later expanded to include production and characterization of the chemically blown and syntactic foams over the range of densities obtainable by these techniques. The characterization tests included the determination of the compressive and tensile strength over the temperature range from -100° F (-74° C) to 700° F (374° C), thermal conductivity, and specific heat. The results of this characterization indicate that both types of Pyrrone foam show promise as thermal structural materials for aerospace applications.

138.00 Korshak, V. V.; Doroshenko, Yu. E.; Teplyakov, M. M.; Fedorova, R. D.; and Volkov, B. V.: Effect of Synthesis Conditions on the Properties of Poly(amino amido acids). *Vysokomol. Soedin., Ser. A*, vol. 12, no. 3, 1970, pp. 677-680.

The polycondensation of 3,3',4,4'-tetraaminodiphenylmethane with pyromellitic anhydride (I) in HCONMe_2 , AcNMe_2 , and N-methyl-2-pyrrolidinone at -30° to $+20^\circ$ gave polymer II. The molecular weight of II was maximum at -20° and was substantially increased when 5% molar excess of I was used; HCONMe_2 or AcNMe_2 were the best solvents. Thermal dehydration of II gave polycyclic stepladder polymers of increased mechanical strength.



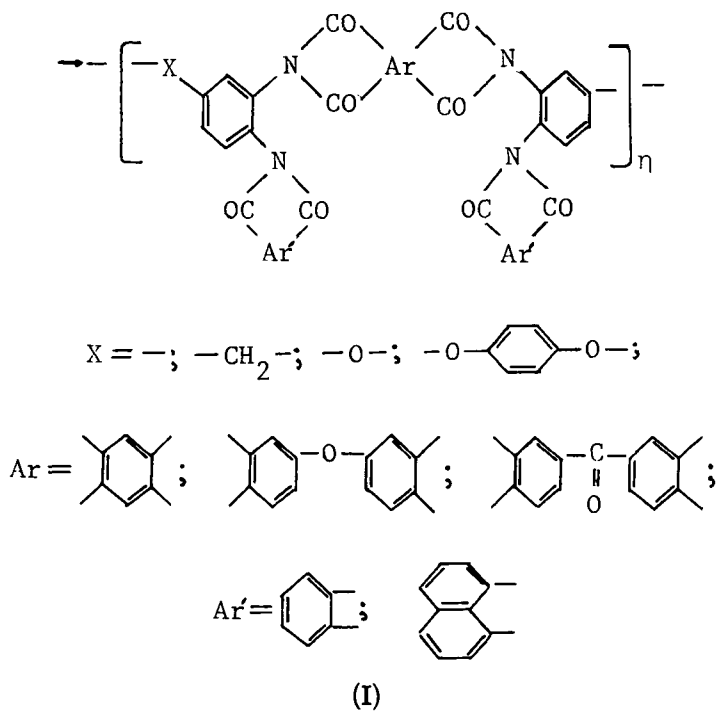
(II)

139.00 Korshak, V. V.; and Rusanov, A. L.: Reaction of Polyfunctional Aromatic Nucleophils With Derivatives of Aromatic Polycarboxylic Acids. *Izv. Akad. Nauk SSSR, Ser. Khim.*, no. 2, 1970, pp. 289-294.

This paper discussed and classified the reactions of aromatic diacyl chlorides and dianhydrides with various substituted aromatic diamines, including tetraamines, on the basis of the differences in electron densities of the principal amine pairs and the nucleophilic atoms ortho or adjacent to the amino functions. Theoretical conditions which should be met in order to attain linear polymers and high molecular weights were suggested.

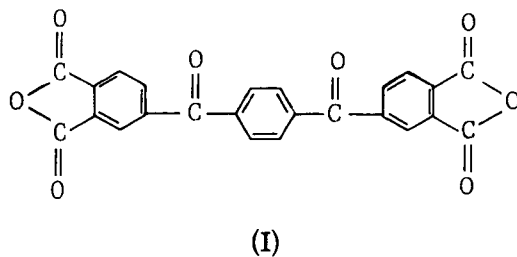
140.00 Korshak, V. V.; and Rusanov, A. L.: Synthesis of Heat-Resistant Soluble Polyimides. *Izv. Akad. Nauk SSSR, Ser. Khim.*, no. 10, 1968, p. 2418.

A description is given of the synthesis of heat-resistant soluble polyimides (I) containing arylimide rings in the o-position to the imide rings of the polymer backbone. The polyimides (I) were prepared by allowing poly(aminocarboxy)amides to react with aromatic dicarboxylic anhydrides at room temperature, and heating the resulting prepolymers at $50-250^\circ\text{C}$ in vacuum. The synthesized polyimides had high degradation temperatures ($400-500^\circ\text{C}$). Most of the polyimides dissolved in strong acids and amide solvents.



141.00 Korshak, V. V.; Rusanov A. L.; and Katsarava, R. D.: Poly(benzimidazopyrrolones). U.S.S.R. Pat. 295,779, Feb. 12, 1971. (From Otkrytiya, Isobret., Prom. Obraztsy, Tovarnye Znaki, vol. 48, no. 8, 1971, p. 68.)

1,4-Bis(3,4-dicarboxybenzoyl)benzene dianhydride (I) was polycondensed with aromatic tetraamines followed by cyclization of the resulting poly(aminoamido acids), to give poly(benzimidazopyrrolones).



- 142.00 Korshak, V. V.; Rusanov, A. L.; and Katsarava, R. D.: Poly(benzimidazopyrrolones) From 3,3',4,4'-Tetraaminodiphenylmethane and Pyromellitic Dianhydride. Dokl. Akad. Nauk SSSR, vol. 178, no. 1, 1968, pp. 105-107.

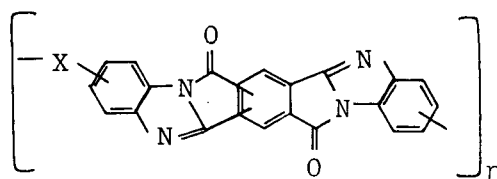
3,3',4,4'-Tetraaminodiphenylmethane was polymerized in HCONMe₂ with pyromellitic dianhydride at -20 to -30°. The IR spectrum of the resultant polymer was compared with a model compound N-(o-aminophenyl)phthalamic acid. The IR spectrum of the polymer had bands characteristic of secondary amides, of carboxyl groups, and of amino and imino groups. When the film was heated in vacuo 5 hr at 160°, bands appeared at 1710 and 720 cm⁻¹, characteristic of imide rings. When the polymer was heated in vacuo at 350° for 2 hr, bands appeared at 1310 and 1470 cm⁻¹, characteristic of tertiary nitrogen atoms and vibration of C:N groups, respectively. The fully cyclized polymer was insoluble in common solvents, including concentrated H₂SO₄.

- 143.00 Korshak, V. V.; Rusanov, A. L.; and Katsarava, R. D.: Synthesis and Examination of Aromatic Poly-(o-amino-o-carboxy)amides and Their Heat Resistant Ring Polymers. Kinetics and Mechanism of Polyreactions, Vol. I, Akadémiai Kiadó (Budapest), 1969, pp. 59-63.

Straight-chain, macromolecular film- and filament-type poly-(o-amino-o-carboxy)amides were produced in the reaction of bis-o-phenylenediamines with the dianhydrides of aromatic tetracarboxylic acids under low-temperature polycondensation conditions in solution. The mechanism of the reaction was reviewed and an interpretation was made in terms of quantum mechanics. During the heating of poly-(o-amino-o-carboxy)amides, "ladder" polymer polybenzoylene-benzimidazoles were obtained which possessed high thermal characteristics. The low-temperature treatment in solution of poly-(o-amino-o-carboxy)amides with the anhydrides of aromatic dicarboxylic acids, with subsequent heat treatment of the synthesized polymers, produced polyimides which contained aromatic imide groups attached to the basic polymer chain. In the reaction of poly-(o-amino-o-carboxy)amides with o-phenylenediamine in polyphosphoric acid, polymers were produced which contained benzimidazole groups attached to the basic chain of the polymer.

144.00 Korshak, V. V.; Rusanov, A. L.; and Katsarava, R. D.: Synthesis and Investigation of Poly(benzimidazopyrrolones) Containing Ether Linkages in the Main Chains. Dokl. Akad. Nauk SSSR, vol. 182, no. 6, 1968, pp. 1327-1330.

Poly[(p-phenylene oxide)benzimidazopyrrolones] were synthesized, the structures were elucidated using IR spectra, and thermal properties of the compounds were studied. 3,3',4,4'-Tetraaminodiphenyl ether or hydroquinone 3,3'-4,4'-tetraaminodiphenyl ether was polymerized at -20° to -30° in HCONMe_2 with pyromellitic dianhydride. The IR spectra of the resulting polymers showed absorptions at 1640, 1540, and 1305 cm^{-1} , representative of a poly(aminocarboxamide), and were compared with the model compound N-(o-aminophenyl)phthalamic acid. The polymer was heated at $150\text{-}160^{\circ}$ for 5 hr to give a yellow-orange polymer. Its IR spectrum, when compared with those of the model compounds, N-(o-aminophenyl)phthalimide and 2-(o-carboxyphenyl)benzimidazole, showed that the polymer had a poly(aminoimide) structure. Further heating of the polymer to $300\text{-}330^{\circ}$ for 10 hr gave a benzimidazopyrrolone (I, $X = 0$ or p- $\text{OC}_6\text{H}_4\text{O}$); the IR spectra was compared with that of 1,2-dibenzoylbenzimidazole. The compounds had tear strengths of $1000\text{-}1100\text{ kg/cm}^2$ and elongations of 3-4%. They were soluble on heating in concentrated H_2SO_4 and at room temperature in hydrazine hydrate. The compounds were stable to heating at $470\text{-}500^{\circ}$, as shown by thermogravimetric analysis. Thermal mechanical curves showed that the polymers did not decompose at $300\text{-}350^{\circ}$. The X-ray diffraction analysis of the three separate types of polymer showed that all were amorphous.



(I)

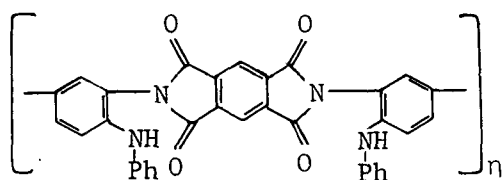
145.00 Korshak, V. V.; Rusanov, A. L.; and Katsarava, R. D.: Synthesis and Studies of Poly(benzimidazopyrrolones) Based on Pyromellitic Dianhydride and Some Bis(o-phenylenediamines). Vysokomol. Soedin., Ser. A, vol. 11, no. 9, 1969, pp. 2090-2101.

