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Three-stage Synthesis of "Ladder" Polyheteroarylenes

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Discussion of the fundamental principles of a general method for synthesising polyheteroarylenes, based on the three-stage reaction of tetrafunctional nucleophiles with tetracarboxylic acids, their derivatives, and analogues, is followed by detailed analysis of optimum procedures, principal characteristics, and fields of practical application of the main classes of "ladder" polymers—polyaroylenebenzimidazoles and related systems, polyisoindoloquinazolinediones, polyaroylene-1,2,4-triazoles, etc. A list of 280 references is included.

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I. INTRODUCTION

In the chemistry of synthetic polymers great attention has been paid to aromatic heterochain polymers, in particular polyheteroarylenes—polymers containing aromatic heterocycles in the main chains of the macromolecules—during the past twenty years [1-5]. The demands of new technology, requiring synthetic materials of ever increasing thermal stability, have caused the development during the past decade of an extremely interesting and peculiar field in the chemistry of polyheteroarylenes—research on "ladder" or "double-chain" polymers possessing, according to calculations by Tessler [6,7], enhanced resistance to the action of high temperatures. A completely or partly "ladder" structure is conferred on polyheteroarylenes by introducing fused aromatic heterocycles into main chains of the macromolecules [8-17].

Research in this field has yielded many polymers containing fused heterocycles in the main chains [8-17], the large majority of them obtained by one of the main methods for synthesising "ladder" structures—polyfunctional polycondensation, primarily its chief variant—polyheterocyclisation [15]. According to the Reviewers' proposed classification [18,19] the reactions involved in the synthesis of most ladder polyheteroarylenes by polyheterocyclisation can be divided into three main groups—(1) two-stage homo- or co-polymerisation of tetrafunctional monomers containing pairs in mutually *ortho*, α, or *peri* positions; (2) two-stage reactions of aromatic dicarboxylic acids of their derivatives with aromatic diamines containing *ortho* to the amino-groups aromatic heterocycles containing labile hydrogen atoms; and (3) three-stage reactions of aromatic tetracarboxylic acids, their derivatives, or analogues with tetrafunctional nucleophilic reagents containing four amino-groups as such or as carbamoyl, hydrazide, and other residues. The last process is the most widely used for synthesising ladder polyheteroarylenes, and can be regarded as a logical extension and development of two-stage polyheterocyclisation, which is very commonly applied in the synthesis of several thermostable polyheteroarylenes [1] and is in turn a complicated variant of the synthesis of linear condensation polymers, e.g. aromatic polyamides.

The transition from the synthesis of aromatic polyamides to that of polyheteroarylenes such as polyimides [20] or polybenzimidazoles [21] in fact requires the use of one potentially tetrafunctional monomer and also an additional stage in the process, actual polycyclisation. Similarly, the transition from the synthesis of polyheteroarylenes by two-stage polyheterocyclisation to that of ladder polyheteroarylenes by three-stage polyheterocyclisation demands that both the initial compounds should be potentially tetrafunctional, as well as an additional stage in the cyclisation process [22].

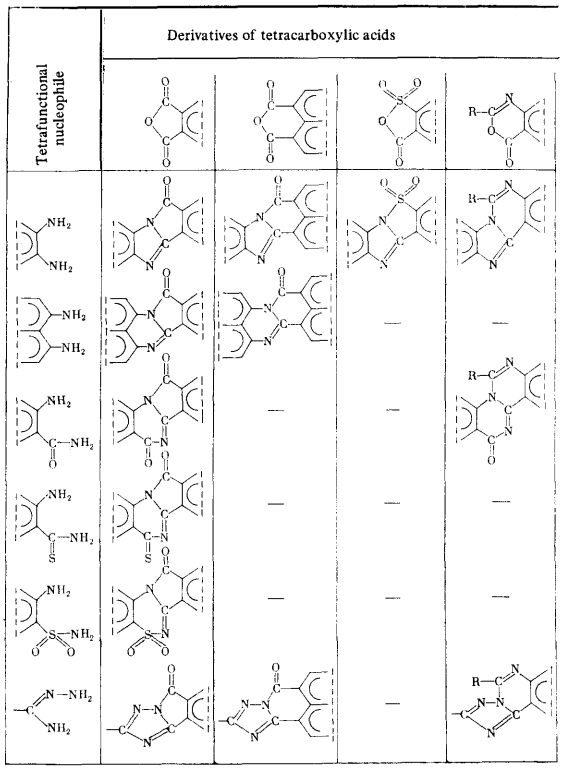
Being a more complicated variant of two-stage polyheterocyclisation, the three-stage synthesis of ladder polyheteroarylenes exhibits all the features of polycyclocondensation processes—the difficulty of selective difunctional polycondensation of potentially tetrafunctional monomers in the first stage, the complication of achieving 100% cyclisation, etc.—with the problems considerably greater than in two-stage polyheterocyclisation. The first stage in the three-stage synthesis actually involves selective polyamidation, which is more successful the greater the difference in nucleophilic reactivity between adjacent reaction centres in the tetrafunctional nucleophilic compound used, the lower the electrophilic reactivity of the acylating agent, and the lower the reaction temperature [23,24]. The nature of the solvent also has a considerable influence on the course of the process.

The tetrafunctional character of both monomers creates in several cases not only difficulties in achieving high selectivity of polyamidation but also the possibility of the formation in the first stage of polymers containing isomeric groups and thus essentially "heterounit" polymers [25]. The problem of such heterogeneity in ladder polyheteroarylenes is still more clearly evident in the second stage—polycyclisation giving polymers containing comparatively simple heterocycles *ortho* to functional substituents in aromatic rings—when the "heterounit" character of the polymers is due not only to incomplete cyclisation but also to the participation of different kinds of *ortho*-substituents, with the possible formation of at least two kinds of *ortho*-substituted polyheteroarylenes. In the third stage, finally, which usually requires more severe conditions, increase in the number and types of "foreign" units may be due to incomplete cyclisation and to secondary reactions of the heterocycles formed.

These considerations demand the most careful choice of method for the synthesis of each class of ladder polyheteroarylenes, so that in each individual case the polymers may correspond as closely as possible to the specified structure and so that their inherent properties may

be most fully realised. The three-stage synthesis of ladder polyheteroarylenes can be accomplished in different ways—(i) multistage polycyclocondensation with isolation of soluble products of the first stage, their processing into articles, and subsequent cyclisation as finished articles by gradually raising the temperature; (ii) polycyclocondensation in the melt under the conditions of the so called "Marvel reaction"[26]; or (iii) high-temperature polycyclocondensation (without isolation of intermediate polymeric structures) in solvents of high boiling point, in particular acids[27-30]. Many compounds of various classes can be used as tetrafunctional monomers in the three-stage synthesis, which is responsible for the structural diversity of the heterocycles present in the main chains of the required ladder polyheteroarylenes (see Table).

Typical monomer units and "ladder" polyheteroarylenes based on them.

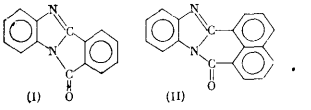


II. POLYAROYLENEBENZIMIDAZOLES

Among the ladder polyheteroarylenes whose structural units are shown in the Table the first to attract the attention of research workers were products of the reaction of aromatic bis-*o*-diamines—also termed bis-*o*-phenylenediamines—and aromatic tetramines with aromatic tetracarboxylic acids or their derivatives.

These polymers are macromolecular compounds of the polyaroylenebenzimidazole type. The main achievements in the synthesis, processing, and application of the polymers have been summarised not only in monographs[1-5] and reviews concerned with ladder polymers as a whole[8-17] but also in several specialist reviews[31-36]. Nevertheless, many aspects of the chemistry of polyaroylenebenzimidazoles continue to be extremely controversial.

