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# Ladder Polyheteroarylenes—Progress and Problems

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Survey of the present state of the chemistry of these polymers and examination of their resistance to various types of degradation show that a ladder structure does not guarantee great stability, although a high degree of structural perfection and highly stable heterocycles confer significantly improved heat resistance, thermal stability, non-flammability, radiation resistance, etc. relative to traditional heteroarylenes. The principal methods for synthesising ladder polyheteroarylenes of high degrees of cyclisation are considered, various modes of practical application are examined, and their prospects are noted. A list of 260 references is included.

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## I. INTRODUCTION

The development of several modern technologies—primarily aviation, rocket manufacture, electrical engineering, electronics, etc.—made it necessary to produce polymeric materials with operating temperatures around 300°C. Solution of this problem largely involved the elaboration of novel thermostable polymers. For this reason many investigations were undertaken in the USSR and abroad from the mid-1950s with the aim of creating new thermostable macromolecular compounds[1]. These investigations led to a considerable number of heteroorganic[1-9] and aromatic carbon-chain polymers[1,3,4,6-19] possessing a combination of valuable properties, but the greatest development occurred in the chemistry of aromatic polymers containing different heterocycles in the main chains—so called polyheteroarylenes[1,3,4,6-16,20-40].

The most widely used polyheteroarylenes have been polyimides[1,4,6-10,20,22,41,42] and polyazoles[1,4,6-10,21-32,40,43-47], whose development and introduction into industry solved the problem of producing polymeric materials capable of prolonged operation at temperatures up to 300°C. However, these polyheteroarylenes and materials made from them do not meet the constantly increasing demands, in particular for operation at temperatures above 300°C. During the mid-1960s, therefore, the development was undertaken of polyheteroarylenes that would surpass known heterocyclic polymers in a combination of properties, primarily in heat resistance and thermal stability. This problem could in principle be solved in several ways.

(1) Replacement of heterocyclic fragments in macromolecules of polyheteroarylenes by more thermostable heterocycles—an approach suggested by the preferential degradation of polyheteroarylenes at the heterocyclic fragments[48-56]—required a detailed study of the comparative thermal stability of individual heterocyclic systems[57-59] and the development of methods for synthesising polyheteroarylenes containing heterocycles of maximum thermal stability. This approach has now been followed quite successfully, although by no means all syntheses of highly thermostable aromatic heterocycles can be readily and successfully extended to polyheteroarylenes of high molecular weight.

(2) Polyheteroarylenes can be synthesised containing hetero-organic groups—e.g. organoboron[60,61] and organosilicon[62,63] groups.

(3) The production of polyheteroarylenes having a completely or partly ladder structure is the most promising approach, although quite controversial from various points of view. Ladder polymers—also termed "strip"[1], "double-chain", "ordered linear-spatial", and "non-randomly cross-linked"[64] polymers—attracted the close attention of investigators after the publication by Tessler[65,66] of results indicating that such polymers should be considerably more resistant to various types of degradation than are ordinary, "single-chain" polymers. The "period of enthusiasm" following his publications (1966-1970) saw the preparation of a considerable number of different classes of polyheteroarylenes, having a complete or partial ladder structure as a consequence of the introduction into the main chains of highly fused aromatic heterocycles[67-77]. Since in several cases such polymers differed little in thermal stability from the traditional polyheteroarylenes, interest in the ladder polymers diminished appreciably, and the "enthusiasm" was followed by a "period of scepticism", although research has continued on individual classes of ladder polymers.

Current views on ladder polyheteroarylenes can be summarised in the following statements: (i) partial and complete ladder structures can be expected to be more resistant than traditional polyheteroarylenes to various types of degradation; (ii) at the present time this potential advantage has not been realised; and (iii) the comparatively poor stability of known ladder polyheteroarylenes is due to the low degrees of cyclisation characterising all ladder polyheteroarylenes. All these statements are true within certain limits, but absolute acceptance of any of them will lead to erroneous conclusions, in particular to an unduly pessimistic assessment of ladder polyheteroarylenes.

An attempt has now been made at an objective survey of the present state of the chemistry of these polymers and their prospects.

## II. RESISTANCE TO VARIOUS TYPES OF DEGRADATION—PRECONDITIONS AND REALITY

According to Tessler[65,66] great stability towards degradation of polymers having a complete or partial

ladder structure, in comparison with single-chain macromolecules, is a consequence of the following considerations. Any reaction involving rupture of the macromolecular chains of single-chain polymers will lead to a decrease in molecular mass of the latter and hence a decrease in their strength characteristics. Double-chain (ladder) polymers can undergo rupture of any one bond without decrease in molecular mass and impairment of strength properties. Moreover, random rupture of several bonds may also be unaccompanied by decrease in molecular mass, and only two "concerted" chain breakages, occurring at strictly defined sites, will lead to fracture of the macromolecule into two fragments with all its consequences.