The authors prepared a series of polymers of high thermal stability by condensing pyromellitic dianhydride (I) with several tetraamines $[3,4\text{-(NH}_2)_2\text{C}_6\text{H}_3]_2\text{R}$, where $\text{R} = \text{-, -CH}_2\text{-, -O-, and -O-p-C}_6\text{H}_4\text{-O-}$. The condensations were carried by the slow addition of a solution of I in HCONMe_2 to a solution of II in HCONMe_2 at $-25 \pm 5^{\circ}$ with vigorous

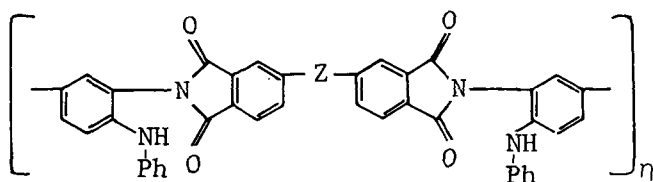
stirring. The low temperature and slow addition of I toward the end of the reaction were essential to avoid cross-linking which was favored by similar electron densities on the N atoms in the neighboring amino groups. Only by strictly observing these precautions was it possible to obtain linear polymers soluble in organic solvents. In vacuo at 150-160° in 5-6 hr the polymers underwent dehydrocyclization to poly(aminoimides) which were insoluble in organic solvents. In high vacuum at 300-350° for 10 hr, further dehydrocyclization transformed the polyimides into poly(benzimidazopyrrolones), which were crimson to red and had softening temperatures of 400-500°. They exhibited a high tensile strength (1000-300 kg/cm²), but low elasticity, the elongation at rupture being only 3-4 percent.

146.00 Korshak, V. V.; Rusanov, A. L.; Katsarava, R. D.; and Tugushi, D. S.: Synthesis of New Polyimides. *Izv. Akad. Nauk SSSR, Ser. Khim.*, no. 7, 1968, p. 1654.

Polyimides (Ia-c) were prepared from 4,4'-dianilino-3,3'-diaminobiphenyl and aromatic tetracarboxylic acid dianhydrides via the appropriate polyamides (II). II formed transparent brittle films which on heating at 150-300° in vacuo became transparent and durable. I were soluble in boiling HCONMe₂, AcNMe₂, and strong acids. They decomposed in air at 400-450°.



(Ia)



(Ib) Z = O

(Ic) Z = CO

147.00 Korshak, V. V.; Teplyakov, M. M.; and Fedorova, R. D.: Synthesis and Investigation of Polybenzimidazoles Containing Alkyl Substituents in Aromatic Nuclei. *J. Polym. Sci., Pt. A-1*, vol. 9, 1971, pp. 1027-1043.

Polybenzimidazoles were synthesized from 3,3'-diamino-5,5'-dimethylbenzidine, 3,3',4,4'-tetraamino-5,5'-dimethyldiphenylmethane (I), bis(3-amino-4-methylamino)phenylmethane, bis(3-amino-4-methylamino-5-methyl)phenylmethane, and diphenyl esters of adipic, sebacic, isophthalic, and terephthalic acids and 4,4'-dicarboxydiphenyl oxide by solid-phase polyheterocyclization. Properties of the polybenzimidazoles were studied. The polymers had high thermal stability. They were soluble in a number of organic solvents and gave strong, elastic films. Solubility and thermal stability of polybenzimidazoles were determined by the methyl group position in the polymeric chain. The influence of other alkyl substituents on properties of polybenzimidazoles was investigated. The polymer structure was studied by infrared and PMR spectroscopy and elemental analysis. Compound I was polymerized with pyromellitic acid dichloride to give a Pyrrone polymer insoluble in organic solvents.

148.00 Koton, M. M.; Florinskiy, F. S.; Rudakov, A. P.; Vlasova, K. N.; Bessonov, M. I.; and Layus, L. A.: Polyimidazopyrrolones. U.S.S.R. Pat. 293,011, Jan. 15, 1971. (From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki*, vol. 48, no. 5, 1971, p. 106.)

Polyimidazopyrrolones were produced by polycondensation of aromatic tetracarboxylic dianhydrides with aromatic tetramines, followed by thermal cyclization of the resulting poly(amidoamino acids). Dianhydrides of aromatic tetracarboxycyclic acids containing two or more ether bonds between aromatic radicals were used as the dianhydride component to increase the relative elongation of the polymers and to decrease their water capacity.

149.00 Lander, L. L.: Time and Temperature Dependent Modulus of Pyrrone and Polyimide Moldings. NASA CR-1946, 1972.

Moldings of four polymers, two Pyrrones and two polyimides, were used in this investigation. One Pyrrone, an oligomer type designated Pyrrone A, was synthesized from benzophenone tetracarboxylic acid dianhydride (BTDA) and diaminobenzidine (DAB). A second Pyrrone, a salt-like intermediate designated Pyrrone L, was synthesized and molded from the same monomers (BTDA and DAB). The two polyimides were both available commercially, and details of the synthesis and molding of these polymers are not

generally available. However, one polyimide, designated polyimide B, is thought to be synthesized from BTDA and meta phenylenediamine (mPDA). The other polyimide, designated polyimide P, is thought to be synthesized from pyromellitic dianhydride (PMDA) and oxydianiline (ODA).

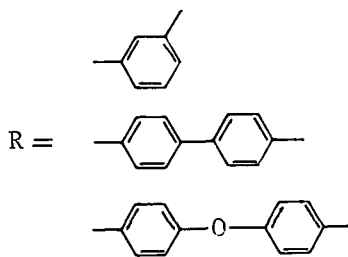
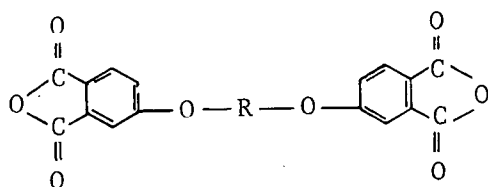
Although most of the polymer moldings had no reinforcing agents or additives, one group of Pyrrone A contained 15 weight percent graphite. Some of the moldings had received either thermal aging or electron irradiation before testing. Since such treatment had no significant effect on the time-temperature analysis in this report, only average values of modulus and damping were reported and no distinction was made as to the pretest treatment.

Three types of thermomechanical tests were performed. The dynamic modulus and damping factor were determined in the temperature range of 100° to 500° K. The technique used was that of a fixed-free resonating beam. Compressive stress relaxation tests to 10² seconds were performed over the range from 350° to 700° K with one series extending from 160° to 700° K. The thermal expansion was measured with quartz tube dilatometers over the range of 100° to 500° K.

150.00 Layus, L. A.; Bessonov, M. I.; Koton, M. M.; and Florinskiy, F. S.: Study of the Formation of Polyimidazopyrrolones by the Method of IR Spectroscopy. *Vysokomol. Soedin., Ser. A*, vol. 12, no. 8, 1970, pp. 1834-1840.

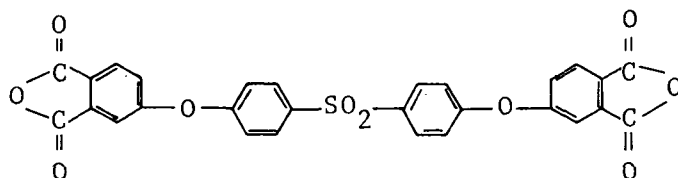
The cyclization of several polyaminoamido acids (PAAA), to form polyimidazopyrrolones (Pyrrones), was studied by infrared analysis of heat treated 4-5 micron PAAA films. The films were heated in nitrogen in increments of 30° C for 10-minute periods through the range of 80 to 400° C. The results indicated that Pyrrone ring formation began before the first stage (imidization) of cyclization was completed. Differences were noted for the cyclization process for those polymers in which the ring-forming functional groups were separated by a system of conjugated bonds, in contrast to a second group, in which the conjugation was disrupted by aromatic ether bonds. With the first group, the formation of imide and Pyrrone rings began at higher temperatures than with the second group. Furthermore, the rate of formation of Pyrrone for the first group was high at lower stages of imidization, and as a result, the degree of imidization never exceeded a value of 0.3-0.4. The temperature range in which PAAA, PAI(polyamino-imide), and Pyrrone coexisted was very large, varying from 150 to 250° C. For the second group of polymers, the range for onset of imide and Pyrrone ring formation was shifted 30-50° C lower. Within the groups containing aromatic ether bonds, the greater separation in temperatures for imide and Pyrrone ring formation resulted in a degree of imidization approaching 80-90 percent.

The polymers were made by the reaction of 3,3',4,4'-tetraaminodiphenyl ether with pyromellitic dianhydride and the three dianhydrides listed below:



151.00 Lubowitz, H. R.; Jones, R. J.; Cassey, H. N.; Vaughan, R. W.; and Burns, E. A.:
An Experimental Feasibility Study for the Preparation of Thermo-
Oxidatively Stable Pyrrone Laminates. NASA CR-1404, 1969.

This report describes the preparation from a sulfone dianhydride of Pyrrone laminates which would be suitable for long-term exposure to extreme thermal and oxidative environments. The feasibility study was divided into three principal tasks: (1) monomer synthesis, (2) polymer synthesis and characterization, and (3) laminate processing and evaluation. Pyrrone resins were prepared from bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (I) and 3,3'-diaminobenzidine. Suitable conditions were determined for preparing laminates from completely soluble Pyrrone precursors. The laminates, which were made under relatively mild processing conditions, had medium void content and had mechanical properties similar to other state-of-the-art condensation polymers. The polymer gave neat resin and composite properties similar to or exceeding those published for state-of-the-art Pyrrone polymer systems.



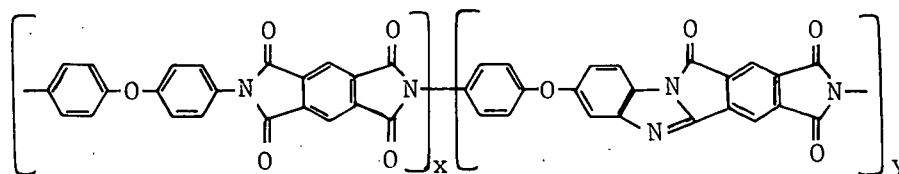
(I)

152.00 McLain, Allen G.; and Kelliher, Warren C.: Flight- and Ground-Test Evaluation of Pyrrone Foams. NASA TN D-6711, 1972.

Two Pyrrone materials, pure Pyrrone foam with a density of 481 kg/m³ (30 lbm/ft³) and hollow-glass-microsphere-Pyrrone composite with a density of 962 kg/m³ (60 lbm/ft³), were tested in the Langley 20-inch hypersonic arc-heated tunnel at pressure levels from 0.06 to 0.27 atm (1 atm = 101.3 kN/m²) and heating rates from 1.14 to 11.4 MW/m² (100.45 to 1004.50 Btu/ft²-sec). The 481-kg/m³ Pyrrone foam was also flight tested as an experiment aboard a Pacemaker test vehicle. The results of the ground tests indicated that the thermal effectiveness of the 481-kg/m³ Pyrrone foam was superior to the 962-kg/m³ glass-sphere-Pyrrone composite. The 481-kg/m³ Pyrrone foam had approximately one-half the thermal effectiveness of low-density phenolic nylon. The 481-kg/m³ Pyrrone foam experienced random mechanical char removal over the entire range of test conditions. Char thermal-property inputs for an ablation computer program were developed from the ground-test data of the 481-kg/m³ Pyrrone foam. The computer program using these developed char thermal properties, as well as the measured uncharred material properties, adequately predicted the in-depth temperature histories measured during the Pacemaker flight.