Although polyaroylenebenzimidazoles are often regarded as a single class of polyheteroarylenes, whose properties vary within narrow limits, they can be quite validly divided into two large classes—polybenzoylene- and polynaphthoylene-benzimidazoles—differing both in methods of synthesis and in properties, whose units are modelled by the compounds



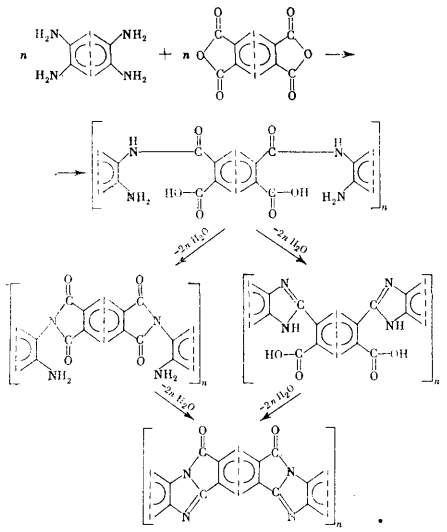
An equally valid classification distinguishes polymers obtained from tetracarboxylic acids or their derivatives of high or low electrophilic reactivity. Such differences in the initial tetracarboxylic acids, connected primarily with the charges on the carbonyl carbon atoms, are responsible for significant differences not only in the course of their acylation of bis-*o*-diamines but also in the electron densities on the carbonyl carbon atoms in the terminal heterocycles, influencing the resistance to hydrolysis of the latter, the action of nucleophilic reagents, etc. The two proposed classifications coincide in considerable measure, since in general bisphthalic acids and their derivatives are considerably more strongly electrophilic than are bisnaphthalic acids and derivatives. In several cases, however, departures from the above general principles are encountered.

1. Polybenzoylenebenzimidazoles

The first polyaroylenebenzimidazoles to attract the attention of investigators were polybenzoylenebenzimidazoles, known also as polyimidazopyrrolones, polybenzimidazopyrrolones, or "pyrrones"[41]. Since the initial publicity[37] attributed to these polymers extraordinarily high thermal stability, high resistance to deformation, and the ability to be processed into articles, they attracted the attention of a considerable number of research workers.

Polybenzoylenebenzimidazoles can be prepared by the interaction of aromatic bis-*o*-diamines or their salts with diesters[38-40], tetraesters[42], and also dichlorides of diesters of tetracarboxylic acids[43-45], but bisphthalic dianhydrides have found the greatest application. This reaction was conducted under conditions of "hot reactive extrusion" of the monomers[46,47], by melting the initial compounds together[48], under conditions of high-temperature polycondensation in solution in an organic solvent—nitrobenzene[49], phenol[50], or an amide solvent[49-51]—or in polyphosphoric acid[50,52-59], and also under conditions of low-temperature polycondensation at the interface[60] and in solution followed by cyclisation of the resulting initial polymers. In most cases dipolar aprotic solvents are used in the reactions of aromatic bis-*o*-diamines with

tetracarboxylic dianhydrides, when the poly-*N*-*o*'-aminophenylphthalamic acids obtained in the first stage undergo cyclodehydration to the polybenzoylenebenzimidazoles:



Considerable numbers of patents [61-98] and papers [38,43,44,50-55,99-122] have dealt with the synthesis by this scheme of completely aromatic polybenzoylenebenzimidazoles containing also various aromatic carbocyclic and/or heterocyclic rings. Polybenzoylenebenzimidazoles have been obtained also by the use of dianhydrides or cycloaliphatic tetracarboxylic acids [123-128]. Furthermore, polyesterbenzoylenebenzimidazoles [129] and polyamidobenzoylenebenzimidazoles [130-134] have been synthesised from bis-*o*-diamines and bisphthalic dianhydrides containing ester and amide groups respectively.

The first stage in the preparation—the synthesis of poly-*o*-amino-*o*'-carboxyamides—is usually conducted under conditions of low-temperature polycondensation in a dipolar aprotic solvent, such as dimethylformamide, dimethylacetamide, *N*-methylpyrrolid-2-one, hexamethylphosphoramide, dimethyl sulphoxide, etc. Thermochemical investigations indicate that the interaction of the most widely used bis-*o*-diamines and bisphthalic dianhydrides [135-137] is characterised by considerable exothermic effects, which are responsible in all cases for the high equilibrium constants (owing to the insignificant contribution by the entropy component to the Gibbs free energy) and hence potentially high degrees of polymerisation [138].

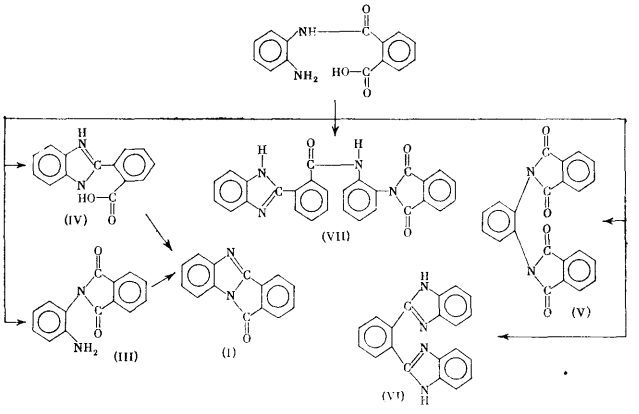
The only problem complicating synthesis of the poly-*o*-amino-*o*'-carboxyamides is the possibility of gel formation, since bis-*o*-diamines in particular are nucleophiles with neighbouring amino-groups of closely similar nucleophilic reactivities, while bisphthalic dianhydrides are the most active of the acylating agents shown in the Table. Therefore, although quantum-chemical calculations [23,24] and thermochemical investigations [137] indicate that, after the first amino-group has undergone acylation, the amino-group *ortho* to the acylated amino-group is the most strongly deactivated, the latter remains sufficiently reactive to react with dianhydrides, forming initially branches and then intermolecular "cross-links". The possibility of gel formation increases in the concluding stage, when the number of *o*-amino-groups exceeds considerably the number of amino-groups at the ends of the macromolecules.

In conformity with the above principles [23,24] success in selective polyamidation depends significantly on the temperature of the reaction and the nature of the solvent. Selectivity is actually increased by cooling from room temperature to −20°C and on passing from dimethyl sulphoxide to dimethylacetamide and thence to dimethylformamide, but gel formation cannot be completely suppressed even by conducting the reaction in dimethylformamide at −20°C. Success therefore requires a continual deficiency of the acylating agent, at least in the last stage: i.e. the last 5–10% of the dianhydride should be added as a solution to the reaction mix.

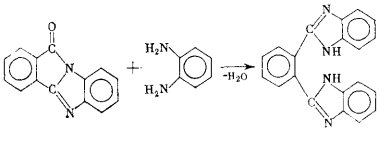
Nevertheless, such addition lowers the viscosity characteristics [139] of poly-*o*-carboxyamides, and this probably applies also to poly-*o*-amino-*o*'-carboxyamides. An alternative procedure for selective polyamidation would be somehow to increase the difference in nucleophilic reactivity between neighbouring reaction centres in the bis-*o*-diamines. With this aim use was made as initial compounds of 5,5'-dichlorobiphenyl-3,3',4,4'-tetramine [106] and also bis-*o*-diamines in which two amino-groups had been protected by preliminary acetylation or ethoxycarbonylation [140-142], and also by "blocking" with hydrogen chloride [70,109]. However, such deactivation of two amino-groups has an adverse effect on the nucleophilic reactivity of the two remaining amino-groups, since bis-*o*-diamines are monomers with interdependent functional groups. This makes it impossible to obtain *ortho*-substituted polyamides of high molecular weight, and also complicates appreciably the process of cyclisation. Hence the preferred method for preparing initial polymers of polybenzoylenebenzimidazoles is the above interaction of unprotected bis-*o*-diamines and bisphthalic dianhydrides in dimethylformamide; the reaction goes especially smoothly in the presence of triethylamine or other base [62,142] that stabilises solutions of poly-*o*-amino-*o*'-carboxyamides against gelation. Workable polymers of high molecular weight, possessing great resistance to deformation, have been obtained by this method from most of the bis-*o*-diamines and bisphthalic dianhydrides used.

