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Thermostable Polymers from Dianhydrides of Aromatic Tetracarboxylic Acids and Tetra-amines

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The preparation, properties, and structure of polymers based on dianhydrides of aromatic tetracarboxylic acids and tetra-amines are surveyed. 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 are examined. A list of 77 references is included.

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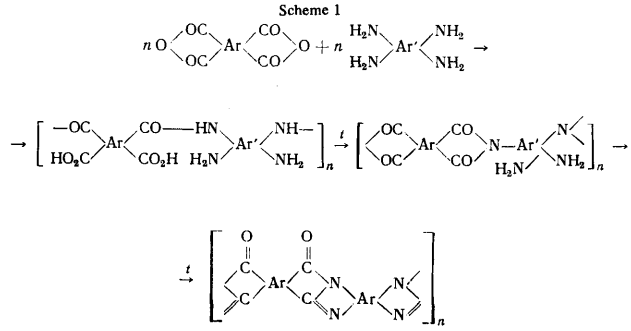
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I. INTRODUCTION

At the present time much attention is paid to the synthesis and investigation of thermostable polymers [1]. This has arisen from the demands made by rapid developments in technology—especially such advanced fields as aircraft and spacecraft construction, nuclear power, and electrical technology—for materials capable of operating under severe conditions of high-temperature gas flows and radiation. During recent years progress has been made in producing a series of polymers having a conjugated system comprising various carbocyclic and heterocyclic rings in a macromolecular chain of ladder and block–ladder structure.

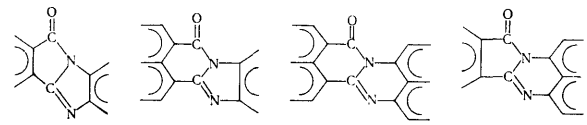
Considerable interest attaches in this series to macromolecular products of the reaction of dianhydrides of aromatic tetracarboxylic acids and tetra-amines (Scheme 1):

Scheme 1



They are polymeric analogues of the highly stable aroylenebenzimidazole dyes [2].

The repeating unit in the macromolecular chains includes a system of fused aromatic carbocyclic and heterocyclic rings



Depending on the type of heterocycles formed in the process the polymers have been termed polyimidazopyrrolones (pyrrones), polyaroylenebisbenzimidazoles or polyaroylenebenzimidazoles, polyperimidinetetrayls, polybisbenzimidazophenanthrolines, etc. In principle none of these names completely represents the structure of the polymers, especially when intermediate groups and complicated fused carbocyclic and heterocyclic rings are present. The Reviewers therefore consider it advisable to use the trivial, but already quite widely employed name "pyrrones" with an indication of the initial components, and only in isolated cases to retain the names of the polymers given in the original papers. The first work on the synthesis of polymers of this class was published in 1965–1966. [3-8] At the present time the preparation and properties of pyrrones are being actively investigated, and these compounds may be expected to find wide application in the immediate future.

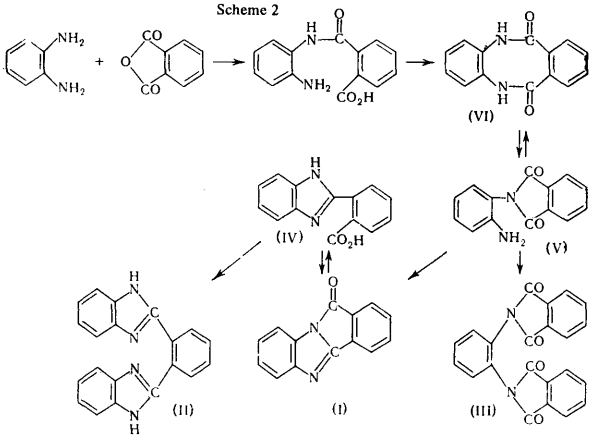
II. REACTION BETWEEN AROMATIC ANHYDRIDES AND *o*-DIAMINES

In the reaction between aromatic dianhydrides and tetra-amines, the formation of the final polymers is preceded by that of several intermediate structures. In

order to elucidate the mechanism of polycondensation, therefore, it is advisable to examine papers on the interaction between aromatic *ortho*- or *peri*-diamines and anhydrides.

Possible reactions in the condensation of phthalic anhydride with *o*-phenylenediamine can be represented by Scheme 2:

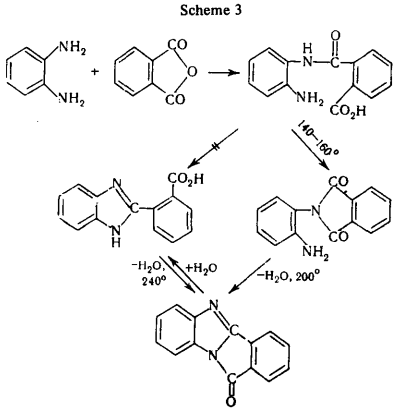
Scheme 2



The reaction products have been described in several papers[2,3,8-10]: depending on the conditions 1,2-benzoylenebenzimidazole (I), *o*-phenylenedibenzimidazole (II), *NN'*-diphthaloyl-*o*-phenylenediamine (III), *o*-benzimidazol-2'-ylbenzoic acid (IV), and *N*-*o'*-aminophenylphthalimide (V) have been isolated. Stetter[11] obtained a substance containing an eight-membered ring (VI) by reaction between phthaloyl chloride and *o*-phenylenediamine. Porai-Koshits and Antoshul'skaya[12] obtained the compounds (II)–(V) by fusing the components in various proportions, and established that compound (III) is formed with the greatest difficulty, whereas (II) and (IV), which contain imidazole rings, are formed more readily. Arient and Marhan found[13] that small quantities of (V) and (VII) are formed initially in methanol at moderate temperatures. At the boiling point only (V) is present in the mixture initially, and the imidazole derivative (IV) is formed. On further heating the composition of the mixture remains almost unchanged: the product contains the two compounds in the approximate proportions 1 : 1.

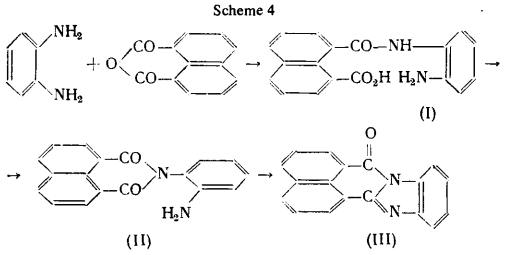
Dawans and Marvel[4] used nuclear magnetic resonance to investigate the products obtained by conducting the reaction in dimethyl sulphoxide: the n.m.r. spectra indicated the presence of a mixture of the final products. It was assumed[4] that competitive formation of the acid (IV) and the amine (V) takes place, one or other product predominating according to the reaction conditions. Colson et al. established[8] that only the amino-imide (V) is formed when *o*-phenylenediamine is heated with phthalic anhydride at 140–160°C for 30 min. Heating this product to 100°C converted it into benzoylbenzimidazole. The latter cannot be formed from the acid (IV) below 240 to 250°C, which is additional evidence for the scheme of cyclisation given by Colson and his coworkers (Scheme 3).

Scheme 3



These results are consistent with those given by Arient[2] showing that *o*-benzimidazolylbenzoic acid is formed only by hydrolysis of 1,2-benzoylenebenzimidazole. If the process takes place in anhydrous medium (in acetic anhydride or in the melt), the reaction halts at the first stage.

Scheme 4



Naphthalic acid reacts with *o*-phenylenediamine in various solvents at temperatures up to 60°C with gradual formation of the amide (I) and from it *N*-*o*-aminophenylnaphthalimide (II). In all cases the final reaction products are the imide (II) and a small quantity of 1,2-naphthoylenebenzimidazole (III).[14] The compound (III) was obtained at higher temperatures. The reaction goes very easily and in quantitative yield[15-17]. 1,2-Naphthoylenebenzimidazole is more stable than 1,2-benzoylenebenzimidazole on prolonged boiling in acid and in alkaline medium. As a consequence, reaction between *o*-phenylenediamine and naphthalic acid ceases at the stage of formation of 1,2-naphthoylenebenzimidazole. On the basis of the above results Scheme 4 has been suggested as the mechanism of the reaction.

Thus it follows from the above results that condensation of aromatic dianhydrides with tetra-amines in anhydrous medium takes place in three successive stages—formation of an amide–amino-acid, cyclisation of the latter to an amino-imide†, and finally conversion of this product into an aroylenebenzimidazole.

†It has been shown recently[18] that the amino-amide is not formed in the reaction of 1,8-naphthylenediamine with phthalic anhydride.

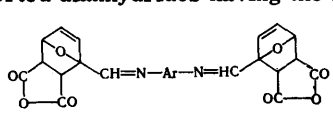
III. SYNTHESIS OF THE POLYMERS

Pyrrones were synthesised by Bell and Pezdirtz [3], Dawans and Marvel [4], the present Reviewers [5], and several other investigators [6-8] almost simultaneously and independently of each other. They used dianhydrides of various *ortho*- and *peri*-tetracarboxylic acids and various tetra-amines (Table 1). In isolated cases the dianhydrides were replaced by the more reactive symmetrical dimethyl dichlorocarbonyl-dicarboxylates, and the stable tetrahydrochlorides have been used instead of readily oxidised tetra-amines.

Table 1. Initial tetra-amines and dianhydrides for the synthesis of pyrrones.

Component	Abbreviation	References
Tetra-amines		
Benzene-1,2,4,5-tetra-amine	BTA	3,4,19-22
Biphenyl-3,3′,4,4′-tetra-amine	BPTA	3,4,5,7,8,19,21, 24-34
4,4′-Oxydiphenylene-1,1′,2,2′-tetra-amine	ODPTA	3,4,8,19,28,31, 34-38
Diphenylmethane-3,3′,4,4′-tetra-amine	DPMTA	19,28,31-34,39
Naphthalene-1,4,5,8-tetra-amine	NTA	4,21,22,40
Benzophenone-3,3′,4,4′-tetra-amine	BOTA	41
p-Phenylenedioxy-4,4′-diphenylene-1,1′,2,2′-tetra-amine	PDODPTA	34;38
Dianhydrides of tetracarboxylic acids		
Pyromellitic	PMDA	3,4,7,8,19,23,27-29, 33,38,39,42-44
Biphenyl-3,3′,4,4′-tetracarboxylic	BPDA	32
4,4′-Oxydiphenylene-1,1′,2,2′-tetracarboxylic	ODPDA	7,34
Benzophenone-3,3′,4,4′-tetracarboxylic	BODA	3,19,28,34,41
Naphthalene-1,4,5,8-tetracarboxylic	NDA	5,20,24-26,31,33, 35,36,40,42,43
Perylene-3,4,9,10-tetracarboxylic	PTDA	5,7,25,31,37
2,8′:2′,8-Dioxy-1,1′-binaphthyl-4,4′,5,5′-tetra-carboxylic	DOBNDA	45

Polymers have been synthesised from dianhydrides of alicyclic tetracarboxylic acids—those of bicyclo[4,2,2]-decane-2,3,7,9-tetracarboxylic acid and its 9-methyl derivative, butane-1,2,3,4-tetracarboxylic acid, and cyclopentane-1,2,3,4-tetracarboxylic acid [33]—and also from hitherto unreported dianhydrides having the structure [26,37,46]



and several others [34].