153.00 Minami, M.; Maekawa, H.; Kubota, T.; Tsuda, Y.; Kitamura, K.; Tatsuno, Y.; Watanabe, M.; and Kawabata, Y.: Polyamide-Acid Amines. U.S. Pat. 3,498,948, Mar. 3, 1970. (See also Jap. Pat. 69 19,878, Aug. 27, 1969.)

Polymer solutions convertible into heat resistant polymers were described. Pyromellitic anhydride and m-cresol were heated to form a homogeneous solution, 4,4'-diaminodiphenyl ether and 3,4,4'-triaminodiphenyl ether were added, pyridine was added slowly, the solution was cast on a glass plate, and heated to give a tenacious film of I, a random copolymer of imide and imide-imidazopyrrolone structures.



(I)

154.00 Morgan, P. E. D.; and Scott, H.: Simultaneous Polymerization and Molding of Pyrrone Polymers. NASA CR-1737, 1971.

The feasibility of simultaneously polymerizing and molding Pyrrone polymers and obtaining high strength, high modulus, dense thermally stable moldings by starting with monomeric materials was demonstrated. Typical properties of the moldings were: density, 1.29 g/cc; diametral tensile strength, 10 700 psi (7.377×10^7 Pa); ultrasonic modulus, 1.3 million psi (8.963×10^9 Pa); hardness, 83 Rockwell B; and thermal stability in air (at 0.5 C/min), 400 C. Optimization of molding and properties was attempted only for the PMDA (pyromellitic acid or anhydride) DAB (3,3'-diamino benzidine) system. A method designed to mix monomers at a molecular level by preparing 1:1 salts of pyromellitic acid and DAB improved moldability and thermal stability as well as reproducibility of polymer properties. Interrelationships between molding powder characteristics and molding conditions required to achieve optimum polymer properties were investigated. This demonstration of the feasibility of molding Pyrrones directly from salt monomers may now be expected to lead to rapid improvements in the molding of other systems, such as the NTCA (naphthalene tetracarboxylic acid) DAB system.

155.00 Morgan, P. E. D.; and Scott, Harvey: Strong, Dense, Thermally Stable Polymers by Reactive Hot Pressing of Solid Organic Monomers. J. Polym. Sci., Pt. B, vol. 7, no. 6, 1969, pp. 437-442.

An equimolar mixture of pyromellitic dianhydride and 3,3'-diaminobenzidine (I) was ball milled, placed in a mold lined with porous graphite, pressed at 4000 psi (2.758×10^7 Pa), heated at 5°/min to 450°, and heated at 450° for 1 hr. After cooling, the pressure was released to give a dark orange-brown, easily polished pellet having Knoop hardness (100 g load) 56.0, Rockwell E hardness E116, tensile strength 13 000-16 000 psi (8.963×10^7 - 1.103×10^8 Pa), and high thermal stability (i.e., 6% and 30% weight losses at 400° and 1000°, respectively). The pellet was insoluble in cold H₂SO₄, Me₂SO, and AcNMe₂ and had the E.S.R. spectrum of a poly(imidazopyrrolone) or "Pyrrone" polymer. A bis(benzimidazo)benzophenanthroline polymer (II) was also prepared by the above method from 1,2,5,8-naphthalene(tetracarboxylic acid) dianhydride and I. II had been prepared as a fiber in solution, but had not been molded previously.

156.00 Nechtschein, Jacqueline; Reboul, Angeline; and Traynard, Philippe: Polymers With Conjugated Structures. III. Influence of Structure on the Catalytic Properties of Conjugated Polymers. Bull. Soc. Chim. Fr., no. 3, 1967, pp. 960-968.

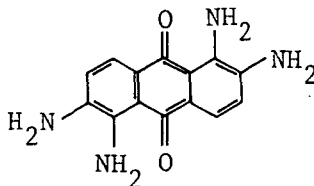
The effect of structural factors on the catalytic activity of polypyromellitimides and poly(indoloimidazoles) was investigated by determining the initial decomposition rate of N_2O . The catalytic activity of imperfectly conjugated polymers was dependent only on the number of π bonds between the conjugation breaks and, to a lesser degree, on the condensation of the elements, and essentially independent of other variations, such as presence of a heteroatom, chain length, and configuration. The catalytic properties of the paramagnetic centers in polymers with regular alternating double and single bonds were not related to structural factors, but rather to the carbon enrichment or the tendency of the structure to order itself in a crystalline manner. The activation energy of polymers in both groups tended to diminish as the number of π bonds between two breaks in conjugation increased.

157.00 Paufler, Robert M.: Heterocyclic Polymers Prepared From Tetracarboxylic Acid Dianhydrides and Tetramines. U.S. Pat. 3,414,543, Dec. 3, 1968. (See also Neth. 6,500,698, Fr. 1,429,425, Belg. 658,494.)

Tetramines were treated with tetracarboxylic dianhydrides to give linear amino polyamide acids (I), which were shaped and then cyclodehydrated to yield heterocyclic polymers (II). I had inherent viscosities (N_{inh}) ≥ 0.1 dl/g (30° , 0.5 wt % in Me_2SO). II had $N_{inh} \geq 0.3$ dl/g (30° , 0.5 wt % in H_2SO_4) and thermal stability at $>500^\circ$. Thus, a solution of pyromellitic dianhydride (III) in Me_2SO was slowly added dropwise with vigorous agitation to 3,3'-diaminobenzidine (IV) in Me_2SO to yield II with N_{inh} 0.92 dl/g directly. The IR spectra of II indicated the presence of bisbenzimidazo[1,2-a:1',2'-a']-benzo[1,2-c:4,5-c']dipyrrole and bisbenzimidazo[1,2-a:1',2'-a']benzo[1,2-c:5,4-c']dipyrrole units. Collected II solutions were concentrated at $40-5^\circ/1$ mm to 25% solids, heated to 55° , and dry spun into a N stream heated to 255° . Resulting fibers were drawn 1.2 times original length at both 283° and 500° and relaxed at 350° to give fibers (tenacity 3.7 g/denier, elongation 21%, modulus 82 g/denier) whose properties were unchanged after overnight exposure to 10% NaOH solutions at $85-95^\circ$ or air at 400° . Similar II were prepared by cyclodehydration of I prepared by treating IV with tricyclo[4.2.2.0^{2,5}]dec-9-ene-3,4,7,8-tetracarboxylic dianhydride (V), and by treating 1,2,4,5-tetraaminobenzene with V.

158.00 Pense, Rolf; and Marvel, C. S.: Polymers Containing Anthraquinone Units: Polyimidazoles and Polypyrrolones From 1,2,5,6-Tetraaminoanthraquinone. J. Polym. Sci., Pt. A-1, vol. 8, 1970, pp. 3189-3198.

1,2,5,6-Tetraaminoanthraquinone (I) was condensed with isophthalaldehyde and terephthalaldehyde and their bisulfite addition compounds to yield new heat-stable polymers. I was also condensed with pyromellitic anhydride to give the pyrrolone. The highest viscosities were obtained in polymers prepared with acid catalysts. The polymers were nearly all soluble in concentrated sulfuric acid but not in organic solvents. Those soluble in sulfuric acid could also be solubilized by reduction with sodium dithionite and potassium hydroxide in aqueous organic solutions. A few polymers were apparently crosslinked, since they would not dissolve in either sulfuric acid or in base after reduction. Weak fibers were obtained by spinning the reduced alkaline solutions of the polymers into aqueous acid.



(I)

159.00 Pezdirtz, George F.; and Bell, Vernon L.: An Exploratory Study of a New Class of Stepladder and Ladder Polymers - Polyimidazopyrrolones. NASA TN D-3148, 1965.

A new class of aromatic-heterocyclic polymers were prepared from the room-temperature reaction of tetraamines with tetraacids or their respective derivatives. The polymers are polyimidazopyrrolones or "Pyrrones." Exploratory experiments indicated that they had excellent thermal and radiolytic stability. The polymers combine the chemical structures of the aromatic polyimides and polybenzimidazoles. Since they were formed through an intermediate stage which was soluble, typical solution property measurements were used for basic molecular characterization. A reaction scheme for the conversion of the soluble intermediate was presented. Applied properties such as ease of fabrication, mechanical strength, and molding characteristics were discussed.

160.00 Price, Howard L.; and Bell, Vernon L.: Preparation and Compression Molding of Salt-Like Intermediate Pyrrone (BTDA-EG-DAB). Technical Papers, Vol. XV, Soc. Plast. Eng., Inc., 1969, pp. 617-623.

Compression molding processes for three molecular forms of Pyrrone salt-like intermediate molding powders were reported. Three different procedures were investigated to compression mold the Pyrrones. The one-pressure procedure, in which a pressure of 6500 psi (4.482×10^7 Pa) was applied at room temperature and a 450° F (234° C) curve temperature was used, was not satisfactory. A modified one-pressure procedure, in which the die was charged with previously heated powder and the pressure was applied at 500° F (262° C), permitted small moldings to be made at 700° F (374° C). A two-pressure molding procedure was used successfully to mold both small and large disks. The results of this investigation showed that the critical factor in molding the Pyrrones was the elimination of volatiles.

161.00 Price, Howard L.; and Bell, Vernon L.: Radiation Stability of Unfilled Pyrrone Moldings. Materials and Processes for the 70's, SAMPE Vol. 15, Soc. Aerosp. Mater. Process Eng., 1969, pp. 335-346.

The stability of unfilled moldings of poly(imidazopyrrolones) (Pyrrone) to electron irradiation in air was studied. A Pyrrone molding powder was prepared by heating a AcNMe₂ solution of benzophenonetetracarboxylic acid dianhydride (I) and diaminobenzidine (II) of 1:1 I-II stoichiometry, and precipitating the powder with MeOH. Salt Pyrrone was prepared by heating I and II in ethylene glycol, separating the precipitate, and washing it with MeOH. The unfilled moldings were pressed into disks. The moldings were exposed to 1 MeV electrons at 10⁹ rad/hr. As the molding temperature increased, the flexural properties also increased. Compression molding parameters, physical changes during post-cure, were also discussed.