The most common method of cyclising poly-*o*-amino-*o*'-carboxyamides to polybenzoylenebenzimidazoles is thermal solid-phase cyclodehydration of the polymers in a vacuum while the temperature is gradually raised to 350°C. Investigation of the thermodynamics [49,143,144], kinetics [111,112], and mechanism [99,101,111,112] of this process has shown that, although formation of both intermediate polymeric structures—poly-*o*-aminoimides and poly-*o*-carboxyphenylbenzimidazoles—is allowed thermodynamically under the temperature conditions of the first stage of cyclisation (up to 200°C), poly-*o*-aminoimides are formed predominantly. Since both *N*-*o*-aminophenylphthalimide (III) and *o*-benzimidazol-2'-ylbenzoic acid (IV) [49,120,145] were found among the products of the model cyclisation of *N*-*o*'-aminophenylphthalamic acid occurring in the melt under the same temperature conditions, it was suggested [146] that (IV) was formed as a result of the isomerisation of (III), which involved a mutual rotation of the moieties of the molecule. Such rotation is difficult in the case of a solid-phase polymer reaction, so that the cyclisation of poly-*o*-amino-*o*'-carboxyamides to polybenzoylenebenzimidazoles occurs predominantly via poly-*o*-aminoimides. Furthermore, investigation of the cyclisation of poly-*o*-amino-*o*'-carboxyamides has shown [111,112] that imidisation and formation of the benzoylenebenzimidazole ring are superimposed on one another: i.e. the second stage of cyclisation begins before completion of its first stage.

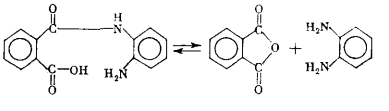
In contrast to earlier results[50] it has now been established that, with few exceptions[56,57], the polymers lose their solubility during cyclisation, and the final polybenzoylenebenzimidazoles in most cases do not dissolve in any of the solvents tested. This is explained not only and not so much by the rigidity of the macromolecular chains as by the three-dimensional structure of the final polymers resulting from a series of secondary processes. Indeed, among the products of the model cyclisation of *N*-*o*'-aminophenylphthalamic acid were detected, together with compounds (III), (II), and (I), respectively intermediate and final products of cyclisation, also *o*-phenylene-*NN*'-diphthalimide (V), *o*-phenylene-2,2'-bisbenzimidazole (VI),[49,120,145], and *o*-benzimidazol-2"-yl-*o*-phthalimidobenzanilide (VII):[145]



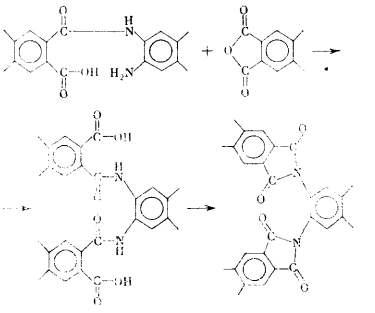
The structure of the last three products gives an idea of the nature of the intermolecular "cross-links" in the final polybenzoylenebenzimidazole structures, while the reactions involved in their formation indicate the processes occurring on the heat-treatment of poly-*o*-amino-*o*'-carboxyamides. The most important of the reactions governing the formation of "side" model compounds are most closely connected with the nature of the initial dianhydrides and occur more easily the greater the electrophilic reactivity of these compounds. Thus the product (VII) is formed from (III) and (IV) more readily the larger the positive charge on the carboxyl carbon atom. Formation of *o*-phenylene-2,2'-dibenzimidazole from *o*-phenylenediamine and 1,2-benzoylenebenzimidazole[147-149]



proceeds more easily the higher the positive charge on the carbonyl carbon of the second reactant. Finally, in the formation of (V) the strongly exothermic character of the reaction of bis-*o*-diamines with dianhydrides (becoming stronger with increase in the reactivity of the latter) is responsible for shifting the equilibrium towards the monomers with rise in temperature (also more marked the more reactive the dianhydride):

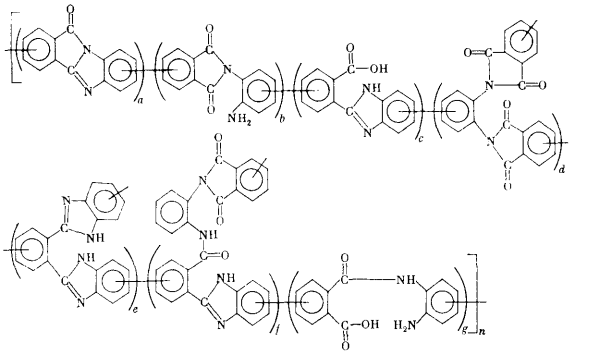


The regenerated anhydride groups react preferentially with regenerated *o*-phenylenediamine groups but, because of the relatively high temperature and hence diminished selectivity of reaction, some of them interact with amino-groups of the *N*-*o*'-aminophenylphthalamic acid:



This reaction also, of course, occurs more readily the more reactive is the initial dianhydride. Subsequent dehydration of the resulting *o*-phenylene-*NN*'-bisphthalamic acid yields (V).

According to these results polybenzoylenebenzimidazoles obtained from the most common bisphthalic dianhydrides would be more correctly represented as "heterounit" polymers having a random distribution along the chain of such units as



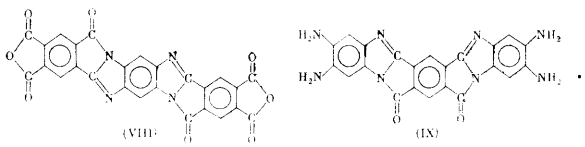
This by no means complete set of structural units present in polybenzoylenebenzimidazoles obtained by the solid-phase polycyclodehydration of poly-*o*-amino-*o*'-carboxyamides indicates the high proportion of defects in these systems. Such polymers obtained by polycyclocondensation in polyphosphoric acid would have been less defective, but this method is suitable only for obtaining polymers from dianhydrides of low reactivity[56-59], whereas syntheses using the most common anhydrides terminate in gel formation[49,107,122], caused primarily by interaction of terminal *o*-phenylenediamine groups of some macromolecules with benzoylenebenzimidazole rings of other macromolecules, a process which is especially intense in polyphosphoric acid[147-149].

Owing to their "three-dimensional" structure polybenzoylenebenzimidazoles—products of the solid-phase cyclodehydration of poly-*o*-amino-*o*'-carboxyamides—are infusible and insoluble, and can therefore be worked into articles, mainly at the poly-*o*-amino-*o*'-carboxyamide stage, the subsequent cyclodehydration being conducted on the ready made articles. This procedure has been used to obtain polybenzoylenebenzimidazole films[44,100,150-153] possessing high radiation resistance and photoconductivity, able to compete successfully with cellulose acetate films in the preparation of membranes for the deionisation of

water by reverse osmosis. Such films possess comparatively high tensile strength (up to 1500 kg cm^{-1}) but fairly low elongation (up to 10%) at break. The same method has been used to obtain polybenzoylenebenzimidazole fibres[61], extruded and cast articles, adhesives for glass plastics[140,141,154-161], and also foams[162-164] possessing high radiation stability. These and other possible fields of application of the polymers have been surveyed[164].