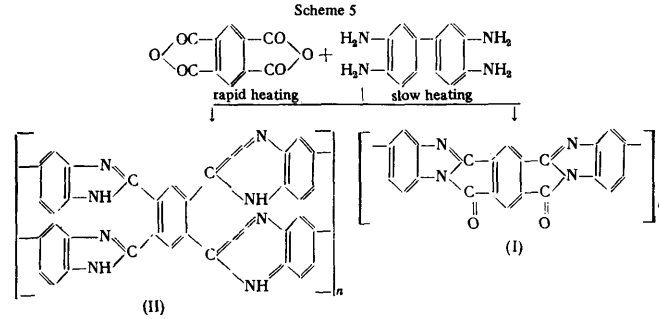
Tetra-amines with spiran structures have also been used for the synthesis [42,43].

Pyrrones have been obtained by conducting the polycondensation in the melt, in the solid phase, and in solution. Two-stage and one-stage methods of synthesis in solution have become most widely used.

1. Polycondensation in the Melt and in the Solid Phase

Polymers have been synthesised from molten pyromellitic dianhydride and various tetra-amines [4]. The mixture of dianhydride and tetra-amine was heated in nitrogen, the temperature being raised gradually to 220°C, and then in a high vacuum at 300–330°C for a few hours. The resulting polymers had predominantly the linear structure (I) (Scheme 5). They were soluble in formic and concentrated sulphuric acids, but in most cases they were insoluble in organic solvents. Their intrinsic viscosity was 0.2–0.5 dl g^{-1}. A rapid rise in temperature during synthesis yields predominantly polymers with network structure (II).

Scheme 5



(II) (I)

Polymers of high molecular weight are formed when the initial reactants are present in equimolecular proportions. Excess of the anhydride increases the yield of polymer (I), but its molecular weight is lower. In most cases the elementary composition of the polymers was consistent with the suggested structure. In order to promote intramolecular cyclisation Dawans and Marvel [4] attempted to dehydrate non-cyclised polymers at low temperatures in the presence of sulphuric acid or acetic anhydride. However, heating with sulphuric acid produced partial sulphonation of the polymer; and in the presence of acetic anhydride (pure or diluted in pyridine) these workers observed acetylation instead of dehydration.

Polymers have been obtained by polycondensation in the solid phase of naphthalene-1,4,5,8-tetracarboxylic dianhydride and biphenyl-3,3′,4,4′-tetra-amine. A mixture of the starting materials was heated under slight applied pressure of nitrogen at 285–295°C for 4 h. The reaction products were cooled in an atmosphere of nitrogen, and dissolved in concentrated sulphuric acid. After supercooling, the logarithmic viscosity of the resulting polymer was 0.22 dl g^{-1}.

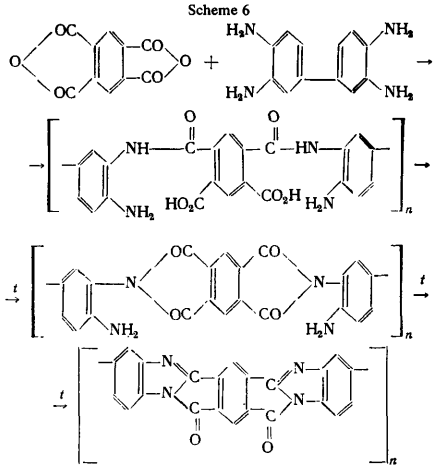
Morgan and Scott [47] have recently proposed a method for preparing polymers of the present type directly at the stage of fabrication into articles. An equimolecular mixture of the dianhydride (of pyromellitic or naphthalene-1,4,5,8-tetracarboxylic acid) and the tetra-amine (biphenyl-3,3′,4,4′-tetra-amine) under high pressure (280 atm) was heated slowly to 450°C in a porous reaction chamber (porous graphite lining). Gaseous and liquid products were driven off under pressure and at a high temperature. The resulting polymers possessed superior mechanical properties and high thermal stability.

2. Polycondensation in Solution

Polycondensation can be conducted in solution in one or two stages. A soluble macromolecular polyamide-amino-acid (PAAA) is obtained in the first stage of the two-stage synthesis. The solvents which have been used are pyridine, dimethyl sulphoxide (DMSO), *NN*-dimethylacetamide (DMAA), *NN*-dimethylformamide (DMFA), 1-methyl-2-oxopyrrolidine [MOP], tetramethylurea, and hexamethylphosphoramide [3-5,31,36,37]. In the second stage the polyamide–amino-acid undergoes polycyclodehydration on heating, with formation of a pyrrone. In the single-stage method the initial reactants are heated to

180–230°C in such solvents as polyphosphoric acid (PPA) or 2,5,8-trioxanonane (diglyme) to yield directly the final polymers.

Scheme 6



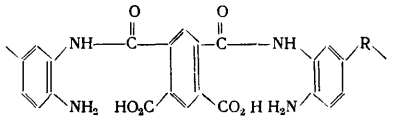
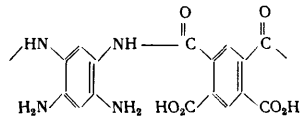
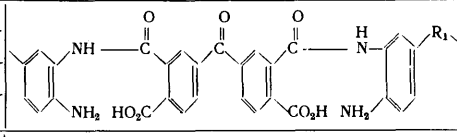
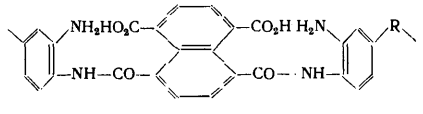
From an investigation of the interaction of model compounds Colson et al.[8] suggested the above sequence of reactions (Scheme 6) in the polycondensation of pyromellitic dianhydride with a tetra-amine.

(*a*) Low-temperature polycondensation—synthesis and properties of polyamide–amino-acids

The first stage in the synthesis of pyrrones—the formation of polyamide–amino-acids—and to a less extent the stage in which polyamino-imides are formed are reversible, so that the molecular weight of the polymers depends on many factors. Low-temperature polycondensation is usually conducted in an aprotic solvent. The optimum reaction temperature depends on the reactivity of the dianhydride used. Acid dianhydrides lie in the sequence—pyromellitic > naphthalene-1,4,5,8-tetracarboxylic > perylene-3,4,9,10-tetracarboxylic— according to their activity in forming polyamide–amino-acids[25,31,36,37]. Such passivation of the dianhydrides in this sequence is due to increasing compensation of the positive charges on the carbon atoms of the anhydride ring by the increasing electron-donating power of the aromatic portion. Polyamide–amino-acids with the highest molecular weights have been obtained from pyromellitic dianhydride at temperatures between −30° and +20°C [27–29,39] and from the naphthalenetetracarboxylic dianhydride at 65–80°C.[24,31,35–37]. The perylenetetracarboxylic dianhydride did not give appreciable yields even when the reactants were heated to 150–160°C. Only on prolonged heating at 170–200°C were partly cyclised polymers obtained[25,31], having composition similar to polyamino-imides (Table 2).

The Reviewers have recently been able to lower considerably the temperature of the first stage by using lithium salts. On investigating the synthesis of polyamide–amino-acids from naphthalenetetracarboxylic dianhydride and the tetra-amine of diphenyl ether they

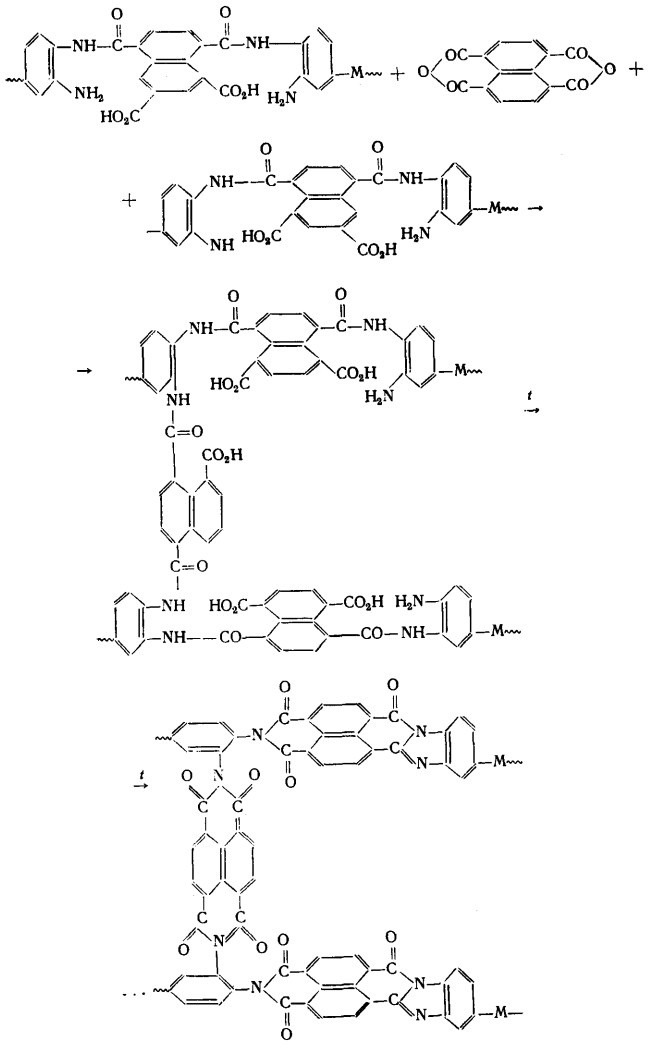
Table 2. Polyamide–amino-acids obtained by low-temperature polycondensation.