162.00 Pruckmayr, Gerfried: Amino-Polyamide Ester Adhesive Binders. U.S. Pat. 3,567,684, Mar. 2, 1971.

Low melting amine-amide-ester prepolymers, useful as metal adhesives, were prepared by polymerizing tetraphenyl benzophenone-3,3',4,4'-tetracarboxylate (I) or tetraphenyl 3,3',4,4'-oxydiphthalate with 3,3'-diaminobenzidine (II) or 3,3',4,4'-tetraaminodiphenylmethane in an inert solvent or in the melt with or without a suitable catalyst. The prepolymers could be applied to metal substrates as dry powders or polymer solutions and cured to form bonds having lap shear strengths ≤ 2400 psi (1.655×10^7 Pa) at room

temperature and ≤ 1600 psi (1.103×10^7 Pa) at 300° . Thus 3.3/g I and 1.07 g II were heated at 200° under N. The amine-amide-ester prepolymer products were used directly as metal adhesives for bonding stainless steel plates. The powdered prepolymer was mixed with an equal weight of Al dust and the mixture was applied to the end of a stainless steel strip, either directly as a dry powder or in the form of a piece of glass fabric impregnated with a solution of the prepolymer or with a melt of the adhesive. Another steel strip was brought into contact with the 1st stainless steel strip to provide a 0.5 inch (1.27×10^{-2} m) overlap. The assembly was heated to approximately 300° for 2 hr under 100 psi (6.89×10^5 Pa) to convert the prepolymer to a polybenzoylenebenzimidazole. The average lap shear strength of the bonds was 2000 psi (1.379×10^7 Pa) at room temperature and 1100 psi (7.584×10^6 Pa) at 300° , as determined by ASTM-D-1002.

163.00 Reucroft, P. J.; Scott, H.; Kronick, P. L.; and Serafin, F. L.: Electrical Characteristics of Pyrrone Polymers. NASA CR-1367, 1969.

Polyimidazopyrrolone or Pyrrone polymers, a new class of aromatic-heterocyclic polymers which have outstanding thermal and radiolytic stability, were studied. A detailed determination of the alternating current and direct current electrical properties of Pyrrone polymer films and the effect of high energy radiation on these properties were described.

164.00 Reucroft, P. J.; Scott, H.; Kronick, P. L.; and Serafin, F. L.: The Effect of High Energy Radiation on the Electrical Characteristics of Pyrrone Polymers. J. Appl. Polym. Sci., vol. 14, no. 5, 1970, pp. 1361-1372.

Gamma radiation-induced conductivity and permanent conductivity effects produced by high doses of 2 MeV electrons were measured in two polyimidazopyrrolone polymers. Radiation-induced conductivity levels were small compared to those found in many common insulating polymers. Permanent increases in dark conductivity produced by accumulated doses of 5×10^9 rad at temperatures up to 300° C were not sufficient to inhibit ultraviolet-visible photoconductivity. High doses of 2 MeV electrons (5×10^9 rad) under the same temperature conditions produced no discernible effect on dielectric properties. Both radiation-induced conductivity and permanent dark conductivity increases were much smaller in one polymer (BTDA-DAB), suggesting the possibility of optimizing radiation resistance in this class of polymers by means of chemical structure variation. The radiolytic and thermal stability reported previously for this class of polymers was generally confirmed, with particular reference to electrical properties.

165.00 Reucroft, P. J.; Scott, H.; and Serafin, F. L.: Photoconducting Pyrrone Polymers. *J. Polym. Sci., Pt. C*, no. 30, 1970, pp. 261-270.

Pyrrone polymers were found to exhibit substantial photoconductivity, photocurrent-dark current ratios of up to 300 being obtained with incident intensities of polychromatic light of 10-20 mW/cm². The condensation product obtained from 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-diaminobenzidine (BTDA-DAB) was about 4 to 5 times more photoresponsive than the product obtained from pyromellitic dianhydride and the same diamine (PMDA-DAB). Maximum photoresponse was obtained when samples were cured for at least 24 hours at 300° C. A linear dependence of photocurrent on voltage was found in the range 10² to 10⁵ volts/cm. The temperature dependence of photocurrent indicated that photocarriers were produced by more than one mechanism in the temperature range from room temperature to 300° C. Photoresponse was found to be maximum in the ultraviolet-visible region, with a peak response at 610 mμ for PMDA-DAB and 550 mμ for BTDA-DAB.

166.00 Russo, Mario: A New Class of Stepladder and Ladder Polymers – The Polyimidazopyrrolones. NASA TT F-13136, 1970. (Translated from *Materia'le Plastics Elastomeri*, vol. 33, no. 11, 1967, pp. 1167-1171.)

This review summarized the initial American publications on the preparation of stepladder and ladder polyimidazopyrrolones in light of comparisons with graphitized inorganic and organic materials.

167.00 Scott, H.; and Serafin, F. L.: Evaluation of Pyrrones as Membranes. NASA CR-1648, 1970.

The facile absorption of water by polyimidazopyrrolones (Pyrrones) suggested a feasibility study to use films of the polymers as membranes for the purification of water by reverse osmosis. This report describes direct osmosis measurements of water, salt, and urea fluxes through Pyrrone membranes. The data indicated comparable flux values and superior water-to-salt permeabilities of the Pyrrones relative to symmetric cellulose acetate membranes. Coupled with better mechanical strength and chemical resistance, these results suggested that the successful fabrication of asymmetric Pyrrone membranes could lead to substantial improvements over asymmetric cellulose acetate, from which the best reverse osmosis membranes have been currently prepared.

168.00 Scott, Harvey; Serafin, F. L.; and Kronick, P. L.: Polyimidazopyrrolone Reverse Osmosis Membranes. *J. Polym. Sci., Pt. B*, vol. 8, no. 8, 1970, pp. 563-571.

Membranes of polyimidazopyrrolones or Pyrrone polymers, noted for their thermal oxidative stability, high modulus, and outstanding irradiation resistance, had exceptionally high water permeability and salt rejection properties. A high reflection coefficient was measured under direct and reverse osmosis conditions. The membranes were cast with an adjustable clearance film applicator and thermally cured on polished glass plates using a polyamic prepolymer prepared by treating 3,3'-diaminobenzidine and pyromellitic anhydride or 3,3',4,4'-benzophenonetetracarboxylic dianhydride in AcNMe₂. Although the permselectivity of various Pyrrone films measured by direct osmosis varied considerably, the observed values generally fell in a range well beyond that observed with symmetrical cellulose acetate membranes. The relatively rigid Pyrrone ladder polymers, which did not swell significantly in water, possessed similar reversible water uptake, water permeability, and permselectivity characteristics as cellulose acetate and other water-swellaible polymer membranes. The Pyrrone polymers are probably organic structural analogs of inorganic molecular sieves.

169.00 Sillion, Bernard; and Reboul, Angeline: Polymères conjugués utilisés comme catalyseurs: les poly (isoindolobenzimidazoles) et dérivés (Conjugated Polymers Used as Catalysts - Poly(isoindolobenzimidazoles) and Their Derivatives.) *Compt. Rend. Acad. Sci., Ser. C*, t. 262, Feb. 7, 1966, pp. 471-474.

Poly(isoindolobenzimidazoles) were prepared by 2-stage condensation of diaminobenzidine with dianhydrides in AcNMe₂ under an inert atmosphere. The prepolymer was cyclized by thermal treatment in vacuo at 350°. The B.E.T. specific surfaces for a temperature increase of 60°/hr were: 19 (and 495 with different surface preparation) for pyromellitic; 51 for 3,4,9,10-perylenetetracarboxylic; 13.5 for 3,3',4,4'-tetracarboxybenzophenone; and 3.5 for 3,3',4,4'-tetracarboxydiphenyl ether anhydrides. The E.P.R. were similar to those of other conjugated polymers. The density of free spins was 10¹⁶ - 10¹⁹ spins/g for polymers treated at 350°. The products catalyzed the decomposition of N₂O, whose activation energy was decreased to 20 kcal/mole (8.36 × 10⁴ J/mole), depending on the structure of the polymer.

170.00 Suzuki, Munehiko; Hosokawa, Etsuo; Hirata, Shinsuke; and Hoshino, Tetsuo:
Poly(imidazopyrrolones). Jap. Pat. 69 26,314, Nov. 5, 1969.

The title resins were prepared by reaction of a tetracarboxylic dianhydride with a tetraamine in an organic polar solvent in the presence of a monoamine or diamine or acid anhydride to form a cyclic polyamine, followed by dehydrative condensation. Thus, 0.085 mole of pyromellitic dianhydride (I) was slowly added at 10-20° with stirring to N-methyl-2-pyrrolidinone (II) containing 0.10 mole 3,3',4,4'-tetraminodiphenylmethane (III), and a further 0.005 mole of phthalic anhydride and 0.01 mole of I was added in the same way. The resulting resin solution was shaped into films, dried 30 minutes at 120-300° in air, and heated 10 minutes at 300° to give strong and flexible films. Resistance to heat and alkali of the films were better than those of the films made from diaminodiphenylmethane (instead of III) in the same way.

171.00 Teleshov, E. N.; Fel'dblyum, N. B.; and Pravednikov, A. N.: Thermal Dehydrogenating Cyclization of Polyaminoamidoacids and the Degradation of Polybenzimidazopyrrolones. Vysokomol. Soedin., Ser. A, vol. 10, no. 2, 1968, pp. 422-428.

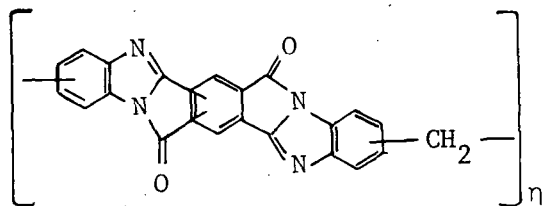
Thermal cyclodehydration of polyaminoamidoacids into polybenzimidazopyrrolones was studied by infrared spectroscopy. The reaction was shown to proceed in two stages with formation of an intermediate polyaminoimide. Kinetic of thermal degradation of polybenzimidazopyrrolones was studied. Comparison of composition of gaseous products of the polymer degradation with kinetics of cyclization and thermal degradation demonstrated that the process occurred mainly as degradation of uncyclized amide units.

172.00 Teleshov, E. N.; and Pravednikov, A. N.: Synthesis and Properties of Polybenzimidazopyrrolone. NASA TT F-10985, 1967. (Translated from Dokl. Akad. Nauk SSSR, vol. 172, no. 6, 1967, pp. 1347-1349.)

A new polymer with an aroylenebenzimidazole structure was synthesized from the polycondensation of 3,3'-diaminobenzidine with the dianhydride of pyromellitic acid in a solution of dimethylformamide. The mode of addition of the monomers was most important since a change in the order produced an insoluble gel rather than the desired polymer solution. Films of the polyamidoamino acid (stage I) were studied by infrared spectroscopy, subjected to cyclization, and the cured films (benzimidazopyrrolone, stage II) again studied.