Polybenzoylenebenzimidazoles can thus be used to obtain the most diverse goods, but they differ little in thermal stability from the usual "single-chain" polyheteroarylenes: under the standard conditions of dynamic thermogravimetric analysis in air most of the former polymers already lose weight at 450°C, and under the corresponding isothermal conditions appreciable losses in weight are observed at 350°C even after a short period (up to 10 h). Most investigators link the relatively poor thermal stability[43,44,111,113,165-175] with the comparatively low degree of cyclisation of these polymers, roughly 70% according to thermochemical[143,176] and mass-spectrometric[169] results (this must be regarded as an approximate value, since in both cases only contributions by the main structural units of the polymers were taken into account).

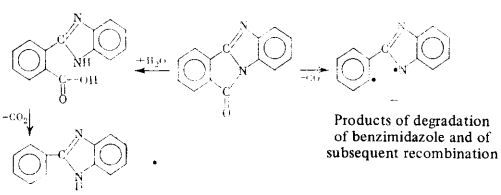
Attempts have therefore been made to raise the degree of cyclisation by "chemical plasticisation" of the macromolecules by saturating them with ether bonds[90,95,112-114], as well as by using as initial compounds oligomers already containing 1,2-benzoylenebenzimidazole rings and possessing degrees of polymerisation of 1.5–5.5,[66] e.g.



(VIII) (IX)

However, neither method produced any considerable increase in thermal stability of the polymers.

The question that arises naturally from these results, whether it is fundamentally possible to produce highly thermostable polymers containing 1,2-benzoylenebenzimidazole rings, can be solved only by examining the degradation of model compounds free from the influence of "defective" units, end groups, etc. Investigation of the hydrolytic[177] and thermal[178] stability of the simplest model compound (I) has shown that hydrolysis to (IV) with decarboxylation of the latter begins at 400°C, and homolytic decomposition of the heterocycle with evolution of carbon monoxide at 435°C:



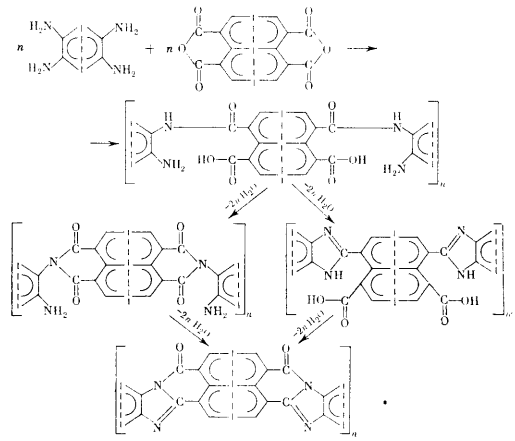
Such mechanisms of hydrolytic and homolytic degradation of (I), which are consistent with several other results[101,165,166,169], indicate that the C–CO and N–CO bonds are the least stable in this compound, a conclusion consistent also with calculation of the molecular diagram of (I) by the Hückel π-electron approximation in the LCAO–MO method[178]. The comparatively low temperatures of the start of hydrolytic and homolytic decomposition of (I) are evidence that the limited thermal stability of polybenzoylenebenzimidazole is due both to the marked "heterounit" character of the polymers and to the chemical nature of the heterocyclic system itself.

2. Polynaphthoylenebenzimidazoles

1,2-Naphthoylenebenzimidazole (II) is considerably more thermostable than I.[178] Quantum-chemical calculations by the LCAO-MO method to the Hückel π-electron approximation indicate that the C–CO and N–CO bonds are the weakest in (II) as in (I), but their bond orders are considerably higher in (II) than in (I), while the positive charge on the carbonyl carbon atom is lower in (II) than in (I).[178] Hydrolytic degradation of (II) therefore begins at 475°C, and homolytic degradation at 525°C.[178]

A considerable amount of research, the main results of which have appeared in several patents[70-75,179-186], and papers[52,53,108,109,187-214], has been done on the synthesis of polymers modelled by (II)—polynaphthoylenebenzimidazoles, also termed polybisbenzimidazobenzophenanthrolines and polybenzobisbenzimidazophenanthrolinediones.

Two main methods—multistage polycyclocondensation[181,203-205,208-214] and single-stage high-temperature polycyclocondensation in an acid solvent[52-58,70-75,108,109,179,180,182,204-209,212,214]—are used to obtain these polymers. The multistage polycyclocondensation of bis-*o*-diamines with bisnaphthalic dianhydrides is conducted in dimethyl sulphoxide containing an inorganic salt (e.g. lithium chloride) to increase the polarity of the solvent, and is followed by solid-phase heat-treatment of the initial polymers:

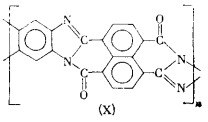


Because of the low reactivity of bisnaphthalic dianhydrides the first stage—the production of film-forming poly-*o*-amino-*peri*-carboxyamides—is accomplished at 80°C or above. In the second stage the thermodynamically advantageous six-membered imide ring is formed preferentially, according to infrared spectroscopy[214]; cyclisation is completed when the temperature is raised to 300°C. Polynaphthoylenebenzimidazoles obtained by multistage polycyclocondensation, owing to the rigidity of their macromolecular chains, which prevents effective solid-phase polycyclisation, probably contain a considerable proportion of incompletely cyclised groups. However, processes leading to three-dimensional structures, similar to those considered above for polybenzoylenebenzimidazoles, do not take place in the present case, so that the

present polymers dissolve in sulphuric acid, methyl hydrogen sulphate, and polyphosphoric acid. The most thermostable polynaphthoylenebenzimidazoles obtained by multistage polycyclocondensation retained 90% and 50% of their initial weight after isothermal heat-treatment in air at 316°C for 140 and 210 h respectively.

High-temperature polycyclocondensation in acid solvents, according to the above scheme but without isolation of initial or intermediate polymer structures, has found considerably wider use. Both bis-*o*-diamines and their salts can be used as monomers, and the acid components can be bisnaphthalic acids and their dianhydrides. The most convenient acid solvents have proved to be polyphosphoric acid alone [52,58,70-75,108,109,179,180,182,183,187-195,198-200,202,204-209,212,214] or mixed with sulphuric acid [201] or a Lewis acid [184], as well as various Lewis acids [30,75,185,186,196,197]. The absence of gel formation is attributed to the lower reactivity of bisnaphthalic than of bisphthalic dianhydrides, the ease of formation of a six-membered heterocycle, and the greater stability of the 1,2-naphthoylbenzimidazole than of the 1,2-benzoylenebenzimidazole ring towards nucleophilic reagents [178].

Naphthalene-1,4,5,8-tetracarboxylic acid and its dianhydride are the most generally used acid components; and 3,3′-diaminobenzidine, bis-3,4-diaminophenyl ether, and benzene-1,2,4,5-tetramine are the bis-*o*-diamines. Reaction between the last compound and the dianhydride gave the completely "ladder" polymer

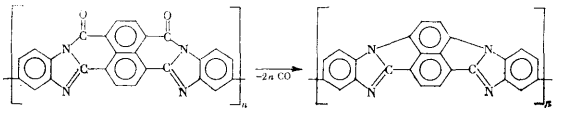


(X)

of high molecular weight, soluble in sulphuric acid, methyl hydrogen sulphate, and polyphosphoric acid, and beginning to lose weight appreciably at ~550°C according to the results of dynamic thermogravimetric analysis [190]. However, the polymer of partly ladder structure based on the more readily available 3,3′-diaminobenzidine has become more common. This polymer is also completely soluble in the three acid solvents, can be obtained with an intrinsic viscosity exceeding 6 dl g^{-1}, and is closely similar to the completely ladder polymer in thermal characteristics [190]. Because of the complexity of the nomenclature of these polymers, the polynaphthoylenebenzimidazole obtained from benzene-1,2,4,5-tetramine is usually denoted as BBL, and that based on 3,3′-diaminobenzidine as BBB.