Initial components		Repeating unit	Synthesis conditions			Viscosity	Ref.
dianhydride	tetra-amine		R	temp., °C	solvent		
PMDA	BPTA		—	20	DMFA	0.81–0.99[a]	19, 27
	BPTA, 4HCl		—	20	DMAA	0.47[a]	19
	ODPTA		—O—	20	DMFA	0.25[b]	4
				20	DMAA	0.59[a]	19
	DPMTA		$-CH_2-$	20	DMAA	0.74[a]	19
				−20÷+30	DMFA	—	39
Dimethyl 4,6-dichloro-carbonyl-isophthalate	BTA		—	20	DMSO	0.25[c]	8
	BTA, 4HCl		—	20	DMSO	0.77[a]	19
BODA	BPTA		—	20	DMFA	1.45[a]	19
	ODPTA		—O—	20	DMAA	1.11[a]	19
	DPMTA		$-CH_2-$	20	DMAA	0.72[a]	19
	BOTA		—CO—	20	DMFA	0.43[d]	19
NDA	BPTA		—	75	DMSO	0.43[d]	31
	ODPTA		—O—	75	DMSO	0.79[d]	31
				80	DMFA	0.59[r]	
	DPMTA		$-CH_2-$	75	DMSO	0.36[d]	31

[a]Intrinsic viscosity at 25°C in solvent used for synthesis. [b]Specific viscosity of 0.5% solution in formic acid at 20°C. [c]Intrinsic viscosity in DMSO at 30°C. [d]Specific viscosity of 1% solution in DMFA at 25°C.

established[31,36,37] that up to 50°C the viscosity of the reaction solution increases very slowly and does not exceed 0.2 dl g^{-1}, over the range 65–80°C the increase accelerates considerably, and when the temperature is raised to 100°C individual amino-imide fragments are formed as a result of cyclisation in the chain of the polyamide–amino-acids. This sequence and the rate of addition of the reactants have a substantial effect on the rate of increase in the molecular weight of the polyamide–amino-acids.

Scheme 7



The same factors govern the possibility and time of gel formation. With slow addition of a dianhydride to a solution of a tetra-amine the rate of increase in the molecular weight of the polyamide–amino-acids is small, since transamination plays an important role in this case. Gel formation is observed in the later stages of polycondensation[36]. The time to gel formation decreases with increase in the temperature, the rate of increase in molecular weight of the polyamide–amino-acids, and also the local concentration of dianhydride in the solution. Gels are partly soluble in aprotic solvents and to a considerable extent in concentrated sulphuric acid. On prolonged standing they pass into a product which swells but is insoluble in sulphuric acid. The gels differ little in composition from soluble polyamide–amino-acids, and like the latter have an amorphous structure.

High-temperature cyclisation of a gel, in contrast to the soluble polyamide–amino-acids, yields polymers which are insoluble in sulphuric acid[36]. The main reaction in which polyamide–amino-acids are formed can evidently be accompanied by a secondary reaction between the dianhydride and amino-groups in the chain of the resulting polyamide–amino-acid. Although the basicity and hence the reactivity of these groups is low, the probability of their interaction with the dianhydride increases in the later stages of polycondensation, when little free tetra-amine and few reactive terminal amino-groups are present (Scheme 7).

The intensity of transamination and the probability of secondary reactions leading to gel formation depend significantly on the basicity of the tetra-amine and the reactivity of the dianhydride. Thus addition of pyromellitic dianhydride to a solution of a tetra-amine leads in all cases to the formation of a large quantity of gel. When the solutions are mixed in the opposite sequence, the whole of the polymer is instantly precipitated as a gel. When naphthalene-1,4,5,8-tetracarboxylic dianhydride and various tetra-amines are added together, gel formation is observed only after 2–6 h.[31,36]

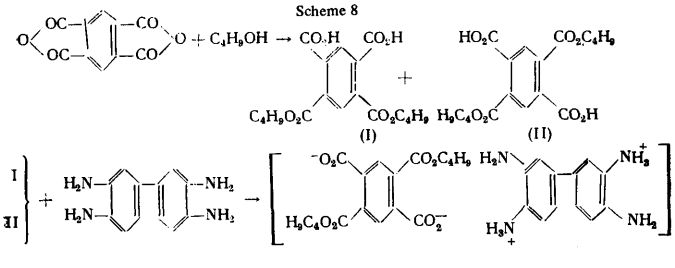
Tetra-amines of low basicity, e.g. bis-3,4-diaminophenyl sulphone, play an active part in transamination. However, their use diminishes the difference in basicity between terminal amino-groups and those in the chain of the polyamide–amino-acids, which favours intermolecular cross-linking of the chains. By using inorganic salts the Reviewers have been able also to vary the optimum conditions for the synthesis of polyamide–amino-acids of high molecular weight and eliminate the possibility of gel formation.

Korshak and his coworkers[39] also observed fairly rapid gel formation at room temperature in the polycondensation of pyromellitic dianhydride with diphenylmethanetetra-amine. A linear product could be obtained by lowering the temperature of the synthesis to between −20° and −30°C. Polycondensation at a high temperature leads to partial imidisation. The temperature at which this latter process begins in an aprotic solvent is determined by the nature of the dianhydride and of the tetra-amine.

Imidisation is accompanied by the separation of a certain amount of water, in whose presence of dianhydride is converted into the less reactive tetracarboxylic acid. A slight (1–2%) excess of the dianhydride is necessary to restore equivalence. Further increase in the excess (above 2%) of pyromellitic dianhydride in the reaction with tetra-amines leads to increased viscosity of the polyamide–amino-acids and rapid gel formation[19]. The synthesis of polyamide–amino-acids from naphthalene-1,4,5,8-tetracarboxylic dianhydride and tetra-amines is characterised by a diminution in viscosity when the excess of dianhydride exceeds 2%.[36] A fall in viscosity is observed also when excess of the tetra-amine is used (Scheme 8).

Bell[48] achieved strict equimolecularity of the components by first obtaining the salts from *m*- or *p*-dialkyl pyromellitates and the tetra-amines:

Scheme 8



Heating these salts in dimethylacetamide gave polymers having predominantly the structure of polyamide–amino-acids. Heating the dry salt in a vacuum or in an inert atmosphere yielded polybenzimidazopyrrolones.

The best solvents for the reaction are dimethylacetamide, dimethyl sulphoxide, and 1-methyl-2-oxopyrrolidine [31,36,37]. The reduced viscosity of polyamide–amino-acids depends on the concentration of the reactants. The presence of moisture in the solvent lowers the viscosity of the resulting precondensates.

Easily oxidisable tetra-amines, e.g. benzene-1,2,4,5-tetra-amine, have been replaced by their stable tetrahydrochlorides for polycondensation with dianhydrides [3,19]. A solution of pyromellitic dianhydride was added over 2–20 h to a suspension of the tetrahydrochloride in the presence of an acceptor for hydrogen chloride. The resulting polymers were identical in structure and properties with those obtained by other methods. Bell and Jewell [19] replaced the dianhydride, which reacts very slowly with tetra-amine tetrahydrochlorides, by dimethyl 4,6-dichlorocarbonylisophthalate. In this case tertiary amines are ineffective as acceptors of hydrogen chloride, while use of the free amine leads to precipitation of the polymer.

Polyamide–amino-acids are coloured (pale yellow to brown) powders soluble in aprotic solvents. Keeping dilute (1–2%) polymer solutions at 20°C decreases the viscosity of the polyamide–amino-acids. A more substantial fall in viscosity occurs in a moist solvent. Gel formation was observed on the prolonged storage of 10% solutions of polyamide–amino-acids (from naphthalene-1,4,5,8-tetracarboxylic dianhydride and 4,4′-oxydiphenylene-1,1′,2,2′-tetra-amine). [36]

Available data on the molecular-weight characteristics of polyamide–amino-acids usually consist merely of an indication of the intrinsic or the reduced viscosity. Osmometric measurements on polymers obtained from pyromellitic dianhydride and certain tetra-amines gave molecular weights of 7000–20 000, while the intrinsic viscosity was 0.4–1.5 dl g^{-1} (in dimethylformamide at 25°C) [19,30].

Most polyamide–amino-acids form strong transparent films when their solutions are evaporated. Polymers having intrinsic viscosity $\geqslant 0.4$ dl g^{-1} are suitable for the preparation of films. The strength of films dried at 125°C (obtained from pyromellitic dianhydride and tetra-amines) is 700–1050 kgf cm^{-2}, their relative elongation 25–35%, and the modulus of elasticity 14 000–28 000 kg cm^{-2}. [29,30] The tensile strength of the polyamide–amino-acid films based on naphthalene-1,4,5,8-tetracarboxylic dianhydride and tetra-amines was 850–950 kgf cm^{-2}. [31,36] These films usually contained 9–12% of solvent.

(*b*) Transformation of polyamide–amino-acids

The conversion of polyamide–amino-acids into pyrrones represents the second stage of polycondensation, and consists in intramolecular polydehydration accompanied by formation of a polyaminoimide and then the final polymer. Polycyclisation is accomplished by heat-treating the polyamide–amino-acid films or powders in a vacuum or in an inert atmosphere, and also by heating their solutions in polyphosphoric acid. Heating involved raising the temperature either smoothly or in steps to 200–400°C and maintaining the polymers at these temperatures.

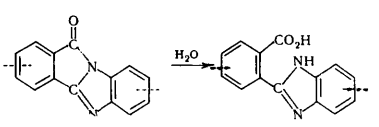
Thermogravimetric analysis proved to be unsuitable for the kinetic study of the polydehydration of films [3,35], since the solvent forms with the polyamide–amino-acid a complex which decomposes at temperatures corresponding to the start of cyclisation of the acid. The thermogravimetric method has been used to investigate the kinetics of the cyclodehydration of various polyamide–amino-acid powders (formed by biphenyl-3,3′,4,4′-tetracarboxylic dianhydride with biphenyl-3,3′,4,4′-tetra-amine, 4,4′-oxydiphenylene-1,1′,2,2′-tetra-amine, and diphenylmethane-3,3′,4,4′-tetra-amine respectively; and by biphenyl-3,3′,4,4′-tetra-amine with the dianhydrides of pyromellitic and naphthalene-1,4,5,8-tetracarboxylic acids). [32,33] Cyclodehydration is found to be of first order [32] and to occur in two stages [33].