173.00 Twilley, Ian C.; and Lazarus, Stanley D.: Solid State Polymerization of Tetracarboxylic Acids Dianhydrides and Aromatic Tetramines. U.S. Pat. 3,549,594, Dec. 22, 1970.

Thermally stable polymers having exceptionally high melting points with average molecular weights ranging up to about 100 000 were prepared by polymerizing an aromatic tetramino compound with an aromatic dianhydride at temperatures ranging up to about 350° C until a completely condensed linear polymer was obtained which was characterized as having heterocyclic fused rings as recurring units in the polymeric chain.



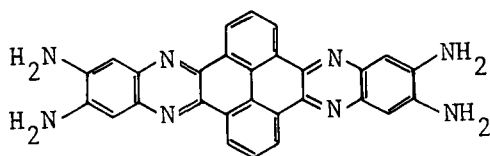
SECTION II – BBB
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200.00 Arnold, Fred E.: Ladder Polymers Containing Heterocyclic Units of Different Structure. *J. Polym. Sci., Pt. B*, vol. 7, no. 10, Oct. 1966, pp. 749-753.

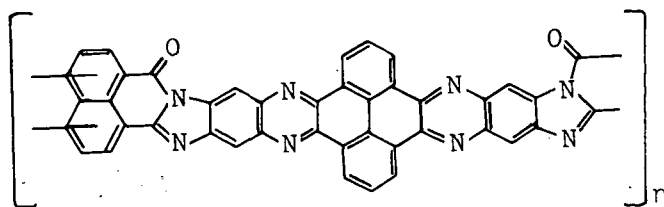
Ladder polymers, consisting of two different aromatic heterocyclic structures occurring in an alternating order sequence along the polymer backbone, were prepared. 2,3,11,12-Tetraaminodiquinoxalino[2,3-e,2',3'-l]pyrene (I) was obtained by the condensation of 1,2-diamino-4,5-bis(p-tolylsulfonamido)benzene with 1,2,6,7-tetraketopyrene yielding 2,3,11,12-tetrakis(p-tolylsulfonamido)diquinoxalino[2,3-e,2',3'-l]pyrene (II), which was detosylated in acid medium to give the free amine I. I was polymerized with 1,4,5,8-naphthalenetetracarboxylic acid in polyphosphoric acid to produce a ladder polymer (III) made up of alternating bisquinoxalinopyrene and bisimidazo naphthalimide structures. Polycondensation of I or II with pyromellitic anhydride yielded ladder polymer IV containing alternating bisquinoxalinopyrene and bisimidazopyromellitide structures. Both III and IV could be cast into films from methanesulfonic acid.



(I)

201.00 Arnold, Fred E.: Ladder Polymers From Tetraaminodiquinoxalpyrene. *J. Polym. Sci., Pt. A-1*, vol. 8, no. 8, 1970, pp. 2079-2089.

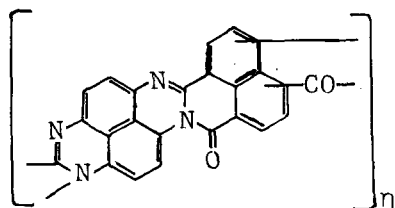
A fused aromatic heterocyclic tetraamine, 2,3,11,12-tetraaminodiquinoxalino[2,3-e,2',3'-l]pyrene was prepared and polymerized with 1,4,5,8-naphthalenetetracarboxylic acid or pyromellitic dianhydride. The resulting ladder polymers (e.g., I) had inherent viscosities of 0.5-1.0 dl/g in methanesulfonic acid and good thermal stability, e.g., initial weight losses occurred at 550-600° in nitrogen and at 430-450° in air.



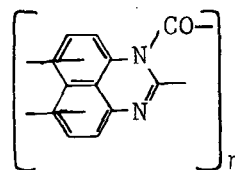
(I)

202.00 Arnold, Fred E.; and Van Deusen, Richard L.: Poly(perimidine-tetrays). J. Polym. Sci., Pt. B, vol. 6, no. 11, 1968, pp. 815-819.

1,4,5,8-Tetraaminonaphthalene was condensed with 1,4,5,8-naphthalenetetracarboxylic dianhydride to give the 6-6 ladder polymer I, while dimethyl 4,5-diamino-1,8-naphthalenedicarboxylate was polymerized in solution, giving the polymer II. Other synthetic routes to these polymers were discussed, and the polymers were characterized.



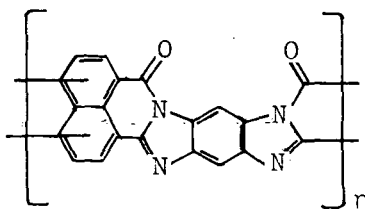
(I)



(II)

203.00 Arnold, F. E.; and Van Deusen, R. L.: Preparation and Properties of High Molecular Weight, Soluble Oxobenz[de]imidazobenzimidazoisoquinoline Ladder Polymer. Macromolecules, vol. 2, no. 5, Sept.-Oct. 1969, pp. 497-502.

The synthesis of double chain or ladder polymers (I) from 1,2,4,5-tetraaminobenzene and 1,4,5,8-naphthalenetetracarboxylic acid was optimized. High ladder polymers of high quality were obtained from the free tetraamine, as well as its hydrochloride salt, in polyphosphoric acid polycondensations at 180°. These ladder polymers were completely soluble in methanesulfonic acid and had intrinsic viscosities ranging from 1 to 6 dl/g. Film-forming and fiber-forming properties were demonstrated. TGA weight losses of less than 10% at 600° in air and less than 5% at 700° in nitrogen were observed. Low-viscosity ladder polymers were obtained from polycondensations in methanesulfonic acid.



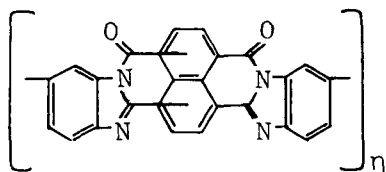
(I)

204.00 Arnold, F. E.; and Van Deusen, R. L.: Unusual Film-Forming Properties of Aromatic Heterocyclic Ladder Polymers. *J. Appl. Polym. Sci.*, vol. 15, no. 8, Aug. 1971, pp. 2035-2047.

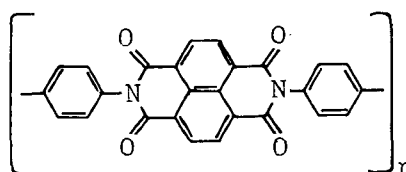
A new method of obtaining films of aromatic heterocyclic ladder polymers was found which circumvents casting from high-boiling acidic solvents. The BBL ladder polymer was formed into tough, durable films by collecting suspensions of the polymer obtained from acid reprecipitations upon a fritted glass funnel. After drying, the polymer was removed as film, with thickness dependent upon the amount of material used. Such a film had a tensile strength of 9600 lb/in² (6.619×10^7 Pa), as compared to a tensile strength of 16 000 lb/in² (1.103×10^8 Pa) obtained from the same polymer when cast from methanesulfonic acid solution.

205.00 Berlin, A. A.; Belova, G. V.; Liogon'kii, B. I.; and Shamraev, G. M.: Thermal and Oxidative Thermal Degradation of Poly(arenediarylbenzimidazoles) and Poly(arylenebisbenzimidides). *Vysokomol. Soedin., Ser. A*, vol. 10, no. 7, 1968, pp. 1561-1569.

Thermal stability of poly(arenediarylbenzimidazoles) such as I, prepared by a two-step method or in polyphosphoric acid, of poly(arylenebisbenzimidides) such as II, and of copolymers of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride and a mixture of 3,3'-diaminobenzidine and 4,4'-diaminodiphenyl oxide at various mole ratios was studied. Curves of thermal and thermal oxidative degradation of the polymers were shown. Mass spectral data of degradation products of some of the polymers were given. An increased resistance to thermal and thermal oxidative degradation was shown by imidazole polymers as compared to imide polymers. The introduction of blocks of imidazole structure into the copolymer increased its thermal stability. The thermal oxidative degradation curves of I, contrary to II, are S-shaped, the activation energies being 28.8 (12.04×10^4) and 9.2 kcal/mole (3.85×10^4 J/mole), respectively. Heating I prior to the degradation resulted in an autocatalytic effect due to the formation of paramagnetic centers.



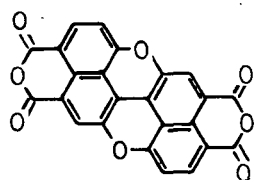
(I)



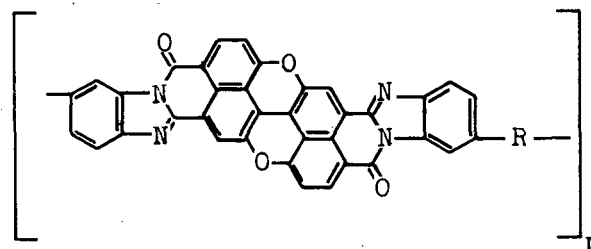
(II)

206.00 Berlin, A. A.; Liogon'kii, B. I.; Belyukh, S. I.; Privalov, V. E.; Rudkevich, M. I.; and Shram, G. I.: Synthesis of Poly[arylenebis(benzimidazoles)] Based on Peri-Xanthenoxanthene-3,4,9,10-Tetracarboxylic Acid Dianhydride. *Vysokomol. Soedin., Ser. B*, vol. 13, no. 3, 1971, pp. 198-201.

The polycondensation of peri-xanthenoxanthene-3,4,9,10-tetracarboxylic acid dianhydride (I) with 3,3'-diaminobenzidine or 3,3',4,4'-tetraaminodiphenylmethane in polyphosphoric acid at 210° gave Poly[arylenebis(benzimidazoles)] (II) (R is single bond or CH₂) which decompose in the air only above 400°. I was prepared by heating 3-hydroxynaphthalic anhydride in boiling PhNO₂ containing CuCl₂. The polycondensation in Me₂SO at 75-80° gave low yields of II and the corresponding poly(amino amido acid) which was converted to II by heating in vacuum at 250°.



(I)

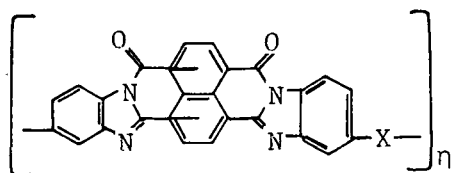


R = NIL, -CH₂-

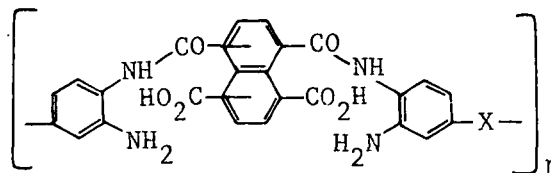
(II)

207.00 Berlin, A. A.; Liogon'kii, B. I.; and Shamraev, G. M.: Synthesis and Properties of Polymers Derived From the Dianhydride of 1,4,5,8-Naphthalene-tetracarboxylic Acid and Aromatic Tetramines. *Vysokomol. Soedin., Ser. B*, vol. 10, no. 9, 1968, pp. 678-682.