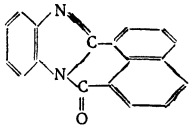
The above arguments were supported by quantitative results obtained by using the Monte Carlo method to analyse randomly occurring degradation processes in ladder and single-chain polymers [65,66]. The calculation was based on several postulates: (i) all bonds in the polymer were equally strong and equally accessible independently of their positions in macromolecules of different chain lengths; (ii) all polymer chains had the same length; and (iii) rates of degradation were proportional to the number of unbroken bonds in the polymer.

The calculations indicate that, for a given number of bonds ruptured in the macromolecules, completely laddered polymers undergo considerably smaller decreases in molecular mass than do single-chain polymers: in particular, the molecular mass of the former remains almost constant when the number of bonds broken would lead to an 80% decrease in single-chain polymers. Partly laddered structures occupy an intermediate position. In developing these principles Tessler [66] calculated rates of loss in weight of polymers of ladder and single-chain structure with increase in the number of bonds destroyed, and showed that in the initial stages of degradation ladder polymers undergo considerably smaller weight losses than do single-chain macromolecules.

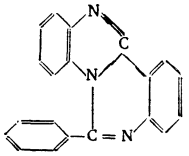
Tessler's scheme is undoubtedly extremely empirical, since it disregards several factors—tending either to hinder or to promote degradation—among which the following may be mentioned. (i) Positive changes in entropy accompanying degradation are larger with ladder than with single-chain polymers, which facilitates such processes. (ii) The energetics of degradative processes may change after the first bond rupture, and in particular the possibility of autocatalytic degradation is ignored [78]. (iii) Ladder polymers are more rigid than single-chain structures. Flexibility of completely ladder polymers can result only from microdeformations of the macromolecular lattice (i.e. deformations of valence angles and bonds) during its thermal vibrations [79,80]; the great rigidity of ladder polymers hinders the development of concerted movements of the segments—even at very high temperatures—which significantly retards the start of degradative processes [81,82]. (iv) Development of the "cage effect" [83,84] involves retention in the vicinity of the radicals formed after rupture of any bond, which can thus readily recombine after the excess of energy has been dissipated: the construction of ladder polymers from aromatic systems leads after rupture to more ready restoration of the original structure [64,72].

The empiricism of Tessler's scheme is still more evident when we pass from abstract double-chain systems to actual polymers. In particular, one of the principal postulates underlying the scheme—the equal strength of all bonds—is in effect impossible in polyheteroarylenes. Violation of this postulate, of course, nullifies a random character for degradation, and results in its preferential occurrence at the weakest bonds [1,3]. Thus a double-chain structure does not yet guarantee enhanced thermal stability in comparison with single-chain polymers, so that improved thermal characteristics in relation to traditional polyheteroarylenes cannot be expected from all ladder polyheteroarylenes, but only from those from which weak bonds are definitely absent.

Quantum-chemical calculations on several model compounds of ladder polyheteroarylenes and study of their degradation [85-88] have convincingly demonstrated significant differences in stability to thermal and thermohydrolytic degradation between models of different types of ladder polyheteroarylenes. In particular, 1,2-1',8'-naphthoylenebenzimidazole (I) and 2-phenylbenzimidazolo-[1,2-*c*]quinazoline (II)

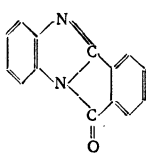


(I)



(II)

undergo degradation at temperatures 75 deg above that at which degradation of 1,2-benzoylenebenzimidazole (III)



(III)

begins [86,87]. Still more significant differences have been observed in the degradation of the polymers modelled by the above compounds and of other ladder polyheteroarylenes [88]. These differences are so considerable (up to 100–150 deg) that it is evidently inappropriate to speak of the thermal stability of ladder polyheteroarylenes as a whole.