Cyclisation has been studied by infrared spectroscopy [3,8,24,31,41,44,50,51]. Polyamide–amino-acids obtained from pyromellitic dianhydride and tetra-amines show characteristic absorption bands due to secondary amides in the region of 1660, 1650, 1540, 1505, 1305, and 1280 cm^{-1}, bands in the region of 1720 and 1605 cm^{-1} due to the presence of carboxy-groups, and bands in the range 3200–3400 cm^{-1} due to amino- and imino-groups. On cyclisation of these acids absorption appears at 1710 and 1720 cm^{-1}, which is characteristic of imide rings, absorption at 1310 cm^{-1} due to the presence of a tertiary nitrogen atom, and a band at 1470 cm^{-1} characteristic of C=N stretching vibrations.

Similar changes in the infrared spectra on passing from polyamide–amino-acids to the final polymers were on the whole observed with naphthalenetetracarboxylic and several other dianhydrides [24,31,50,51]. The most characteristic aspect of the transition to the final polymers is the preservation of only one intense band, usually in the range 1695–1720 cm^{-1}, and the absence of the other bands between 1680 and 1800 cm^{-1} which are characteristic of the unfinished polymers. This is consistent with the infrared spectra of corresponding model compounds.

The retention of other bands (at 1775, 1760 cm^{-1}, etc.) on the cyclisation of polyamide–amino-acids based on *oo′*-tetracarboxylic dianhydrides and *oo′*-tetra-amines [41] probably indicates that they are difficult to cyclise in comparison with those based on the corresponding *peri*-compounds.

Pravednikov et al. showed [44] that heating at 150–160°C polyamide–amino-acid films obtained from pyromellitic dianhydride and tetra-amines yields mainly polymers of amino-imide structure. At these temperatures, however, the rate of formation of imide rings is low, and the degree of conversion rapidly reaches a limiting value. Raising the temperature to 200°C did not effect complete cyclisation of the polyamide–amino-acids. This is due to entropy factors (increasing rigidity of the polymer chains) [8,35,52] and also to the possibility that carboxybenzimidazole repeating units may be formed from units in the final structure as a result of hydrolysis by water liberated during cyclisation [8]:

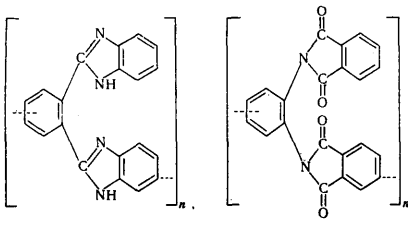


A high degree of conversion of polyamide–amino-acids into the final polymers was achieved at 250–400°C. The

infrared spectra and the elementary composition of polyamide–amino-acid films and powders obtained from naphthalenetetracarboxylic dianhydride and tetra-amines showed, after vacuum heat-treatment, that cyclisation was almost complete at 300–350°C.[31,36,40]

Cross-linking may occur in this temperature range, with the formation of a certain amount of insoluble polymers[31,36]. The intensity of intermolecular cross-linking depends on the mobility of the molecular chains, and is minimal with polymers containing no $-CH_2-$ or $-O-$ hinge groups. A certain quantity (< 5%)of units probably remain uncyclised at these temperatures, and they do not appear in the infrared spectra.

Korshak et al.[34,53] obtained polyimides containing pendant arimide groups attached to the main chain by the interaction of polyamide–amino-acids in solution with anhydrides of aromatic dicarboxylic acids and subsequent heat-treatment. Reaction of polyamide–amino-acids with *o*-phenylenediamine in polyphosphoric acid gave polybenzimidazoles containing benzimide pendants on the main chain of the polymer



(*c*) High-temperature polycondensation in solution

High-temperature polycondensation differs from the low-temperature process in occurring at 115–240°C and yielding polymers predominantly of amino-imide or aroylenebenzimidazole structure. The solvents used were molten phenol, pyridine, dimethylacetamide, dimethyl sulphoxide, 1-methyl-2-oxopyrrolidine, 2,5,8-trioxanonane, and polyphosphoric acid.

Dawans and Marvel[4] heated pyromellitic dianhydride and biphenyl-3,3′,4,4′-tetra-amine in boiling pyridine for 70 h to obtain a 90% yield of a polymer (with $[\eta]_{H_2SO_4}$ = 0.65 dl g^{-1}) corresponding in structure to a polyaminopyromellitimide. Heating the product in a vacuum to 300°C gave a pyrrone. A partly cyclised polymer of higher molecular weight ($[\eta]$ = 0.94 dl g^{-1}) was obtained by heating the reactants in dimethylacetamide at 160°C. Heating the starting materials in a mixture of 2,5,8-trioxanonane and pyridine to 240°C yielded a polymer having a high degree of cyclisation.

Polymeric products, which according to their infrared spectra and elementary composition were similar in structure to a polyaminoimide, were obtained by the reaction of perylenetetracarboxylic dianhydride with biphenyltetra-amine, and also with oxydiphenylenetetra-amine or with diphenylmethanetetra-amine in 1-methyl-2-oxopyrrolidine or dimethyl sulphoxide at 160–200°C, and also in boiling dimethylacetamide[5,7,25,31,37]. They were not soluble in organic solvents, but dissolved in concentrated sulphuric acid and in polyphosphoric acid. The polymers were cyclodehydrated by heating in a vacuum at 350°C.[25,31]

Conducting the single-stage synthesis of pyrrones in polyphosphoric-acid solution enables aromatic tetra-amines that are relatively unstable in air to be replaced by their stable salts, and hence the required proportions of the components to be maintained extremely accurately. Pyrrones with a high degree of cyclisation and the highest molecular weights are obtained in polyphosphoric acid[5,21,24]. Departure from equimolecular proportions of the initial components results in a decrease in the molecular weight of the resulting pyrrones[4,31,36], in contrast to what happens in aprotic solvents.

The temperature of polycondensation in polyphosphoric-acid solution was usually 180–220°C (Table 3). Dawans and Marvel[4] obtained polybenzimidazopyrrolones in this solvent by heating tetra-amine tetrahydrochlorides with pyromellitic dianhydride at 200°C for 2–40 h. The concentration of the reactants was 0.6–3.0 wt.% based on the solvent. The resulting polymers were infusible powders, insoluble in organic solvents but soluble in concentrated sulphuric acid and in polyphosphoric acid. Berlin and his coworkers[5,24,25,31,35–37], as well as Van Deusen et al.[20–21,40], prepared polynaphthoylenebisbenzimidazoles from naphthalenetetracarboxylic dianhydride and tetra-amines. The viscosity (Table 4) and the solubility of the polymers obtained are affected not only by the final temperature of the synthesis but also by the rate of rise in temperature. The optimum temperature is 200–210°C.[31,37] The most rapid rise in viscosity occurs during the first 2 h, after which the rate of rise in viscosity is very small; the reaction can be regarded as almost complete after 6–8 h.

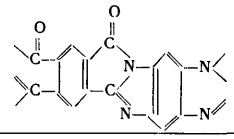
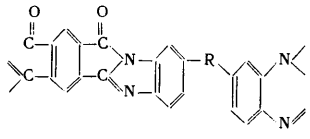
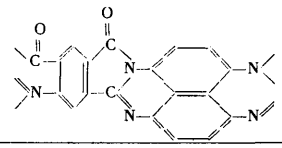
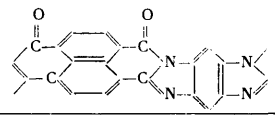
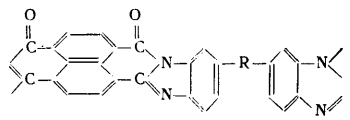
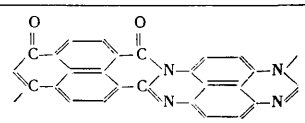
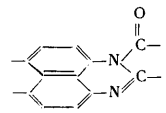
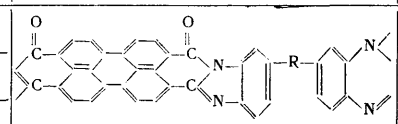
The polymers are soluble in concentrated sulphuric, 85% phosphoric, polyphosphoric, benzenesulphonic, and methanesulphonic acids. They do not decompose on being heated to 320–425°C (the temperature limits of the apparatus)[20,24]. Polymers based on naphthalenetetracarboxylic dianhydride and biphenyltetra-amine dissolve relatively slowly. Solutions of 5–10% concentration have been obtained at ~ 100°C. With polymers based on the same dianhydride and oxydiphenylenetetra-amine or diphenylmethanetetra-amine 5–6% solutions in sulphuric acid can be obtained at room temperature[20]. A method has been worked out for improving the solubility of the polymers by freeze-drying the moist products. This has enabled a porous polymer to be obtained, which is consequently more readily soluble.

Heating pyrrones in a vacuum above the temperature of their synthesis in polyphosphoric acid increases their molecular weight[20,31,37], probably owing to solid-phase polycondensation at the terminal groups. Thus when polynaphthoylenebisbenzimidazole ($[\eta]$ = 0.9 dl g^{-1}) was heated in a vacuum at 215°, 250°, 275°, 300°, and 325°C for 4 h, the intrinsic viscosity of the polymer increased to 1.3 dl g^{-1}; no products insoluble in concentrated sulphuric acid were formed[31,37].

Pyrrones obtained from naphthalenetetracarboxylic dianhydride and a series of tetra-amines possess fibre-forming properties[21,54,55]. X-Ray examination of the polymers shows them to be either amorphous or polycrystalline materials.

Berry and Fox[51] succeeded in reducing a polynaphthoylenebisbenzimidazole (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) with dithionite in aqueous pyridine solution. The soluble polymer obtained oxidised readily in the air. The scattering of a laser beam was used to measure the molecular weights of various fractions of the polymer (M = 81 000–167 000 for $[\eta]$ = 2.02–5.48 dl g^{-1}).

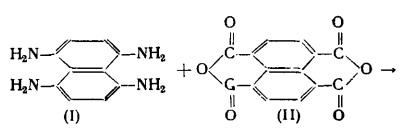
Table 3. Pyrrones obtained by high-temperature polycondensation in solution.