Poly(arylenebenzimidazoles), denoted by structure (I) where X = 0 or CH₂, were prepared by reacting naphthalene-1,4,5,8-tetracarboxylic 1,8:4,5-dianhydride with 3,3',4,4'-tetraaminodiphenylmethane and 3,3',4,4'-tetraaminodiphenyl ether, respectively. Polycondensation in N,N-dimethylformamide or N,N-dimethylacetamide at low temperatures gave polymer intermediates (II) where X = 0 or CA₂ which were cyclized at 300° in vacuo to polymers denoted by formula I. Polycondensation was also accomplished in polyphosphoric acid by gradual heating to 200°. IR spectra of the polymers were shown and discussed. Thermogravimetric curves were recorded and electrical properties of the polymers were tabulated. The polymers were stable at ≤450° in air; 30 percent weight loss occurred at ≤800° in vacuo.



(I)



(II)

208.00 Berlin, A. A.; Liogon'kii, B. I.; and Shamraev, G. M.: Synthesis and Studies of Some Polyaminoamidoacids. *Vysokomol. Soedin., Ser. A*, vol. 12, no. 4, 1970, pp. 938-947.

Polyaminoamidoacids were synthesized from 1,4,5,8-naphthalenetetracarboxylic acid dianhydride and different aromatic tetraamines. Effects of the solvent, concentration and order of mixing of the reagents, temperature and duration of the reaction on molecular weight of the polyaminoamidoacids were investigated. Cyclization of the polymers and their magnetic and electrical behavior were studied.

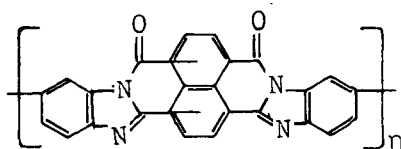
209.00 Berlin, A. A.; Liogon'kii, B. I.; and Shamraev, G. M.: Thermostable Polymers From Dianhydrides of Aromatic Tetracarboxylic Acids and Tetraamines. *Russ. Chem. Rev.*, vol. 40, no. 3, 1971, pp. 284-300. (Translated from *Usp. Khim.*, vol. 40, no. 3, 1971, p. 513.)

The preparation, properties, and structure of polymers based on dianhydrides of aromatic tetracarboxylic acids and tetraamines were surveyed through 1970. Compounds of this type possess excellent thermal stability, resistance to radiation and chemicals, catalytic activity, and semiconductor properties. The fields of practical application of the polymers were examined. A list of 77 references was included.

210.00 Berlin, A. A.; Liogon'kii, B. I.; Shamraev, G. M.; and Belova, G. V.: Heat-Resistant Polymers With Semiconducting Properties – Poly(aroylene-bisbenzimidazoles). *Izv. Akad. Nauk SSSR, Ser. Khim.*, no. 5, 1966, p. 945.

1,4,5,8-Naphthalenetetracarboxylic dianhydride and 3,3'-diaminobenzidine, in polyphosphoric acid at 140-200° or in 2 stages in HCONMe₂, gave polymers of formula I

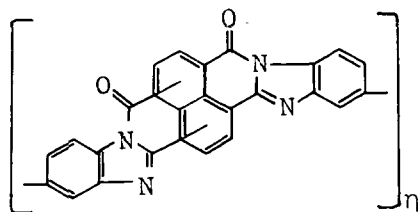
soluble in concentrated H_2SO_4 and polyphosphoric acid. After 24 hr at 200° in vacuum, the polymers retained their solubility. A model for I is Indanthrene Red. The structure of the polymer was confirmed by its ir spectrum. Similar polymers were prepared from tetracarboxylic acids of pyrene, naphthalene, and similar aromatic hydrocarbons. The polymers decomposed in air at $\sim 550^\circ$ and I was stable in air at 400° for 7 hr. The products were paramagnetic and the conductivity of heat-treated products in the $300\text{-}400^\circ$ range was 10^{-6} to 10^{-4} ohm $^{-1}$ cm $^{-1}$.



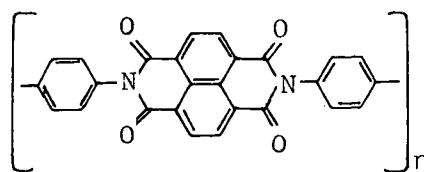
(I)

211.00 Berlin, A. A.; Liogon'kii, B. I.; Shamraev, G. M.; and Belova, G. V.: Poly(naphthalenebisbenzimidazoles). *Vysokomol. Soedin., Ser. A*, vol. 9, no. 9, 1967, pp. 1936-1945.

Heat-stable polymers were prepared from 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (I) and 3,3'-diaminobenzidine (II) by a two-stage synthesis. Structure, heat resistance, and magnetic and electrical behavior were studied. Polybenzimidazoles and polybenzimidides were prepared via the polyaminoamido acid or the polyamido acid with $\text{H}_3\text{CCONMe}_2$ or HCONMe_2 , then cyclodehydrated with polyphosphoric acid. For example, I was polymerized with II at 25° C to give poly[(3-amino-p-phenylene)iminocarbonyl(5,8-dicarboxy-1,4-naphthylene)carbonylimino-2-amino-p-phenylene] (III). III was treated with 116% polyphosphoric acid at 200° C to afford poly(6,9-dihydro-6,9-dioxobisbenzimidazo-[2,1-b:1',2'-j]benzo[lmn][3,8]phenanthroline-2,13-diyl) (IV). Poly[p-phenylene-(1,4,5,8-naphthalenetetracarboxylic 1,8:4,5-diimide-N,N'-diyl)-p-phenylene] (V) was prepared in the same manner, using benzidine instead of II, via poly[p-phenyleneimino-carbonyl(5,8-dicarboxy-1,4-naphthylene)carbonylimino-p-phenylene] (VI) with HCONMe_2 . Thermomechanical curves showed that the temperature for a maximum rate of cyclodehydration was $100\text{-}200^\circ$. E.P.R. spectra and electrical properties were reported for the polymers.



(IV)



(V)

212.00 Berry, Guy C.: Dilute and Concentrated Solutions of a Heterocyclic Polymer (BBB). Discuss. Faraday Soc., no. 49, 1970, pp. 121-136.

Light scattering, viscometry, f.p. depression, and X-ray diffraction studies of the heterocyclic polymer prepared from 1,4,5,8-naphthalenetetracarboxylic acid and 3,3'-diaminobenzidine showed that the polymer behaved as a flexible coil in dilute solutions and in very concentrated solutions of the polymer or bulk polymer there were short-range interactions giving stacked aggregates with spacings of 3.5-3.6 angstroms.

213.00 Berry, G. C.; and Fox, T. G.: Properties of Heterocyclic Condensation Polymers. J. Macromol. Sci. - Chem., vol. A3, no. 6, Oct. 1969, pp. 1125-1146.

Basic questions concerning heterocyclic polymers were reviewed. Initial investigations on the heterocyclic polymer BBB prepared from naphthalene-1,4,5,8 tetracarboxylic acid and 3,3'-diaminobenzidine were described. These included infrared absorption studies of the structure of the polymer, fractionation of the polymer by exclusion chromatography on a porous substrate, and light scattering and dilute solution viscometry on fractions of the polymer dissolved in a strong acid. From these data, the following conclusions were made: (1) in dilute solutions BBB behaves as a "flexible coil" macromolecule, with perhaps relatively free rotation about the single bond connecting the long, inflexible, nearly planar repeat units; (2) a sufficient amount of interchain complex formation occurs in the solid state to give the linear, noncrystalline polymer some of the physical properties of a highly cross-linked network polymer.

214.00 Berry, Guy C.; and Yen, S. P.: Structure and Properties of a Heterocyclic Polymer. Advan. Chem. Ser., no. 91, 1969, pp. 734-756.

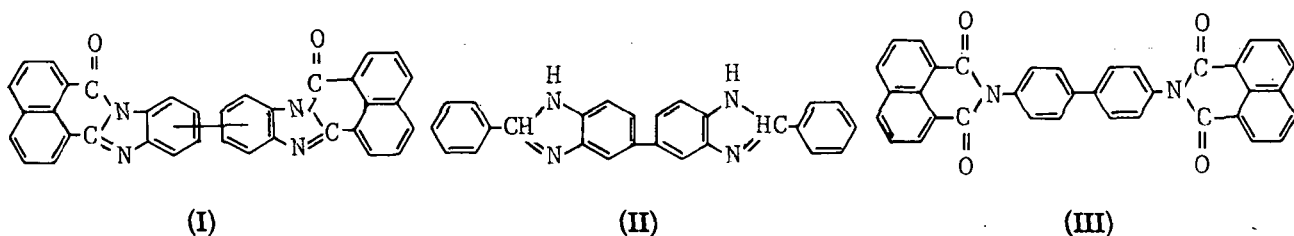
Investigations on the heterocyclic polymer (I) prepared from 1,4,5,8-naphthalene-tetracarboxylic acid and 3,3'-diaminobenzidine were described. These included infrared absorption studies of the structure of the polymer, fractionation of the polymer by exclusion chromatography on a porous substrate, and light scattering and dilute solution viscometry on fractions of the polymer dissolved in a strong acid. In dilute solutions I behaves as a "flexible coil" macromolecule, perhaps with relatively free rotation about the single bond connecting the long, inflexible, nearly planar repeat units. A sufficient amount of interchain complex formation occurs in the solid state to give the linear, noncrystalline polymer some of the physical properties of a highly crosslinked polymer.

215.00 Gaudiana, Russell A.; and Conley, Robert T.: Weak-Link Versus Active-Carbon Degradation Routes in the Oxidation of Aromatic Heterocyclic Systems. III. *J. Macromol. Sci. - Chem.*, vol. 4, no. 2, 1970, pp. 463-480.

A polybenzimidazolone prepared by the condensation of 1,4,5,8-naphthalenetetracarboxylic acid and 3,3'-diaminobenzidine and several model compounds were thermally degraded (300-500^o) under inert and oxidative conditions. In every case only small fragments, i.e., C oxides, cyanogen (trace), and H₂O, were detected by spectroscopic and chromatographic analysis of all phases of the pyrolysis products. The significance of these results was discussed in light of the mechanism by which this aromatic heterocyclic system underwent oxidative degradation.