Detailed investigations of the thermal characteristics of polynaphthoylenebenzimidazoles have shown that they surpass the corresponding polybenzoylenebenzimidazoles not only under conditions of dynamic thermogravimetric analysis but also under isothermal conditions both in a vacuum and in an inert environment [109,169-172,202-205,214-218]. Thus after isothermal ageing in air at 316°C for 500 h the polymers BBB and BBL retained 58% and 87% respectively of their initial weight. The higher thermal stability of polynaphthoylenebenzimidazoles is explained both by the greater thermal and chemical stability of the 1,2-naphthoylenebenzimidazole than of the 1,2-benzoylenebenzimidazole ring [178] and by the higher degree of cyclisation of the naphthoylene polymers obtained by high-temperature polycyclocondensation in acid solvents, primarily in polyphosphoric acid. Thus several workers have found that the degree of cyclisation of the polymers obtained in this acid is close to 100%. [169,183,190] Such a high value is not surprising, for the polymers are synthesised in solution, so that increase in the rigidity of the macromolecular chains is not so significant as in solid-phase polycyclisation [219-221], and furthermore polyphosphoric acid is not only a solvent but also a dehydrating agent, catalysing cyclisation.

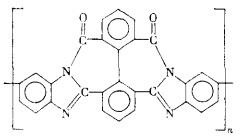
Several methods are now planned for further improving the thermal stability of polymers of this type. In particular, great interest attaches to the use of 1,2,5,6-tetraaminoanthraquinone [195] and 2,3,5,6-tetra-aminopyridine trihydrochloride [109] as initial bis-*o*-diamines. In the latter case the polymers contain only one weak carbon–hydrogen bond, which excludes a quinoid mechanism [222] of thermo-oxidative degradation. As a consequence, polymers obtained from this trihydrochloride and naphthalene-1,4,5,8-tetracarboxylic dianhydride retain 97% of their initial weight when aged at 316°C for 500 h. Another extremely interesting method for improving the thermal stability of polynaphthoylenebenzimidazoles by 40–100 deg consists in removing their weak bonds (C–CO and N–CO) by brief (< 50 ms) insertion into the flame of a propane burner at 1000–1300°C. [223,224] Decarbonylation entails the formation of new polymeric structures, which are assumed to have a ladder structure:



After such pyrolytic treatment the polymers have lost their solubility, but the treatment can be applied directly to ready made articles [223,224].

The excellent thermal properties of polynaphthoylenebenzimidazoles and the comparative simplicity of their synthesis have also attracted great practical interest. In particular, the production of thermostable films [191] and ablation-resistant materials [225-227] has been reported, but the use of these polymers for the production of fibres has attracted the greatest interest [228-232]. Spinning BBB polymer from sulphuric-acid solutions into a precipitating bath of 70% sulphuric acid gave fibres which, after being drawn 1.8–2.2-fold at 525–600°C, possessed a tensile strength of 5 g denier^{-1} at room temperature with an extension of 5% at break. The fibres retained 55–60% of their strength after remaining in air at 600°C for 1 min, or at 360°C for 30 h; they were resistant to moisture and ultraviolet radiation [232]. At the present time these are the most thermostable organic fibres and open up a most promising field for the practical application of ladder polyheteroarylenes.

The attention of research workers has been attracted not only to polymers containing heterocycles representing a combination of two five-membered rings or of a five-membered and a six-membered ring but also to those containing combinations of five- and seven-membered heterocyclic systems. In particular, an attempt was made to synthesis a partly ladder polymer, corresponding to the structural formula

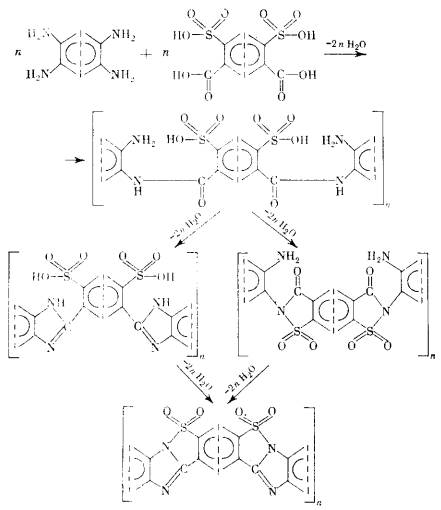


from biphenyl-2,2′,6,6′-tetracarboxylic dianhydride and 3,3′-diaminobenzidine [233]. The reaction was accomplished in polyphosphoric acid, when the dianhydride underwent

decarboxylation to the monoanhydride of fluorenedicarboxylic acid. Only polymers of low molecular weight with a low degree of cyclisation were obtained, which began to degrade at low temperatures.

III. SYSTEMS RELATED TO POLYAROYLENEBENZIMIDAZOLES

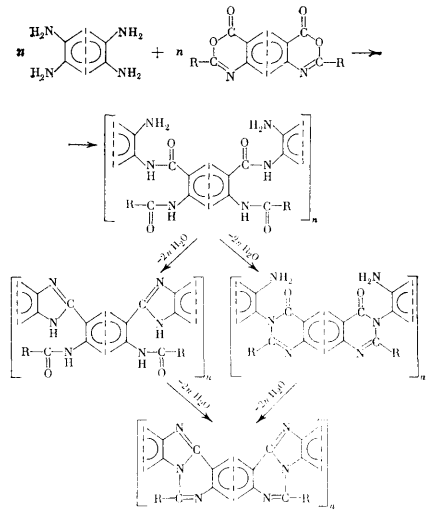
No significant advances have been made by research workers in synthesising sulphimide analogues of polyaroylenebenzimidazoles, containing bisbenzimidazobenzodi-isothiazole tetroxide rings and termed "polythiazones"[234-236]. These polymers were obtained by the polycyclocondensation of bis-*o*-diamines with disulphodicarboxylic acids or their derivatives in the melt, in solution in polyphosphoric acid, or as a multistage process:



The first stage was conducted in dimethylacetamide, and gave polymers—*oo'*-disubstituted polyamides—possessing reduced viscosities up to 1.45 dl g^{-1} when dissolved in sulphuric acid. On heat-treatment these polymers underwent desulphurisation, and the final polymers exhibited comparatively low thermal stability (they began to lose weight below 400°C).

Cyclisation at 420°C of the initial polymers in the presence of triethylamine, i.e. of the triethylammonium salts of the polymers, yielded "polythiazones" that began to degrade above 450°C. Analogous polymers were obtained by conducting the reaction in the presence of triethylamine in the melt[237]. Insoluble "polythiazones" synthesised in polyphosphoric acid began to decompose in air above 450°C.[234-236]. Considerably better thermal characteristics are exhibited by "polythiazones" in an inert atmosphere. Thus the polymer obtained from 3,3'-diaminobenzidine and 4,6-disulphoisophthalic acid does not lose weight when heated in nitrogen to 520°C, and the losses on being heated to 600 and 1000°C are respectively 2.7% and 38.0% of the initial weight.