Initial components: dianhydride	Initial components: tetra-amine	Repeating unit	Synthesis conditions: R	Synthesis conditions: temp., °C	Synthesis conditions: solvent	Additional heat-treatment, °C	[Viscosity] in conc. H_2SO_4	Ref.
PMDA	BTA, 4HCl		—	200	PPA	—	1.10	4
PMDA	BPTA, 4HCl		—	160	diglyme or DMAA	—	0.71—0.94[a]	4
PMDA	BPTA		—	200	PPA	—	1.25—1.80[b]	4
PMDA	ODPTA		—O—	200	PPA	—	1.26	4
PMDA	NTA		—	230—300	diglyme	—	0.34—0.41	4
NDA	BTA		—	190—220	PPA	—	0.34—0.90 5	20, 22, 40
NDA	BPTA, 4HCl		—	110—200	PPA	300	0.57—1.90	5, 20, 24, 31
NDA	ODPTA, 4HCl		—O—	200	PPA	300	1.10	31, 35
NDA	DPMTA		—CH_2—	200	PPA	300	1.40	31, 35
NDA	NTA		—	180	diglyme	350	0.15[c]	40
Dimethyl 4,5-diaminonaphthalene-1,8-dicarboxylate			—	100—250	PPA	—	0.08—0.25	40
4,5-Diaminonaphthalene-1,8-dicarboxylic anhydride			—	100—250	PPA	—	—	21, 40
PTDA	BPTA, 4HCl		—	230	PPA	350	0.21	25, 31
PTDA	BPTA		—	160—175	DMSO DMAA	350	0.32	25, 31
PTDA	ODPTA		—O—	185—190	MOP	350	0.06	31
PTDA	DPMTA		—CH_2—	185—190	MOP	350	0.07	31

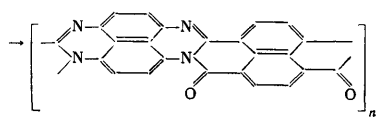
[a]Logarithmic viscosity of 0.25% solution in concentrated sulphuric acid. [b]Intrinsic viscosity measured in DMSO. [c]Logarithmic viscosity in 97% H_2SO_4 at 30°C (0.3 g/100 ml).

The polycondensation of naphthalene-1,4,5,8-tetraamine (I) with naphthalene-1,4,5,8-tetracarboxylic dianhydride (II) and the homopolycondensation of dimethyl 4,5-diaminonaphthalene-1,8-dicarboxylate (III) or the anhydride of the acid (IV) gave polymers (polyperimidinetetrayls) of completely ladder structure[38]:

Scheme 9



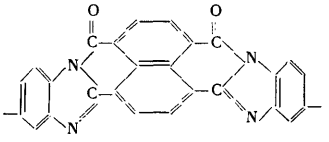
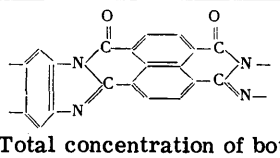
(I) (II)



Since (I) could not be isolated in the free state, it was prepared by catalytic reduction in 2,5,8-trioxanonane, and the dianhydride was added to the resulting solution. The polycondensation was conducted in an atmosphere of nitrogen at 180°C for 12 h; after the trioxanonane had been removed, the polymer was heated in a vacuum at 350°C for 2 h (Table 5). Elementary analysis and infrared

spectroscopy indicated that the polymers were not completely cyclised, which is explained by incomplete reduction of tetranitronaphthalene or oxidation of (I) during polycondensation.

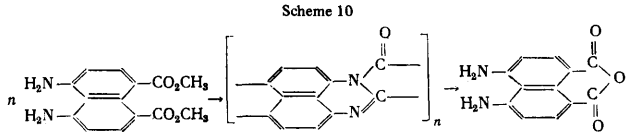
Table 4. Conditions of polycondensation in polyphosphoric acid and viscosity of resulting polymers [20,31].

Repeating unit	Monomer concn., M*	Reaction conditions: temp., °C	Reaction conditions: time, h	Viscosity in conc. H_2SO_4 η
	0.40	110—120	18	0.57
	0.22	180—190	20	1.35
	0.40	200—220	3.5	0.75
	0.12	195—200	8	1.1
	0.12	205—210	8	1.8
	0.20	100—130	18	0.28
	0.18	180—190	20	0.63
	0.13	190—195	24	0.90
	0.19	200—220	4.5	0.34

*Total concentration of both monomers in polyphosphoric acid.

The difficulties associated with the instability of (I) are eliminated by effecting the polycondensation of (III) or (IV) in polyphosphoric acid at 100–250°C:

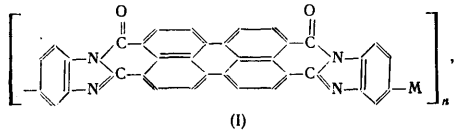
Scheme 10



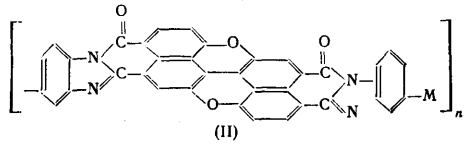
(III) (IV)

Polymers obtained from (III) are soluble in concentrated sulphuric acid. Their elementary composition agrees satisfactorily with calculation. Polymers obtain by the polycondensation of (IV) did not dissolve in concentrated sulphuric acid.

The polycondensation in polyphosphoric acid of the dianhydrides of perylenetetracarboxylic [5,25,31,37] and of 2,8′:2′,8-dioxy-1,1′-binaphthyl-4,4′,5,5′-tetracarboxylic [45] acids with aromatic tetra-amines yields polyaroylenebisbenzimidazoles having the structures



(I)



(II)

The polymer (V) (M absent, $[\eta] = 0.2–0.3$ dl g^{-1}) was obtained by heating the initial components in polyphosphoric acid to 230°C and maintaining this temperature for 16 h.

When other tetra-amines (M = O, CH_2) were used, the polymers (V) were obtained in low yields and having a smaller value of $[\eta]$. Polymers of structure (VI) (with M absent or representing CH_2) were synthesised at 200 to 210°C. With rise in the temperature and increase in the duration of the synthesis the molecular weight of the polymers (VI) ($[\eta] = 0.6$ dl g^{-1}) increased, but at the same time the yield of insoluble products also increased.

Table 5. Conditions of synthesis and properties of polyperimidinetetrayls [40].

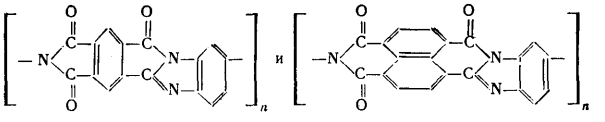
Initial components	Solvent	Temp., °C	Colour of polymer	Logarithmic viscosity**
I + II	diglyme	180 350*	blue	0.15
III	PPA	200	dark blue	0.25
IV	PPA	100	yellow	—
	PPA	200	brown	—

*Temperature of vacuum heat-treatment.
**0.3 g in 100 ml of 97% H_2SO_4 at 30°C.

Pyrrones have been obtained also by using for polycondensation in polyphosphoric acid (at 200°C for 8 h) dianhydrides of bisadducts of diene synthesis between maleic anhydride and various bisfuran compounds [26,37,56].

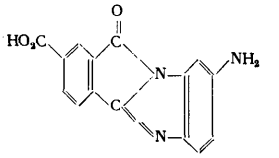
(*d*) Synthesis of polymers akin to pyrrones

D'Alelio and Kieffer [57] obtained high-viscosity polyimidazopyrrolone–imides by the polycondensation of benzene-1,2,4-triamine with the dianhydride pyromellitic and benzophenonetetracarboxylic acids in dimethylacetamide solution followed by thermal cyclisation of the precondensates. The use of naphthalenetetracarboxylic dianhydride gave polymers of very low molecular weight (~ 0.1 dl g^{-1}). The polycondensation of benzene-1,2,4-triamine or its dihydrochloride with pyromellitic or naphthalenetetracarboxylic dianhydride in polyphosphoric acid at 180°C for 12–14 h yielded the polymers



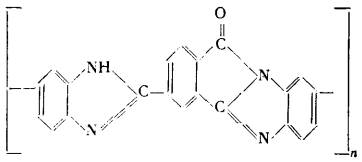
having intrinsic viscosities of 0.63 and 0.88 dl g^{-1} respectively.

The reaction of benzene-1,2,4-triamine with trimellitic anhydride in dimethylacetamide or polyphosphoric acid gave only products of low viscosity, which was attributed to formation of the unreactive compound



Polymers of higher molecular weight ($[\eta] = 0.29–0.45$ dl g^{-1}) have been obtained from trimellitoyl chloride and benzene-1,2,4-triamine in the above solvents in the

presence of triethylamine as acceptor of hydrogen chloride. Polymers ($[\eta] = 0.51$ dl g^{-1}) with the structure



have been obtained by the polycondensation of trimellitic anhydride with biphenyl-3,3′,4,4′-tetra-amine in polyphosphoric acid [57,58].

Copolymers of imidoaroylenebenzimidazole structure were obtained by copolycondensation of the naphthalenetetracarboxylic dianhydride and the biphenyltetra-amine with benzidine or *pp*′-oxydianiline [ODPDA]. [31,59] Various molar proportions of dianhydride, diamine, and tetra-amine (1 : 0.2 : 0.8, 1 : 0.5 : 0.5, 1 : 0.8 : 0.2) were used to synthesise the copolymers. Their synthesis was accomplished either in two stages or as a single-stage process in polyphosphoric acid. The first stage in the two-stage synthesis involved heating the mixture of dianhydride, diamine, and tetra-amine in dimethylacetamide, dimethyl sulphoxide, or 1-methyl-2-oxopyrrolidine at 75–85°C for 6 h. Subsequent vacuum heat-treatment of the precondensates at 200–300°C effects their intramolecular cyclisation to form copolymers of block-ladder imidoaroylenebenzimidazole structure. In the single-stage method polycondensation was conducted in polyphosphoric acid at 200°C for 8 h. Owing to the difference in activity between diamines and tetra-amines the composition of the copolymers differed from that of the initial mixture. The final copolymers were dark, amorphous powders, soluble in polyphosphoric, sulphuric, and formic acids but insoluble in organic solvents. Their intrinsic viscosity was 0.2–0.6 dl g^{-1}.

IV. PROPERTIES OF THE POLYMERS

1. Thermal Stability

The main property which first attracts the attention of research workers to pyrrones is their high heat-resistance and thermal stability. Despite the heightened interest in such polymers, only isolated papers have hitherto been specially concerned with a detailed investigation of their thermal stability. In most publications, however, the thermal stability of the pyrrones obtained is measured by thermogravimetric curves determined with different rates of temperature rise. This makes it difficult to compare the thermal stability of pyrrones differing in structure. Furthermore, very little information is given on the chemistry of the processes occurring in the polymers at high temperatures in oxidising and inert atmospheres and also in a vacuum.