Analysis of published results—extremely contradictory and frequently not comparable—nevertheless indicates that in several cases ladder polyheteroarylenes appreciably surpass traditional heterocyclic polymers in thermal stability. Thus ladder polyquinoxalines obtained by Stille et al. [89-91] begin to decompose, according to dynamic thermogravimetric analysis, in air at 550°C, but in an inert atmosphere at 700°C (Fig. 1). Polynaphthoylenebenzimidazoles exhibit high thermal stability [82,92-99], in full agreement with quantum-chemical calculations and results of a study of the degradation of model compounds [85-88]: under conditions of dynamic thermogravimetric analysis polymers of this type begin to decompose in air at 550°C, but after isothermal aging in air at 316°C for 500 h they retain 60–90% of the initial weight depending on structure [100] (Fig. 2). Polybenzimidazoloquinazolines possess still greater thermal stability, appreciably surpassing polynaphthoylenebenzimidazoles under conditions of isothermal thermogravimetric analysis [101] (Fig. 3). Under conditions of dynamic thermogravimetric analysis polybenzobispyrimidobenzimidazoles occupy an intermediate position between ordinary polyheteroarylenes and graphite [102] (Fig. 4), but under isothermal conditions they undergo no appreciable loss in weight on prolonged heating in air at 400°C. All the polyheteroarylenes examined are characterised not only by highly stable model compounds but also by high degrees of cyclisation. Thus polynaphthoylenebenzimidazoles are nearly 100% cyclised [92,100,103,104],

while polybenzimidazoloquinazolines and polybenzobispyrimidobenzimidazoles are 95% cyclised[105].

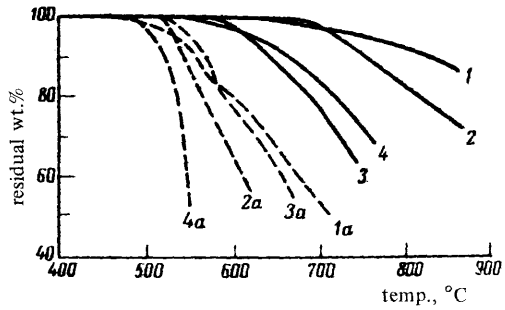
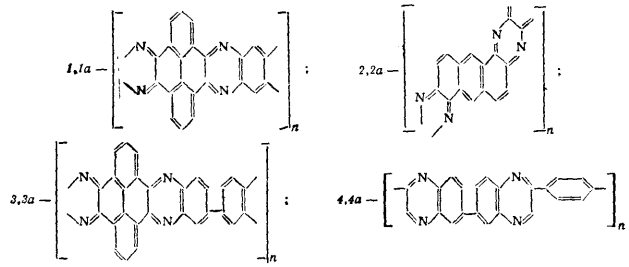



**Figure 1.** Dynamic thermogravimetric analysis curves ($\Delta T$ = 5 deg min$^{-1}$) in: 1)–4) an inert atmosphere; 1*a*)–4*a*) air for the polyquinoxalines:




Apart from ladder polyheteroarylenes possessing exceptionally high thermal stability several polymers of the same type are known whose thermal characteristics either do not surpass or are inferior to those of traditional polyheteroarylenes[106]. Some authors explain the low thermal stability of such ladder polymers either by the presence of readily decomposed groups[107] or by low thermal stability of the heterocycles forming the macromolecular double chain[108,109]. In the majority of cases, however, investigators are inclined to attribute inadequate thermal characteristics to structural defects[92,93,106,110,111], etc. to the heterounit character of the polyheteroarylenes[112–115]. This explanation is used especially frequently to interpret the unsatisfactory thermal stability of polybenzoylenebenzimidazoles, better known as "pyrrones"[92, 93,106,110–117]. The degree of cyclisation of pyrrones is indeed low (≤ 70%), which is confirmed both by experimental results[92,118,119] and by logical computations based on the complicated progress of a model reaction yielding together with the required 1,2-benzoylenebenzimidazole a wide range of products[76,77,120–123], as well as by the difficulties of solid-phase cyclisation in rigid polymer chains[93,124].

The heterounit character of pyrrones is responsible for their low thermal stability and leads in particular to the lower resistance of these polymers to degradation in comparison with the corresponding model compounds[116,117]. However, one deduction that may be made from this premise, formulated as "production of a polybenzoylenebenzimidazole of 100% (or simply a high degree of) cyclisation should yield a polymer of very high thermal stability", seems unsound, since compounds modelling pyrrones are characterised by comparatively low stability under conditions of thermal and thermohydrolytic degradation[85–88], in good agreement with earlier results[125–132] and with the high electrophilic reactivity of bis-1,2-benzoylenebenzimidazoles[133–135]. A similar principle applies also to other classes of ladder polyheteroarylenes having low degrees of cyclisation.