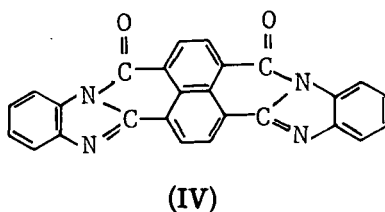
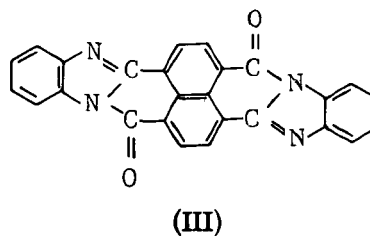
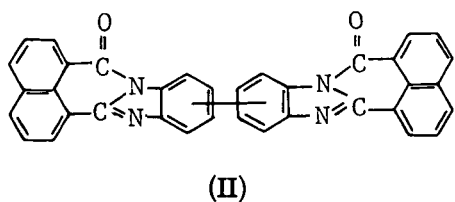
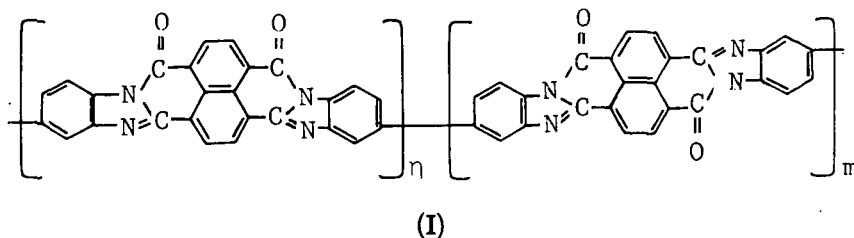
216.00 Gaudiana, R. A.; and Conley, R. T.: Weak-Link Versus Active-Carbon Degradation Routes in the Oxidation of Aromatic Heterocyclic Systems. IV. *J. Macromol. Sci. Chem.*, vol. A4, no. 7, 1970, pp. 1599-1617.

The oxidation of polybenzimidazolone and selected model compounds (e.g., I) including compounds containing benzimidazole (e.g., II) and benzimide ring systems (e.g., III) were investigated at temperatures from ambient to 700^o C. Residue elemental analyses, volatile product distribution differences as a function of time and oxidation temperature, thermogravimetry, and differential thermal analysis studies were reported. The determination of the energy of activation for the over-all initial oxidation processes over the ranges of 0 to 15% weight loss and 100 to 700^o C indicated a value of 35.5 kcal/mole (14.84 × 10⁴ J/mole). The elemental analyses data indicated that significant differences in residue composition existed between model compounds having amine-derived end groups and those systems bearing acid-derived end groups. Data obtained using differential thermal analyses techniques indicated little difference in the thermal behavior of the benzimidazolones in inert or oxygen atmospheres. The changes in the amounts of carbon dioxide and carbon monoxide as a function of temperature and time supported a proposal for simultaneous thermal and thermooxidation processes for the degradation of these systems in oxygen atmospheres at high temperatures.



217.00 Gaudiana, Russell A.; and Conley, Robert T.: Weak-Link Versus Active Carbon Degradation Routes in the Oxidation of Aromatic Heterocyclic Systems. *J. Polym. Sci., Pt. B*, vol. 7, no. 11, 1969, pp. 793-801.

The mechanism by which polymer I degrades in oxidizing atmospheres at elevated temperatures was studied together with the model compounds II, III, IV, 2,2'-diphenyl-5,5'-bibenzimidazole (V), 2,2'-(p-phenylene)dibenzimidazole, 4,4'-naphthalimidobiphenyl (VI), and N,N'-diphenyl-1,4,5,8-naphthalenetetracarboxylic 1,8:4,-5-diimide. The model compounds were prepared by condensing the appropriate mono-, di-, or tetraamine and acid in 115% polyphosphoric acid. Pyrolysis of the polymer and the model compounds at 250-600° gave CO₂, CO, H₂O, and trace amounts of C₂N₂. Degradation of V and VI gave PhCN and 1,8-naphthalic anhydride, respectively. Only the acid-derived portions of the molecules were isolated as degradation products; all attempts to trap or detect condensates from the amine-derived portions of the molecules failed. The failure to obtain N-containing fragments from the amine residues of model compounds indicated that the initial stages of oxidative attack occurred on the benzenoid rings bearing the N and subsequent decomposition of the oxygenated species led to decomposition of the amine portion of the molecule.



218.00 Gibbs, William E.: Synthesis of Certain Aromatic Heterocyclic Polymers. J. Macromol. Sci. - Chem., vol. 2, no. 7, 1968, pp. 1291-1302.

Continued research on the preparation of poly(bisbenzimidazobenzophenanthrolines) by 1-step condensation of 1,4,5,8-naphthalenetetracarboxylic acid and 3,3'-diaminobenzidine in polyphosphoric acid led to good-quality fibers with outstanding resistance to high temperatures and Fade-Ometer aging. The condensation of 4,5-diamino-1,8-naphthalenedicarboxylic acid derivatives produced low-molecular-weight polyperimidines which had good stability. The polyimide from condensation of 2,2',6,6'-biphenyltetracarboxylic acid dianhydride with $(4\text{-H}_2\text{NC}_6\text{H}_4)_2\text{O}$ was insoluble in all solvents tried and showed moderate thermal stability. The completely soluble ladder polymer from condensation of 1,4,5,8-naphthalenetetracarboxylic acid with 1,2,4,5-tetraaminobenzene in polyphosphoric acid was obtained in high-molecular-weight (intrinsic viscosities in MeSO_3H at 30° of >5 dl/g).

219.00 Gloor, W. H.: Fiber Formation and Drawing of Poly(bisbenzimidazobenzophenanthroline). Appl. Polym. Symp., no. 6, 1967, pp. 151-163.

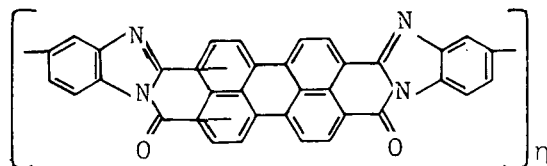
Poly(bisbenzimidazobenzophenanthroline) has been successfully formed into fibers potentially useful in high-temperature Air Force Systems. Polymer from three separate preparations, ranging in intrinsic viscosity from 1.15 to 2.45 (H_2SO_4 , 30° C), was spun from concentrated H_2SO_4 into coagulating baths containing varying amounts of H_2SO_4 . Under optimum conditions, a lustrous, dark green fiber or yarn resulted. As-spun yarn was hot-stretched, both by hand and continuously, at temperatures between 200 and 650° C. Significant strength increases (up to 500%) were obtained at low overall draw ratios (1.5/1 or less). Single fiber strengths in air were measured at temperatures up to 700° C. Approximately 50% of room-temperature strength was retained at 500° C. No evidence of crystallinity was found in X-ray diffraction photographs of as-spun or drawn fiber. The higher mechanical property levels were obtained on yarns and fibers formed from polymer of intrinsic viscosity 2.0 or higher. Best properties to date were about 3.8 gram/denier tenacity and 150-190 gram/denier initial modulus, with low (3-5%) rupture elongation. These were preliminary results and additional effort was expected to increase the overall property levels.

220.00 Gloor, Walter H.: Poly(bisbenzimidazobenzophenanthroline) Fiber and Yarn Properties. Appl. Polym. Symp., no. 9, 1969, pp. 159-166.

The title polymer (I) was formed by solution condensation of 3,3'-diaminobenzidine with 1,4,5,8-naphthalenetetracarboxylic acid in polyphosphoric acid. I formed useful fibers when wet spun from solution in 97% H₂SO₄ (II) into a coagulating bath of ~70% II. Dry-heat drying at 525-600° using 1.8-2.2 draw ratios resulted in I fibers whose properties averaged 5.2 gram/denier at 5% ultimate elongation, 55% strength retention at 600° in air, 1 minute exposure; 50% strength retention after 30 hours in air at 360°, minimum moisture sensitivity, excellent uv resistance, and good loop and knot strength.

221.00 Liogon'kii, B. I.; Shamraev, G. M.; and Berlin, A. A.: Poly(aroylenebisbenzimidazoles) Based on Perylene-3,4,9,10-Tetracarboxylic Acid Dianhydride and 3,3'-Diaminobenzidine. Vysokomol. Soedin., Ser. B, vol. 10, no. 8, 1968, pp. 574-578.

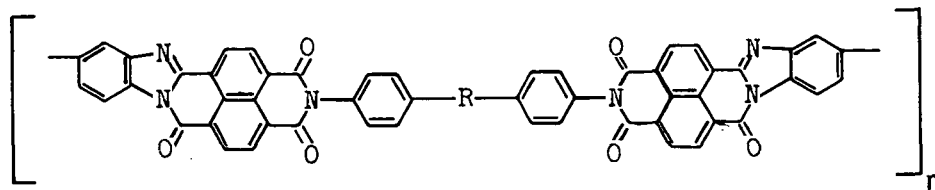
The polymer shown was prepared from 3,3'-diaminobenzidine tetrahydrochloride and perylene-3,4,9,10-tetracarboxylic acid dianhydride using polyphosphoric acid in the first reaction step. The polymerization did not proceed in dimethylformamide or dimethyl sulfoxide. Electrical properties, magnetic properties, and thermal stability of the polymer were determined and compared with those of poly(naphthoylenebisbenzimidazole).



222.00 Liogon'kii, B. I.; Shamraev, G. M.; and Berlin, A. A.: Synthesis and Structural Study of Imidoaroylenebenzimidazole Copolymers. Vysokomol. Soedin., Ser. A, vol. 13, no. 4, 1971, pp. 816-820.

Imidoaroylenebenzimidazole copolymers (I) (R = single bond or O) were prepared by a two-stage polycondensation of 1,4,5,8-naphthalenetetracarboxylic acid dianhydride (II) with 3,3'-diaminobenzidine (III) and benzidine or with III and 4,4'-diaminobiphenyl ether in organic solvents at 75-85° followed by thermal cyclization of the prepolymers at 200-300°. Alternatively, I were prepared by one-stage polycondensation in polyphosphoric acid at 180-220°. The polymers were stable in vacuo and in the air to 500-550° and soluble

in H_2SO_4 and polyphosphoric acid. A narrow EPR signal, characteristic of conjugated system, was observed in these polymers. Increased content of imide segments led to increased resistivity and activation energy of condensation. The copolymers were semiconductors.



R = NIL, -O-

(I)

223.00 Misevichyus, P. P.; Machyulis, A. N.; Liogon'kii, B. I.; Shamraev, G. M.; Berlin, A. A.; and Grigorovskaya, V. M.: Ablation Resistance of Some Thermostable Polymers. *Vysokomol. Soedin., Ser. A*, vol. 12, no. 9, 1970, pp. 2091-2098.