Several workers [60–63], who have investigated the mechanism of the degradation of polymers containing heterocycles in the main chain (polyimides, polybenzimidazoles, polyoxadiazoles, etc.), associate the thermal stability of the polymers mainly with the stability of the heterocycles. This takes no account of the specific natures of the polymers examined, which are governed by the presence of a system of conjugated bonds extending through large sections of the macromolecular chain and by the presence of paramagnetic centres whose structure does not remain constant over a wide temperature range [64,65,67].

Dawans and Marvel [4] used a dynamic thermogravimetric method to study thermal degradation, and showed that polybenzimidazopyrrolones based on pyromellitic dianhydride are stable in an atmosphere of nitrogen up to 450 to 500°C; at 800–900°C they undergo a loss in weight of 25–40%. In air these polymers are oxidised fairly rapidly at 350–400°C. The thermal stability of pyrrones prepared in polyphosphoric acid is superior to that of the same polymers obtained in two stages and in the melt (Fig. 1)‡. The presence of intermediate methylene or oxygen links in the macromolecular chain leads to some diminution in the thermal stability of the polymers (Figs. 2 and 3). Polybenzimidazopyrrolones based on benzophenonetetracarboxylic acid show thermal stability as good as that of the corresponding polymers based on pyromellitic dianhydride (Fig. 3).

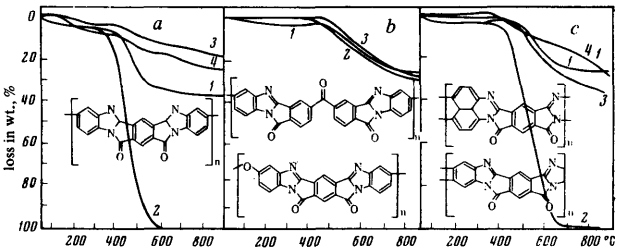
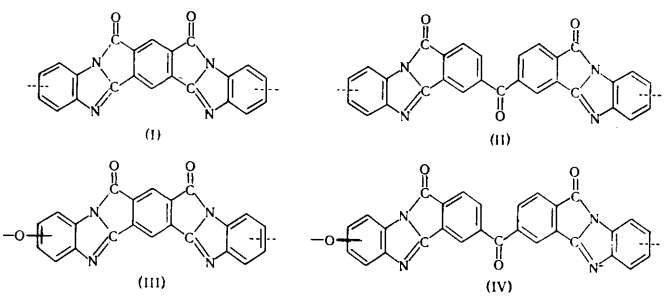


Figure 1. Thermogravimetric curves (rate of rise in temperature $\Delta T = 6$ deg min^{-1}) obtained in air for polymers prepared in: *a*) 1) melt; 2) melt (curve in nitrogen); 3) PPA soln.; 4) two stages; *b*) 1) melt; 2) melt; 3) PPA soln.; *c*) 1) melt; 2) melt (curve in nitrogen); 3) melt; 4) PPA soln.

In a study of the thermal degradation under isothermal conditions of films of the pyrrones



Jewell found [66] that the initial losses in weight were due to removal of absorbed moisture (~ 7 wt. % up to 100–150°C) and to further intramolecular cyclisation. Films which had been preheated at 350°C for 2 h did not lose weight until progressive decomposition of the polymer occurred, which began above 400°C (Fig. 4).

‡Pyrrones obtained in the melt under high pressure possess enhanced thermal stability in air and in an inert atmosphere [47].

The effective activation energy of thermo-oxidative degradation, calculated for the polymers (I)–(IV) from the constant-rate sections over the range 440–460°C, was respectively 31, 34, 28, and 30 kcal mole^{-1}. The authors concluded from the results of differential thermal analysis that the polymers had undergone no phase transitions.

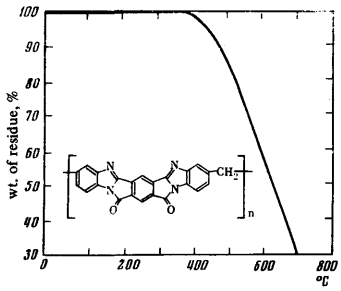


Figure 2. Thermogravimetric curve (ΔT = 4 deg min^{-1}) in air.

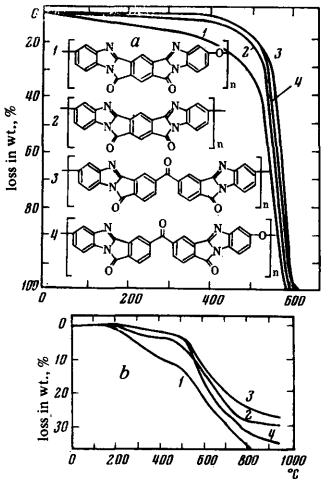


Figure 3. Thermogravimetric curves for pyrrone films (ΔT = 5 deg min^{-1}) in: *a*) air; *b*) vacuum.

When the polymers are heated in a vacuum, the main losses in weight are observed during the initial period of degradation, after which the weight of the residue tends to a limiting value. The total losses in weight of the pyrrones investigated are 28–38 wt. % up to 800°C. The activation energy for degradation of the polymers (I)–(IV) in a vacuum is 47–50 kcal mole^{-1}.

Examination of the products of the degradation of polymer (II) showed that up to 380°C the losses in weight are due to the removal of water. Above 420°C a successive increase in the rate of degradation is observed; it reaches a maximum at 550°C, and drops rapidly at temperatures above 620°C. A large quantity of carbon monoxide and dioxide is evolved in this temperature range. At about 500°C –NCN–groups are also eliminated. With rise in temperature to 650°C these are accompanied by CN– and HCN– groups. Evolution of traces of ammonia is observed only during the main decomposition of the polymer. Thus dehydration occurs in the initial period, and this is followed by thermal rupture of bonds in the macromolecular chain.

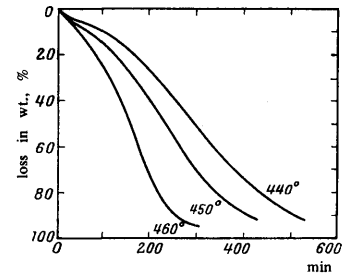


Figure 4. Thermogravimetric curves for pyrrone film (BODA–BPTA) in air.

An investigation of thermo-oxidative degradation undertaken by the Reviewers [5,24,31,35,67] and also by Van Deusen and his coworkers [6,20,40] indicates that polynaphthoylene-bisbenzimidazoles are more stable than the corresponding polyimides and also than pyrrones based on pyromellitic dianhydride (Fig. 5) Their resistance to thermo-oxidative degradation is found to depend, up to a certain limit, on the molecular weight, which is probably an effect of the terminal groups. A particularly substantial decrease in stability was observed with polymers of low molecular weight: when $[\eta]$ = 0.37 dl g^{-1}, progressive breakdown began at a temperature 75 deg lower.

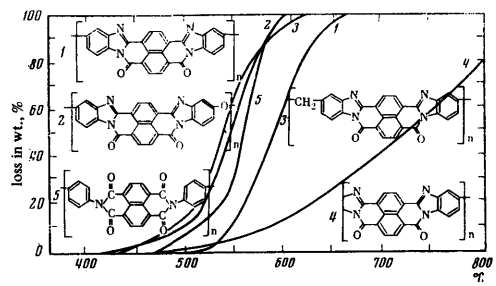


Figure 5. Thermogravimetric curves in air with ΔT = 2 deg min^{-1} (2.5 deg min^{-1} for curve 4).

In a vacuum or in an inert atmosphere the polymers lose 18–30% in weight when heated to 800–900°C. The influence of molecular weight is considerably less evident under these conditions, but even in this case polymers having low molecular weights begin to lose weight at lower temperatures. Polymers obtained from naphthalene-tetracarboxylic dianhydride and biphenyltetra-amine, having intrinsic viscosities of 0.8–1.15 dl g^{-1}, do not

decompose at all when heated in nitrogen to 600°C (Fig. 6), whereas a similar polymer of viscosity 0.12 dl g^{-1} loses up to 10 wt.%. Polymers of completely ladder structure obtained from naphthalenetetracarboxylic dianhydride and benzenetetra-amine, lose 4 wt.% under the same conditions. Several authors [52] explain the lower thermal stability of polymers of ladder structure, probably correctly, by the absence of extensive polyheterocyclisation on rigid macromolecules, i.e. by the presence of a large number of defects.

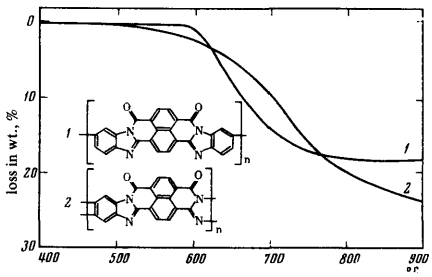


Figure 6. Thermogravimetric curves in nitrogen (ΔT = 2.5 deg min^{-1}).

Differential thermal analysis of a polynaphthoylenebisbenzimidazole (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) (Fig. 7) has shown [31] that reactions involving complicated intra- and intermolecular rearrangements occur when the polymer is heated in an inert atmosphere, in an inert atmosphere contaminated with air, and in air. Heating the polymer to 110–120°C reveals an endothermic peak, indicating the evolution of 4–5% of adsorbed water. Raising the temperature to 270–330°C leads to cyclisation of the repeating units that have remained uncyclised, accompanied by the appearance of an exothermic peak on the curves. Further heating of the polymer in air to 540°C and in argon to 655°C produces insignificant losses in weight, but above these temperatures the specimen breaks down rapidly in air, and loses up to 20–25 wt.% in an inert atmosphere. Breakdown of the polymer is accompanied by cross-linking. The most favourable conditions for carbonisation occur in an inert atmosphere. In air and even with a low oxygen content (7%) degradative processes predominate over cross-linking processes, resulting in progressive weight losses by the polymer.

Tests on the isothermal aging of pyrrones (from naphthalenetetracarboxylic dianhydride and biphenyltetra-amine) showed that they lost only 10 wt.% after being heated in air at 315°C for 1500 h. [20] At 400°C the weight losses for a polymer of the same type do not exceed 10% after 7–8 h.