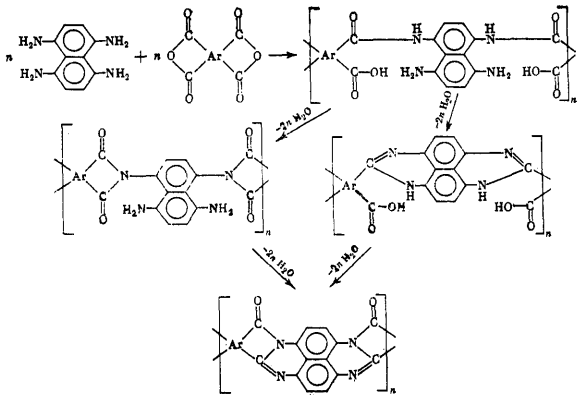
During recent years the attention of research workers has been attracted to polyheteroarylenes and in particular to "ladder" polymers based on "latent" dianhydrides, bisbenzoxazines. Reaction of the latter with bis-*o*-diamines, yielding polymers of completely or partly ladder structure—so called polybenzimidazoloquinazolines—and represented by the scheme



were accomplished by several investigators as a multistage process and as single-stage polycyclocondensation in polyphosphoric acid[238-242]. Multistage polycyclocondensation was achieved by the interaction of bisbenzoxazinones and bis-*o*-diamines in ambipolar aprotic solvents, the most suitable of which was *N*-methylpyrrolid-2-one, followed by solid-phase cyclodehydration of the resulting initial polymers. The low electrophilic reactivity of bisbenzoxazinones—even in comparison with bisnaphthalic dianhydrides—is responsible for the occurrence of this process even at higher temperatures (up to 150°C) without any signs of gel formation, but the same factor makes it difficult to obtain high molecular weights. Attempts to catalyse the process were unsuccessful, and at the present time only initial polymers of polybenzimidazoloquinazolines of comparatively low molecular weight have been obtained. According to spectral data the solid-phase cyclodehydration of these initial polymers involves intermediate formation of poly-*o*-aminoquinazolones, which cyclise to polybenzimidazoloquinazolines with difficulty (owing to the low positive charge on the carbonyl carbon atom of the quinazolone). As a consequence, the polymers formed are shown by spectral data to have a "heterounit" structure determined by the incompleteness of cyclisation, which prevents realisation of the potentially high thermal stability inherent in the benzimidazoloquinazoline ring.

It might have been expected that the problems consequent on the low reactivities of the benzoxazinone and quinazolone rings could be solved by conducting the polycyclocondensation in polyphosphoric acid, but polybenzimidazoloquinazolines of low molecular weight were then obtained, containing according to spectral data other structural residues. Since quantum-chemical calculations and the degradation of model compounds indicate that these rings surpass in thermal stability both 1,2-benzoylene- and 1,2-naphthoylene-benzimidazole rings[243], the search must be continued for methods of synthesising polybenzimidazoloquinazolines of high molecular weight, approaching the idealised structure as closely as possible.

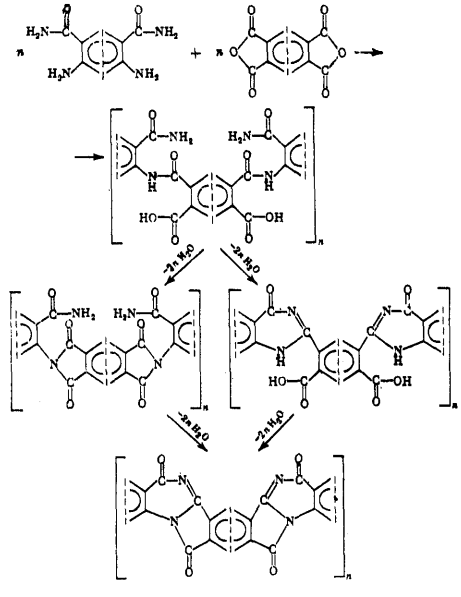
Ladder polyheteroarylenes based on bis-*peri*-diamines are considerably less common than those based on bis-*o*-diamines owing to the relative inaccessibility and very ready oxidisability of the initial compounds, in particular of naphthalene-1,4,5,8-tetramine. Investigations on the interaction of this tetramine with bisphthalic and bisnaphthalic dianhydrides



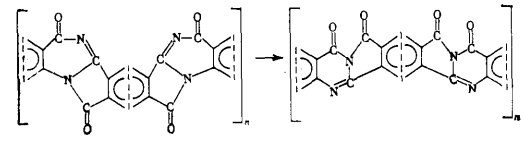
have shown[50,179,244] the theoretical possibility of synthesising such polymers, but workable polymers of high molecular weight could not be obtained.

IV. POLYISOINDOLOQUINAZOLINEDIONES AND RELATED SYSTEMS

Syntheses of polymers of ladder structure from various bis-*o*-amino-amides as tetrafunctional nucleophiles have become quite common. These compounds react with derivatives of bisphthalic acids to form polyisoindoloquinazolinediones[245-256]. The acid derivatives may be either the dianhydrides[245-255] or the dichlorides of diesters[256]. The dianhydrides have been the most widely used:



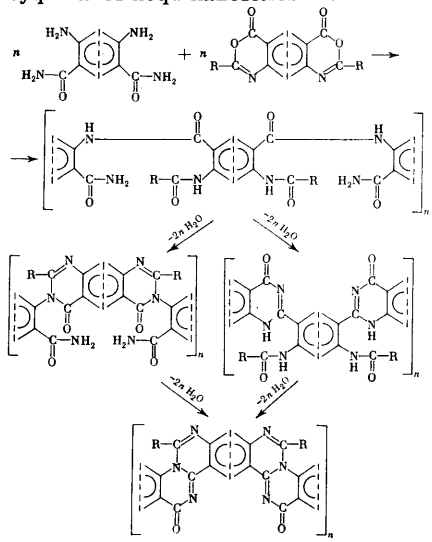
According to Kurihara[246] the final system isomerises into a thermodynamically more advantageous isomer:



Polyisoindoloquinazolinediones have been synthesised by a multistage process[245-250,256,257] and by single-stage high-temperature polycyclocondensation in polyphosphoric acid[251-255]. Multistage polycyclocondensation is effected by low-temperature interaction of the initial compounds in polar solvents followed by solid-phase polycyclodehydration of the resulting poly-*o*-carbamoyl-*o'*-carboxyamides. This process possesses several advantages and disadvantages in comparison with the multistage synthesis of polybenzoylenebenzimidazoles. Its chief merit is that bis-*o*-aminoamides are tetrafunctional nucleophiles whose reactive centres possess markedly different nucleophilic reactivities. As a consequence, the less reactive carbamoyl groups do not undergo acylation, and the first stage is not complicated by the possibility of gel formation[23,24]. On the other hand, the amino-groups are less basic and less strongly nucleophilic than those in bis-*o*-diamines, which in several cases creates difficulties in obtaining initial polymers of high molecular weight. Furthermore, since most investigators find that cyclisation of the polymers involves intermediate formation of poly-*o*-carbamoylimides, the low nucleophilicity of the carbamoyl groups may hinder the formation of isoindoloquinazolinedione rings in the concluding stage. Nevertheless, it has proved possible in several cases to obtain high polymers giving films of strength characteristics approaching those of polybenzoylenebenzimidazole films.

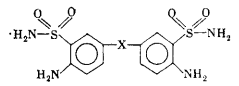
Synthesis in polyphosphoric acid is in considerable measure free from the disadvantage of the multistage process, and can be successfully used to obtain polyisoindoloquinazolinediones of high molecular weight. These polymer structures contain two pairs of weak bonds, N–CO and C–CO, and therefore with few exceptions exhibit limited thermal stability: they begin to lose weight in air at 380–400°C, and in argon above 400°C. In this connection it is somewhat surprising that due attention has not yet been paid to ladder polyheteroarylenes from bis-*o*-aminoamides and bisnaphthalic acids or their derivatives, from which greater themal stability might have been expected than from the polyisoindoloquinazolinediones examined. However, Japanese workers have accomplished the reaction of bis-*o*-aminoamides with

bisbenzoxazinones in polyphosphoric acid, and hence obtained polyquinazolinoquinazolones [258]:

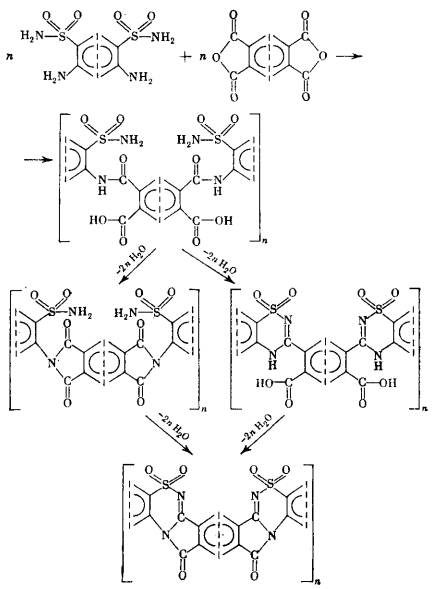


According to the results of dynamic thermogravimetric analysis (in nitrogen with ΔT = 6 deg min^{-1}) the loss of the initial weight at 600°C is 8–13% depending on the structure of the polymers, but it is quite clear that this line of research requires further development.