The ablation resistance of the following polymers towards a stream of hot air was studied: poly(naphthylenebisbenzimidazoles) prepared by the polycondensation of naphthalene-1,4,5,8-tetracarboxylic acid with 3,3',4,4'-tetraaminobiphenyl; poly(peryleneoylenebisbenzimidazoles) prepared by the polycondensation of perylene-3,4,9,10-tetracarboxylic acid with 3,3',4,4'-tetraaminobiphenyl; polyimides prepared by the condensation of naphthalene-1,4,5,8-tetracarboxylic acid with 4,4'-diaminobiphenyl or bis(4-aminophenyl) ether; polyphenylenes; poly(1,4-naphthylenes); and poly(1,4-naphthylene-1,4-phenylenes).

The most resistant to ablation were linear ladder diimides; branching and noncyclic segments decreased the ablation resistance.

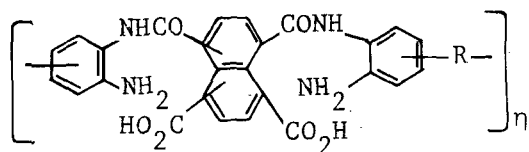
224.00 Mortillaro, Luigi: Poly[bis(benzimidazo)benzophenanthrolines], New Polymers With High Performance. *Mater. Plast. Elastomeri.*, vol. 34, no. 6, 1968, pp. 614-617.

Heteroaromatic, heat-stable, fiber-forming poly[bis(benzimidazo)benzophenanthrolines] with a stepladder structure (I) were prepared by heating 3,3'-diaminobenzidine with naphthalene-1,4,5,8-tetracarboxylic acid II. The ladder structure (III) was prepared by heating II with 1,2,4,5-tetraaminobenzene tetrahydrochloride (IV) in 80-90% yield by polycondensation of II and IV at 220° in polyphosphoric acid, precipitation in H_2O and washing with hot AcNMe_2 . The inherent viscosity of I, measured in concentrated H_2SO_4 solution,

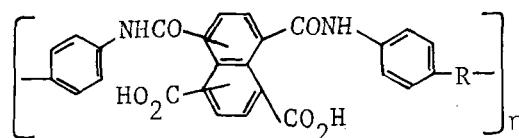
depended on the polycondensation conditions (temp., time, viscosity, given): 110-130°, 18 hr, 0.49; 200-220°, 3 hr, 0.8; 180-190°, 20 hr, 1.15. The viscosity of 0.49 was increased to 0.6 by heating the sample for 14 hr at 165-185° in the solid phase. Both polymer forms were black and soluble in concentrated H₂SO₄, polyphosphoric acid, methane- and benzenesulfonic acids, H₃PO₄ to 85% concentration, and a concentrated aqueous alkaline solution. I, heated for 16 hr at 70-80° in H₂SO₄, showed a viscosity change of 0.80 to 0.79. I had a weight loss of <0.1% on heating to 600°, at 150°/hr, under N, and had <10% weight loss after 1000 hr at 315° in air. Decomposition occurred at 610-620° in air. A fiber was formed by extruding 50 cc of a 10% solution of 40 g polymer in H₂SO₄ from a syringe into a water bath at 45° at 0.3 cc/min. The filament had a tenacity of 0.5 g/denier and a 20% elongation at break. An 8% solution of I of intrinsic viscosity 2.45 (H₂SO₄ at 30°) was similarly extruded to give filament with a tenacity of 1.1 g/denier and 31% elongation. A 6% solution of I gave 1.4 g/denier tenacity and 31% elongation. A 6% solution of I gave 1.4 g/denier tenacity and 48% elongation at break. The filament was washed to remove excess acid and drawn manually at 360-540° to a draw ratio of 1.1-1.29, giving a tenacity of 0.85 to 1.33 and an elongation at break of 7.1-10%. Polymer of viscosity 2.45 was drawn at 380-700° with and without washing treatments which had little effect. The same polymer was drawn in air at 425 and 525° to a draw ratio of 1.23 and 1.31 and had a tenacity of 1.92 and 2.46 g/denier, respectively, and elongation at break of 14.5 and 5.9%, and in Ar at 260-565° to a draw ratio of 1.06-1.59, giving a tenacity of 0.76 and 3.36 g/denier and elongation at break of 34 and 4.1%. Polymer of intrinsic viscosity 2 was drawn to ratios of 0.95-1.76 at 150-650° and gave a filament with a tenacity of 1.56-3.79 g/denier and elongation at break of 18.1-2.9%.

225.00 Shamraev, G. M.; Dulov, A. A.; Liogon'kii, B. I.; and Berlin, A. A.: Thermal Transformations of Some Aromatic Polyamido and Polyaminoamido Acids. *Vysokomol. Soedin., Ser. A*, vol. 12, no. 2, 1970, pp. 401-408.

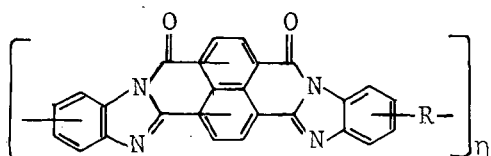
Pyrolysis studies were made on I [R is nil, O, CH₂, or poly(naphthylenebisbenzimidazole)] and II (R is nil or O), whose preparations were reported by A. A. Berlin, et al. (1966-1968). Ir spectroscopy, X-ray diffraction, electron microscopy, and EPR spectroscopy were used to establish that the ordering of I or II proceeds at $\leq 400^\circ$. This was due to formation of the conjugated heterocyclic polymers such as III or IV. At 500° and $\leq 800^\circ$, the structure ordering of III and IV decreased because of thermal degradation.



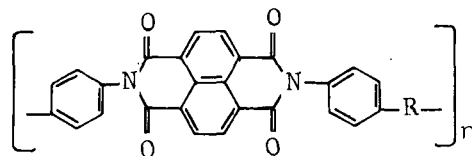
(I)



(II)



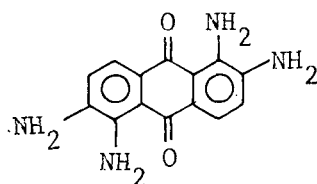
(III)



(IV)

226.00 Szita, Jenó; Brannigan, L. H.; and Marvel, C. S.: Ladder Pyrrolone Structures With Anthraquinone Recurring Units. *J. Polym. Sci., Pt. A-1*, vol. 9, 1971, pp. 691-700.

The reaction of 1,2,5,6-tetraaminoanthraquinone (I) and 1,4,5,8-naphthalenetetracarboxylic acid dianhydride in dimethylacetamide gave a tetrameric prepolymer with balanced endgroups of anhydride and diamine. When this prepolymer was carefully treated with polyphosphoric acid at elevated temperature, it was converted to a soluble polypyrrolone type structure with an inherent viscosity of 2.3-2.7. Polymers of this molecular weight were wet-spun into pliable fibers from methanesulfonic acid. The TGA curve in air showed little weight loss below 550° C. The polymer was also solubilized by reduction with sodium dithionite in alkaline aqueous dimethyl sulfoxide.



(I)

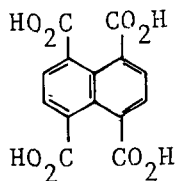
227.00 Van Deusen, R. L.: Benzimidazo-Benzophenanthroline Polymers. *J. Polym. Sci., Pt. B*, vol. 4, no. 3, Mar. 1966, pp. 211-214.

Polycondensation reactions for the synthesis of polymers containing benzimidazo-benzophenanthroline structures were reported. Polymers containing fused six-membered

cyclic diimide structures were also included. The bis(benzimidazo)benzophenanthroline (I) polymers had excellent heat stability. Some samples of I showed no weight loss up to 600°. The structural arrangement of I is one in which a six-membered imide ring is fused between aromatic and imidazole nuclei in a conjugated chain having relatively few single links. Typical polycondensations were carried out by grinding equimolar amounts of monomers under N and stirring in polyphosphoric acid at up to 220°. The intrinsic viscosities were dependent upon the conditions of polycondensation. The benzimidazo-benzophenanthroline ladder-structure polymers were much more difficult to dissolve than I and had some portions that appeared to be insoluble.

228.00 Van Deusen, R. L.; Goins, O. K.; and Sicree, A. J.: Some Properties of Polybenzimidazobenzophenanthrolines. Amer. Chem. Soc., Div. Polym. Chem., Preprints, vol. 7, no. 2, 1966, pp. 528-534.

Polybenzimidazobenzophenanthrolines were prepared by condensations of 1,4,5,8-naphthalenetetracarboxylic acid (I) with either 3,3'-diaminobenzidine or 1,2,4,5-tetraaminobenzene. Soluble polymers with solution viscosities >1.0 (H_2SO_4) were prepared from diaminobenzidine in polyphosphoric acid near 200°. These polymers appeared to undergo some degree of chain extension in secondary solid phase reactions at $>200^\circ$ as reflected by viscosity increases. The more highly fused polymers derived from tetraaminobenzene were found to have solubilities $<0.5\%$ in H_2SO_4 . Inherent viscosities >0.63 were not obtained due to the poor solubility. The highly cyclized structures for these polymers were verified by ir and elemental analysis. Thermal stabilities further tended to confirm this; thermogravimetric analysis (150°/hr) showed that the polymers withstand catastrophic decomposition to 600° in N atmosphere.



(I)

229.00 Van Deusen, R. L.; Goins, O. K.; and Sicree, A. J.: Thermally Stable Polymers From 1,4,5,8-Naphthalenetetracarboxylic Acid and Aromatic Tetraamines. *J. Polym. Sci., Pt. A-1*, vol. 6, 1968, pp. 1777-1793.

Polycondensations of 1,4,5,8-naphthalenetetracarboxylic acid (NTCA) with both 3,3'-diaminobenzidine (DAB) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TAB) in polyphosphoric acid (PPA) were found to produce soluble polymers which exhibit excellent thermal stabilities. Polymer structures were deduced from infrared, thermal, and elemental analyses of model compounds and polymers. Polymer derived from TAB had a ladder-type structure. Polymers with solution viscosities near 1 or above (determined in H₂SO₄) were obtained from polymerizations near 200° C, and analysis showed these to possess a very high degree of completely cyclized benzimidazobenzophenanthroline structure. Less vigorous reaction conditions gave polymers with lower solution viscosities which appeared to be less highly cyclized. Low-viscosity polymer was also prepared from DAB and NTCA by solid-phase polycondensation. Some advancements in the solution viscosities of polymers synthesized from DAB in PPA were caused by second staging in the solid phase.

230.00 Zhilinskaite, L. P.; Machyulis, A. N.; Misevichyus, P. P.; Shamraev, G. M.; Liogon'kii, B. I.; and Berlin, A. A.: The Ablation of Some Heat-Stable Polymers and Their Use as Inhibitors of Ablation Degradation. *Vysokomol. Soedin., Ser. A*, vol. 11, no. 6, 1969, pp. 1214-1220.

A study of the ablative characteristics of a number of polymers disclosed that those with conjugated double bond systems had high resistance to ablation. Of those tested, a naphthoylene-bis-benzimidazole (BBB-type) polymer showed the highest stability to ablative degradation.

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