A kinetic study of the thermo-oxidative degradation of this polymer has been made over the range 450–570°C (Fig. 8). [31,67] The process is clearly autocatalytic in character. The effective activation energy, calculated for sections having a constant rate, is 28.8 kcal $mole^{-1}$ in the temperature range 470–502°C. At higher temperatures the process takes place without an induction period, and its activation energy falls to 7.4 kcal $mole^{-1}$, which indicates a change in the mechanism of thermo-oxidative degradation,

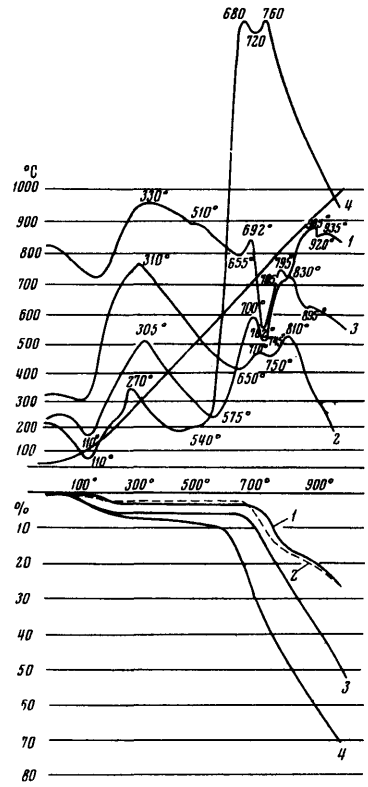


Figure 7. Differential thermal analysis of polynaphthoylenebisbenzimidazole (NDA–BPTA) with ΔT = 6 deg min^{-1} in: 1) argon (under cover); 2) argon (open crucible); 3) argon + 7% O_2; 4) air.

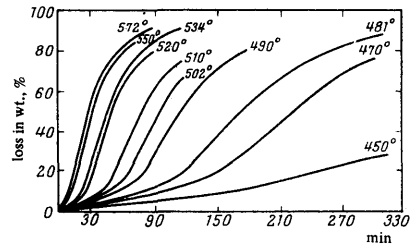


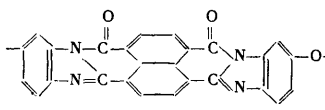
Figure 8. Thermogravimetric curves in air for polynaphthoylenebisbenzimidazole (NDA–BPTA, $[\eta]$ = 1.0 dl g^{-1}).

Small (1%) additions of the previously pyrolysed polymer produce an increase in the maximum rate of degradation. The autocatalytic character of degradation of the polymer and the specific effect of pyrolysed additions are explained in terms of a "local activation effect", which is characteristic of polymers containing a conjugated system [65,67].

Mass-spectroscopic analysis indicates that, when polynaphthoylenebisbenzimidazoles are heated in a vacuum to 800°C, the chief gaseous products are carbon monoxide, nitrogen, and a certain amount of carbon dioxide; hydrogen and steam are also evolved. These results, together with

the composition of the residues (Table 6), indicate the occurrence of processes of carbonisation and the formation of polynuclear fused systems, including conjugated carbocyclic and heterocyclic rings.

Table 6. Change in composition of polymer after being heated in a vacuum [31,37,50].

Repeating unit	Composition	Temperature at which heated, °C				
		300	400	500	600	800
	C/N	5.6	5.8	5.7	9.7	10.9
	C/H	27.7	29.5	30.7	47.5	61.3

Thermogravimetric analysis of the thermal and thermo-oxidative degradation of pyrrones obtained from perylene-tetracarboxylic dianhydride with biphenyltetra-amine, oxydiphenylenetetra-amine, and diphenylmethanetetra-amine respectively (Fig. 9) [24,31,67] indicates that these polymers are less stable in air than are the corresponding polynaphthoylenebisbenzimidazoles of high molecular weight ($[\eta] \geq 1.0$ dl g^{-1}). Nevertheless, they are more resistant to thermo-oxidative degradation than are polynaphthoylenebisbenzimidazoles of low molecular weight ($[\eta] < 0.4$ dl g^{-1}). Such a difference is probably due to the influence of the terminal groups. In a vacuum their thermal stability is equal to or even somewhat surpasses that of polynaphthoylenebisbenzimidazoles of high molecular weight, which is probably due to the stronger intermolecular interaction of polymers containing perylene rings and their greater tendency to cross-linking.

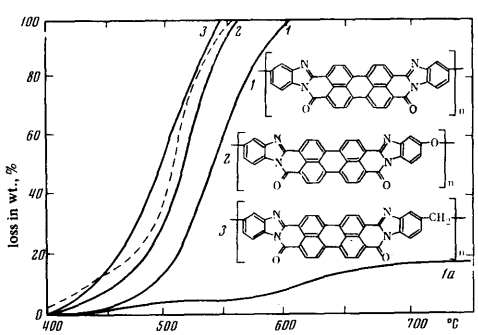
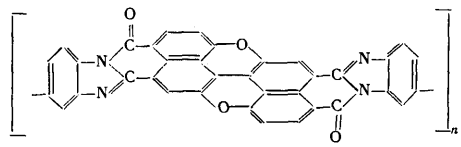


Figure 9. Thermogravimetric curves (ΔT = 2 deg min^{-1}) in: 1)–3) air; 1*a*) vacuum; ---) polynaphthoylenebisbenzimidazole (NDA–BPTA, $[\eta] = 0.37$ dl g^{-1}).

Great thermal stability in air and in a vacuum is shown also by pyrrones prepared in polyphosphoric acid from biphenyltetra-amine and dianhydride bisadducts of maleic anhydride with bisfuran compounds [26,56], and also from this tetra-amine and 2,8′ : 2′,8-dioxy-1,1′-binaphthyl-4,4′,5,5′-tetracarboxylic dianhydride.[45]



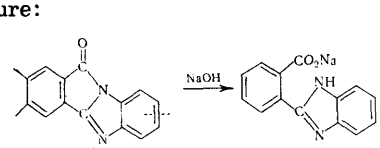
As has been mentioned above, the application of thermostable polymers is most promising in space technology. Such polymers and also compositions based on them are used for the ablation protection of the surfaces of aircraft and propulsion units from the action of high-temperature gas-flows. Prospects have been discussed [68] for the use of heterocyclic polymers of ladder and block–ladder structure as ablation-resistant coatings. Many pyrrones prepared from aromatic tetra-amines and various dianhydrides (of naphthalenetetracarboxylic acid, perylene-tetracarboxylic acid, bisadducts of diene synthesis between maleic anhydride and bisfuran compounds) proved resistant to the action of high-temperature air flows [69–72]. They satisfy such criteria of ablation resistance as low rate of ablation $A_V = \Delta m/\tau F$ kg m^{-2} s^{-1} (where Δm is the loss in weight, F the surface area of the specimen, and τ the duration of the test) and resistance to the action of large temperature gradients. Specimens of the polymers and compositions were prepared by hot pressing.

The rate of ablation of a polymer is almost independent of its molecular weight after the latter has reached a certain value ($[\eta] \geq 0.9$ dl g^{-1}), being determined by its resistance to thermo-oxidative degradation and its tendency to cross-linking. Pyrrones based on naphthalenetetracarboxylic dianhydride, and especially those containing perylene rings, showed the lowest rate of ablation. The introduction of intermediate oxy and methylene groups somewhat increases the rate of ablation. Polymers having a low degree of cyclisation exhibited a sharp drop in ablation resistance. Pyrrones show better ablation resistance than corresponding polyimides and unmodified phenol–formaldehyde resins. The stability of the test specimens to the action of a temperature gradient is greatly improved after they have been heat-treated in an inert atmosphere; it is improved also by hot-pressing polymers containing additives which act as temporary plasticisers.

2. Resistance to Radiation and Chemicals

Pyrrones are extremely resistant to the action of ionising radiation (Table 7). Thus the strength properties of pyrrone films had not deteriorated after exposure to a 10 000-Mrad dose of electrons of energy 2–3 MeV, whereas polyester films are destroyed by a dose of 200 Mrad. [3,19,73,74]

Investigation of the chemical stability of polybenzimidazopyrrolones has shown that the mechanical strength of the films diminishes relatively slowly on standing in 96% sulphuric acid (Table 8). In alkaline solutions the films rapidly lose their strength. The reaction between the polymer and the alkali can be regarded as conversion of the imidazopyrrolone structure into a polycarboxybenzimidazole structure:



Polynaphthoylenebisbenzimidazoles, in contrast to polybenzimidazopyrrolones, are extremely resistant to the action of concentrated sulphuric acid[31,36]. The viscosity of solutions of the polymers is almost unchanged after standing in the acid at room temperature for 700 h. Keeping a polynaphthoylenebisbenzimidazole in 40% alkali (potassium hydroxide) for 2 days produces a decrease in its intrinsic viscosity from 1.8 to 1.1 dl g^{-1}.

Table 7. Effect of radiation on mechanical properties of pyrrone films[3,19].

Pyrrone film	Dose, Mrad	Stress at flow point, kg cm^{-2}	Tensile strength, kg cm^{-2}	Relative elongation, %	Young's modulus, kg cm^{-2}
PMDA-BPTA*	0	930	1 170	3.2	56 800
	1 100	995	1 460	4.5	61 800
	5 500	1 010	1 460	3.9	62 200
	11 000	1 020	1 340	3.1	62 400
	21 000	1 090	1 560	3.3	69 200
	58 300	875	1 070	2.7	57 800
PMDA-ODPTA**	0	647.9	1 260	9.0	51 408
	1 000	859.1	1 183	3.0	58 450
	5 000	1 007	1 422	3.0	57 756
	10 000	1 098	1 218	3.0	60 000

*Temperature of cyclisation 300°C; temperature of exposure 250°C; beam of electrons of energy 3 MeV; dosage rate 5500 Mrad h^{-1}.
**Irradiated with electrons of energy 2 MeV; dosage rate 1000 Mrad h^{-1}.

Table 8. Chemical stability* of polybenzimidazopyrrolone film[19].

Reagent	Young's modulus, kg cm^{-2}	Relative elongation, %	Tensile strength, kg cm^{-2}
Initial film	43 000	5.5	1 560
	27 500	7.5	900
96% H_2SO_4	41 600	4.6	1 190

*Films 0.025 mm thick cyclised at 250°C (for 1 h). Specimen kept at room temperature (for 1 h), washed with water, and dried at room temperature for 1 h.