The possibilities of using bis-*o*-aminothioamides [259] and bis-*o*-aminosulphonamides [260,261] for the synthesis of ladder polyheteroarylenes have been studied still less. The patent literature contains in particular information [261] on a synthesis of such polymers from dianhydrides of aromatic tetracarboxylic acids and bisaminosulphonamides of general formula



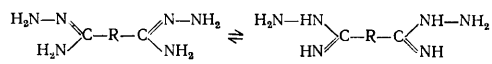
(X = O, CO, CH_2, SO_2, or S), indicating mild interaction of the starting materials in ambipolar aprotic solvents—*N*-methylpyrrolid-2-one, dimethylacetamide, dimethylformamide, dimethyl sulphoxide, hexamethylphosphoramide, etc.—followed by heat-treatment of the resulting poly-*o*-carboxy-*o*′-sulphamoylamides at 200–400°C:



The first stage of this process, like the synthesis of poly-*o*-carbamoyl-*o*′-carboxyamides, is not complicated by gel formation, since the initial nucleophilic monomers contain neighbouring centres differing markedly in reactivity. Furthermore, the amino-groups in the initial bisamino-sulphonamides are relatively strongly nucleophilic, so that in almost all cases poly-*o*-carboxy-*o*′-sulphamoylamides of high molecular weight were obtained, from whose solutions (η_{red} = 0.4–1.2 dl g^{-1}) films having tensile strengths up to 1500 kg cm^{-2} and extensions at break up to 10% were formed. The cyclisation of poly-*o*-carboxy-*o*′-sulphamoylamides, like that of poly-*o*-carbamoyl-*o*′-carboxyamides, occurs predominantly via *ortho*-substituted polyimides. As a consequence, the second stage—the formation of benzoylenebenzothiadiazine dioxide residues by interaction of imide carbonyls with sulphonamide units—is hindered by the diminished nucleophilicity of the *o*-sulphamoyl substituents. The final products of cyclisation are probably "heterounit" polymers containing in the macromolecules all four kinds of residues shown in the fundamental scheme of the reaction, with *o*-sulphamoylimide and benzoylenebenzothiadiazine dioxide groups predominating. Indeed, in several cases these polymers already lose weight at 400–450°C, according to dynamic thermogravimetric analysis in air, with ΔT = 5 deg min^{-1}. The most completely cyclised polymers do not lose weight under similar conditions up to 500°C. Poly(benzoylenebenzothiadiazine dioxide) films possess tensile strengths up to 2500 kg cm^{-2} and elongations at break up to 30%.

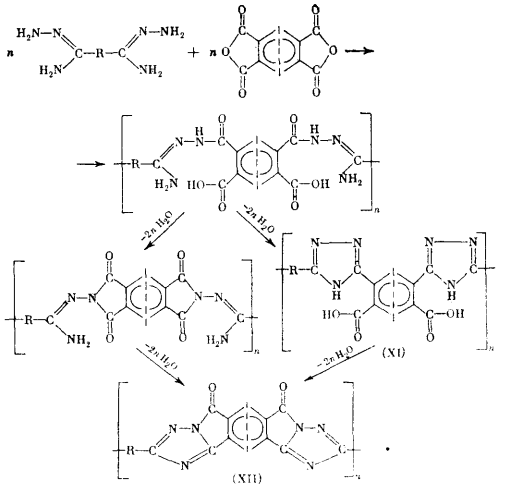
V. POLYAROYLENE-1,2,4-TRIAZOLES

Among tetrafunctional monomers that during recent years have found considerable application for the synthesis of ladder polyheteroarylenes are bisamidrazones of dicarboxylic acids corresponding to the general formula



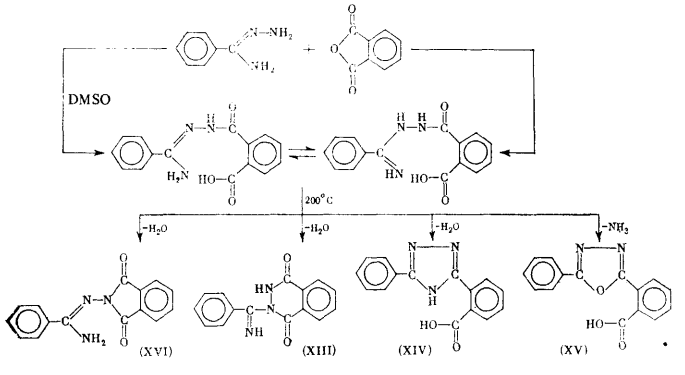
which are relatively easily available, stable compounds [262]. Polymers obtained from bisamidrazones and bisphthalic dianhydrides have been studied in the greatest detail. By 1970 extremely contradictory information had been published on the nature of these products. Thus results obtained by different investigators indicated that the first stage gave poly-*o*-carboxybenzoylamidrazones [263–266], but various structures were ascribed to the final product of

cyclisation, in particular poly-*o*-carboxyphenyl-1,2,4-triazole (XI) [263] and polybenzoylene-1,2,4-triazole (XII): [265, 266]:



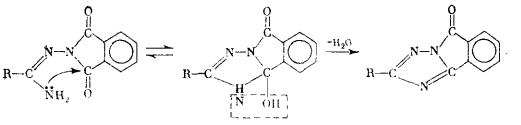
More recent results based on model reactions have shown [19,267-271] that the final products of these reactions are polybenzoylene-1,2,4-triazoles (XII), but these polymers are typical "heterounit" macromolecular compounds, which often hinders unambiguous establishment of their structure.

Several factors are responsible for the "heterounit" character of the polybenzoylenetriazoles. Firstly, although cyclisation of the products of the action of phthalic anhydride on amidrazones, *o*-carboxybenzoylamidrazones, occurs predominantly through the formation of amidino-imides, at least three other modes of cyclisation are possible, with formation of a six-membered cyclic hydrazide (XIII) [272] or of products of cyclisation of the acyl-amidrazone residue—the 3,5-disubstituted 1,2,4-triazole (XIV) and the 2,5-disubstituted 1,3,4-oxadiazole (XV): [273-275]



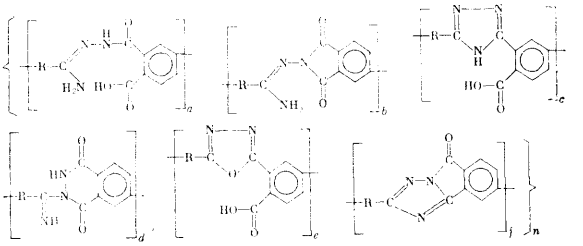
Only two of the four possible intermediate products of cyclisation—(XVI) and the *N*-amidinophthalimide (XIV)—are able to undergo a further stage of cyclisation, whereas the other two products—(XIII) and (XV)—cannot be converted into the final benzoylene-1,2,4-triazole, which is responsible for appearance of the "heterounit" character during synthesis of the polymers. The formation of structures other than (XVI) can be suppressed by treating the reaction mixture with the complex of pyridine and acetic anhydride [267], which acts as an imidisation catalyst [20], but this procedure complicates the synthesis and processing of the polymers.