3. Electrical, Magnetic, and Catalytic Properties

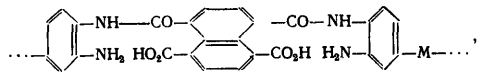
Very little information is available on the electrical properties of polybenzimidazopyrrolones[3,4]. Their resistivity and dielectric strength are typical of insulating organic polymers (Table 9). Polybenzimidazopyrrolones are paramagnetic materials having concentrations of unpaired electrons of 10^{16}–10^{19} g^{-1}.[7]

The magnetic and electrical properties of polymers based on naphthalenetetracarboxylic and perylenetetracarboxylic dianhydrides with aromatic tetra-amines, and also of copolymers of naphthalenetetracarboxylic dianhydride with diamines and tetra-amines, have been studied in greater detail[5,24,25,31,35,50]. The temperature dependence of the conductivity of these polymers is typical of organic semiconductors. Table 10 shows that the conductivity parameters (the activation energy E_σ and the resistance ρ_t) depend substantially on the nature of the dianhydride and the tetra-amine used and on the ratio of diamine and tetra-amine in the case of the copolymers. A break in the conjugated system impairs the conductivity. With increase in the number of fused rings in the initial dianhydride the values of ρ and E_σ for the polymers diminish, probably owing to an increase in intermolecular interaction.

Table 9. Electrical properties of polymers[3,4].

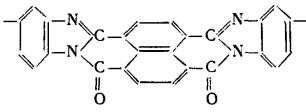
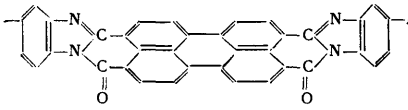
Polymer		Resistivity, ohm cm	Dielectric strength, V cm^{-1}	Dielectric constant
PMDA-ODPTA	PAAA	$6 \cdot 10^9$	$2 \cdot 10^5$	—
	pyrrone	$(3—5) \cdot 10^{12}$	$6 \cdot 10^5$	—
PMDA-NTA	pyrrone	$5 \cdot 10^{10}$	—	4.0

Polyamide-amino-acids have lower conductivities, which depend to a less extent on the nature of M in the formula[31,50]



(where M represents O or CH_2 or is absent).

Table 10. Electrical properties of polyaroylenebisbenzimidazoles and copolymers[31,50].

Polymer		No.	—M—	Conductivity measured up to 200°C	
				E_σ	$\lg\rho_{150°}$
		I	absent	0.47	5.70
		II	—O—	0.67	9.35
		III	$—CH_2—$	0.57	8.35
		IV	absent	0.32	4.60
		V	—O—	0.48	7.10
		VI	$—CH_2—$	0.42	6.50
NDA-BPTA-ODPDA copolymers	1:0.2:0.8	VII	—	0.74	9.75
	1:0.5:0.5	VIII	—O—	0.60	7.60
	1:0.8:02	IX	—	0.59	6.25

Both the final polymers and the precondensates give electron spin resonance signals characteristic of conjugated polymers[5,24,25,31,35,50]. The concentration of paramagnetic centres is considerably lower in polyamide-amino-acids than in cyclised polymers. The paramagnetism of the former compounds has been explained[24] by the possibility of formation of an isoimide structure. In such polymers, moreover, intramolecular and intermolecular transmission of conjugation can be accomplished by complex formation between amino- and carboxy-groups.

A study has been made of the variation in the electrical properties at various stages in the production of polymer molecules when polyamide–amino-acids are heated in a vacuum from 50–100° to 800°C.[31,37,50] The various polyamide–amino-acids show a general tendency for the electrical and magnetic properties to change with the temperature at which they have been heated (Fig. 10). Only intramolecular cyclisation occurs up to 150–200°C. Above 300°C this is accompanied by incipient slight cross-linking (depending on the structure of the polyamide–amino-acid and the polymer), which intensifies at 400°C. In this temperature range the electrical properties of the polymer improve, the narrow e.s.r. signal becomes stronger and narrower, the background in the infrared spectra becomes stronger, and amorphous specimens become polycrystalline.

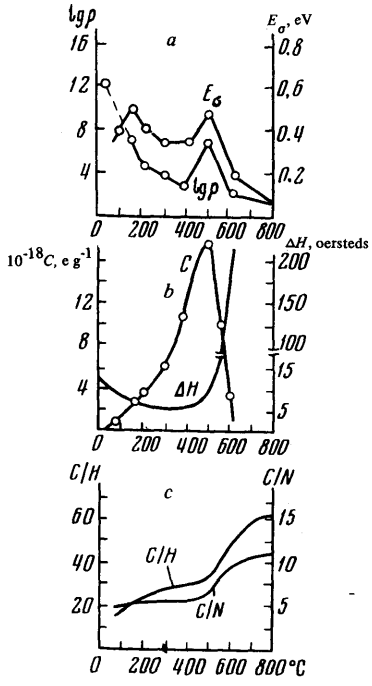


Figure 10. Change in electrical properties—E_σ and ρ_t—and magnetic properties—C (e g^{-1}) and ΔH_{esr} (oersteds)—and in elementary composition of PAAA on heating in a vacuum (for 2 h at each temperature).

Processes involving partial degradation of macromolecules at weak bonds (structural defects) begin at 500°C. They are accompanied by a diminution in the degree of order in the polymer specimen and a sharp deterioration in electrical properties. At 600°C the evolution of gaseous products is accompanied by that of heavier, reactive fragments able to sublime, recombination occurs, blocks previously formed on degradation undergo further cross-linking, the electrical properties of the polymers improve, the intensity of the narrow e.s.r. signal decreases, and a broad e.s.r. signal appears. Raising the temperature of pyrolysis to 800°C leads to a further improvement in the electrical properties and very considerable broadening of the e.s.r. signal of the residues, which contain a notable quantity (up to 8%) of nitrogen and a certain amount of oxygen, and are probably coarse blocks of a polycyclic aromatic including heterocyclic rings.

Pyrrones are catalysts of semiconductor type[7,75,76]. The decomposition of nitrous oxide was found to depend in considerable measure on the type of conjugation in the catalyst macromolecules. Thus the activation energy for this model reaction was 40–52 and 18–27 kcal mole^{-1} when pyrrones of block–ladder and ladder structure respectively were used.

Table 11. Mechanical properties of pyrrone films[19].

Pyrrone	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
PMDA-BPTA	1430	2.8	66 500
PMDA-ODPTA	1530	4.8	57 000
PMDA-DPMTA	975	3.9	37 400
PMDA-BOTA	930	2.6	41 500
BODA-BPTA	1420	4.3	42 000
BODA-ODPTA	1320	3.8	43 800
BODA-DPMTA	680	1.9	41 900
BODA-BOTA	840	3.1	34 800

4. Mechanical Properties

In view of the great thermal stability of pyrrones they show promise for the production of films, adhesives, fibres, and moulded articles. The strength of pyrrone films is high[19], but, as was to be expected with such rigid chains, they have a high modulus of elasticity and low relative elongation (Table 11). The mechanical properties of the films is greatly influenced by the temperature of cyclisation (Table 12) and to a less extent by the atmosphere in which cyclisation occurs (Table 13). The effect of the test temperature on the strength properties of pyrrone films is shown in Table 14.

Table 12. Effect of temperature of cyclisation on mechanical properties of PMDA–BPTA pyrrone films (duration of cyclisation 1 h).[19]

Temp. of cyclisation, °C	Tensile strength, kg cm^{-2}	Stress at flow point, kg cm^{-2}	Young's modulus, kg cm^{-2}	Elongation, %
150	775	1 140	35 600	5.4
225	920	1 200	38 200	4.1
300	1 030	1 320	44 000	3.8

Pyrrone films are far stronger than those obtained from polyamide–amino-acids. For example, the tensile strength of the latter films based on pyromellitic dianhydride and oxydiphenylenetetra-amine is 704–1060 kg cm^{-2}, whereas that of the corresponding pyrrone film[3] is 1060–1550 kg cm^{-2}. Strong films have been obtained from

polyamide-amino-acids prepared from naphthalenetetracarboxylic dianhydride with oxydiphenylenetetra-amine and with diphenylmethanetetra-amine [31,36], their tear strengths being respectively 910 and 850 kg cm^{-2}. After cyclisation at 300°C the strength of the films had improved to 1200 and 1040 kg cm^{-2}. Their mechanical constants can probably be improved by finding optimum conditions for production of the films.

Table 13. Effect of atmosphere on mechanical properties of PMDA-BPTA films (heated at 250°C for 3 h). [19]

Atmosphere	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
Air	1090	4	48 600
Vacuum	1100	3.8	47 600
Nitrogen	990	2.1	60 000

Table 14. Effect of temperature of testing on mechanical properties of PMDA-BPTA films [19].

Temp., °C	Stress at flow point, kg cm^{-2}	Tensile strength, kg cm^{-2}	Elongation, %	Young's modulus, kg cm^{-2}
25	900	1190	2.8	60 000
100	685	1110	3.7	50 000
200	529	800	3.7	36 800

Fibres have been obtained from polymers based on naphthalenetetracarboxylic dianhydride and biphenyltetra-amine [21,54,55,77]. Concentrated sulphuric acid was used as solvent in wet spinning. Polymers having intrinsic viscosity 1.15-2.45 dl g^{-1} have been employed. After drawing (at 360-540°C) the strength of the filaments was 0.85-1.33 g $denier^{-1}$ at draw ratios of 1.10-1.29; the elongation at rupture was 6.8-10.0%. With continuous drawing of filaments at 260-565°C and draw ratios of 1.06-1.31 in an atmosphere of argon and in air their strength reached 2 g $denier^{-1}$ at an elongation of 19%. To obtain strong filaments while preserving high values of the elongation at break, a monofil was subjected to hot drawing in argon. Filaments of strength 4 g $denier^{-1}$ were obtained with 4-5% elongation at break. With a filament which had been drawn at 650°C this elongation had decreased to 3%. According to these workers' results wet spinning from solutions in concentrated sulphuric acid can be used for the practical production of a thermostable fibre. The resulting fibre retains 55% of its initial strength after being kept in air at 600°C for 1 min, and 50% in air at 360°C for 30 h; it is extremely resistant to ultraviolet radiation.

Intensive research is being conducted in the USA into the synthesis of high molecular-weight pyrrones of ladder structure (naphthalenetetracarboxylic dianhydride-biphenyltetra-amine) and the production of fibres from them [21,22].

Methods have recently been found for moulding strong, thermostable articles from pyrrones by adding a temporary plasticiser [31,72]. Polymeric goods obtained directly from the molten monomers under high pressures also possess great strength and hardness [47].

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