Another factor contributing to the "heterounit" character of the polybenzoylenetriazoles (even when the *N*-amidinophthalimide is the sole intermediate product in the cyclisation) is the low nucleophilic reactivity of the amino-group in this intermediate, since the limiting stage is nucleophilic attack by the amino-group on a carbonyl carbon of the imide:



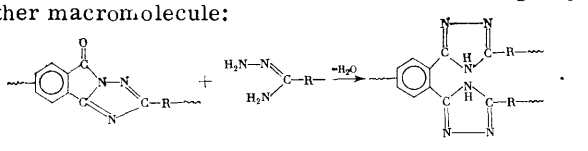
Because of the low nucleophilic strength of the amino-group this reaction is a slow process, but at higher temperatures it may be accompanied both by degradation of the *N*-benzamidinophthalimide at the weak nitrogen–nitrogen bond and by thermal and hydrolytic degradation of the benzoylenetriazole rings.

Taking into account all the above considerations, we must represent the structure of polybenzoylene-1,2,4-triazoles by the "heterounit" system



with the benzoylenetriazole units predominating. The thermochemical method of estimating degree of cyclisation developed and applied to a series of polyheteroarylenes by Korshak, Rabinovich, et al. [143,176], which involves determining heats of combustion, indicates that the final polymers contain ~80% of benzoylene-1,2,4-triazole rings. However, it must be borne in mind that estimation of the degree of cyclisation is based on the postulate that only amidino-imide and the benzoylenetriazole units are present in the polymers.

The above formula suggests that the polybenzoylenetriazoles are linear polymers, so that their heterounit character should be apparent in enhanced solubility. Nevertheless, none of the polymers obtained dissolved in any of the solvents tried. There is no doubt that, as with polybenzoylenebenzimidazoles [49], these products are "cross-linked" structures, in which the intermolecular branch points are most probably *o*-phenylenebistriazolyl residues formed by interaction between a benzoylenetriazole ring of one macromolecule and a terminal amidrazone group of another macromolecule:

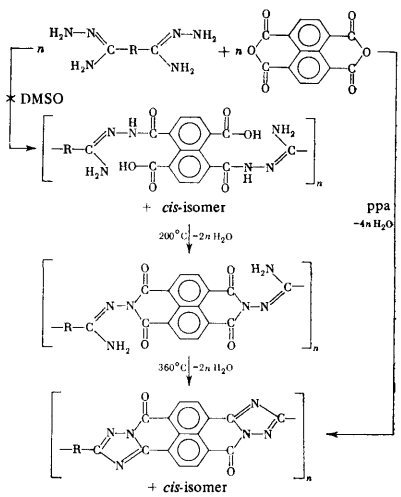


The heterounit character of the polybenzoylenetriazoles has a significant effect on their properties. X-Ray diffraction indicates that they are all amorphous, which is not surprising if they are regarded as copolymers containing various structural units. The effect on the thermal characteristics is very significant: even dynamic thermogravimetric analysis indicates the comparatively low thermal stability of these polymers, which at 350–410

and 400–440°C (rate of heating in air 4.5 deg min^{-1}) lose 5% and 10% respectively of their initial weight. It is interesting that polymers based on pyromellitic dianhydride are in most cases thermally less stable than corresponding polymers obtained from dianhydrides of other tetracarboxylic acids. This is probably caused by the lower degree of cyclisation due to the enhanced rigidity of macromolecules based on pyromellitic dianhydride.

Thus polybenzoylene-1,2,4-triazoles, like polybenzoylenebenzimidazoles, are cross-linked heterounit polymers, undergoing degradation at comparatively low temperatures. Yet the synthesis of their initial polymers, poly-*o*-carboxybenzoylamidrazones, owing to the differences in nucleophilic reactivity between hydrazine and amide amino-groups of amidrazones, is not complicated by branching and gel formation, so that this reaction can be conducted under the most favourable conditions to give poly-*o*-carboxybenzoylamidrazones that can easily be worked into the most diverse articles.

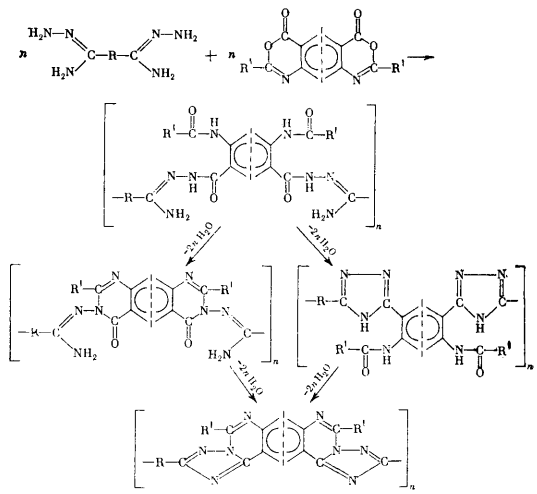
Polynaphthoylene-1,2,4-triazoles—products of the reaction of bisamidrazones with naphthalene-1,4,5,8-tetracarboxylic acid or its dianhydride—differ significantly from the corresponding benzoylene polymers both in methods of preparation and in their main characteristics. Study of model reactions indicates [19,271] that the polynaphthoylenetriazoles can be obtained either by a multistage or by single-stage polycyclocondensation in polyphosphoric acid:



However, attempts to effect polycyclocondensation with any bisamidrazone and the naphthalenetetracarboxylic dianhydride as monomers in a multistage process did not yield macromolecular products, since oligomers having a naphthalimide structure (according to their infrared spectra) separated from the solutions in the early stages. Hence the single-stage polycyclocondensation of bisamidrazones with naphthalene-1,4,5,8-tetracarboxylic dianhydride in polyphosphoric acid was chosen as general method for the synthesis of polynaphthoylene-1,2,4-triazoles [19,271,276–279]. The structure of the products was considerably more nearly perfect than that of the corresponding benzoylene polymers.

The polynaphthoylenetriazoles resemble polynaphthoylenebenzimidazoles in being completely soluble in sulphuric, methanesulphonic, ethanesulphonic, and polyphosphoric acids. Their high viscosities ($\eta_{log} \leq 3.0$ dl g^{-1}) are evidence of their high molecular masses. The most thermostable of these polymers lose 10% of their weight at 520–530°C under the conditions of dynamic thermogravimetric analysis, are stable in air at 400°C under conditions of isothermal thermogravimetric analysis, and do not soften up to 500°C. Polymers of this group possess high ablation resistance, and are of considerable interest as potential fibre-forming polymers.

Summarising these results, we note that on the whole polyaroylene-1,2,4-triazoles are closely similar to polyaroylenebenzimidazoles of corresponding structure and somewhat inferior to the latter in thermal stability. Considerable similarity is evident also on comparing products of the interaction of bisbenzoxazinones with bis-*o*-phenylenediamines and with bisamidrazones. The latter products, polytriazoloquinazolines, obtained in conformity with the general reaction scheme [280]



are closely similar to polybenzimidazoloquinazones. With neither structure has it yet been possible to realise the high thermal characteristics potentially inherent in them, owing to incompleteness of cyclisation and the low molecular weights of the polymers.

Critical analysis of all the above results indicates that the best classes of "ladder" polyheteroarylenes, obtained by three-stage polycyclocondensation, e.g. polynaphthoylene benzimidazoles, are significantly superior to the usual polyheteroarylenes in thermal stability and in operating temperatures. The achievement of the same or still higher thermal stability in other structures, e.g. polybenzimidazoloquinazolines, requires further research aimed at finding methods of synthesising polymers having high molecular weights and high degrees of cyclisation. Overall these polymers may make a significant contribution to the further enhancement of the thermal stability and the operating temperatures of polymeric materials on the solution of several problems facing the chemistry and the technology of ladder polyheteroarylenes—problems of the raw materials base, of processing, and of the production of almost perfect structures.

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