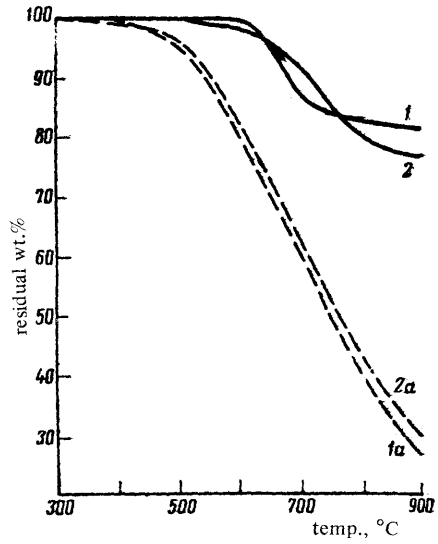
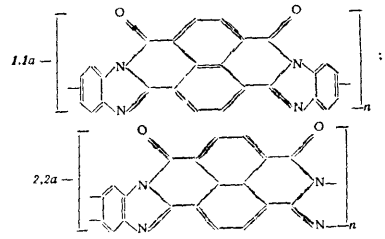



**Figure 2.** Dynamic thermogravimetric analysis curves ($\Delta T$ = 5 deg min$^{-1}$) in: 1), 2) air; 1*a*), 2*a*) an inert atmosphere for the polynaphthoylenebenzimidazoles




The heterounit character of ladder polyheteroarylenes is in principle closely connected with the stability of the heterocycles towards thermohydrolytic degradation and the action of various reagents, since the least stable heterocycles readily undergo all kinds of secondary reactions, tending to intensify the heterounit character of the polymers.

The high thermal stability of several of the above ladder polyheteroarylenes—polyquinoxalines, polynaphthoylenebenzimidazoles, polybenzimidazoloquinazolines, and polybenzobispyrimidobenzimidazoles—is apparent not only in higher temperatures at which they start to lose weight than for traditional polyheteroarylenes but also higher coking values, which in turn are closely related to the enhanced flame resistance of the polymers[136]. Ladder polymers possess considerably higher flame resistance

than traditional polyheteroarylenes: their oxygen indices exceed 0.6, in comparison with 0.3–0.45 for the latter.

Isolated experimental results indicate that ladder systems have a higher ablation resistance than traditional polyheteroarylenes. Polynaphthoylenebenzimidazoles[137,138] and polynaphthoylene-1,2,4-triazoles[139] possess especially high ablation resistance. Some workers[140–142] have noted considerable superiority of ladder polyheteroarylenes, in particular polyaroylenebenzimidazoles, in radiation resistance.

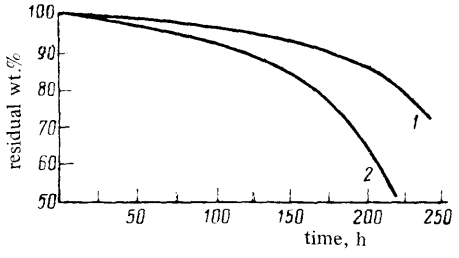
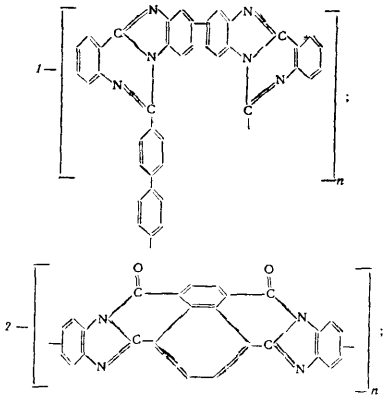



**Figure 3.** Isothermal thermogravimetric analysis curves in air at 361°C for: 1) polybenzimidazoloquinazolines; 2) polynaphthoylenebenzimidazoles:



Ladder systems are indisputably superior to the usual polyheteroarylenes in heat resistance. As a consequence of the great rigidity of polyheteroarylenes having a completely ladder structure their softening points are usually higher than the temperatures at which they begin to degrade. Even saturation by "hinge" groups of the main chains in partly ladder polyheteroarylenes rarely lowers their softening points below 400°C.

Significant advantages of ladder polyheteroarylenes have been found also in studying the working ranges of polynaphthoylenebenzimidazoles, polynaphthoylene-1,2,4-triazoles, polybenzimidazoloquinazolines, etc. Comparison with the corresponding ranges for traditional heterocyclic polymers[143] indicates the considerable superiority of ladder systems both in temperature and in strength parameters: ladder polyheteroarylenes are intermediate between ordinary polyheteroarylenes and sodium or potassium silicate glasses (Fig. 5).

Even the above far from complete analysis shows convincingly the considerable superiority of several ladder polyheteroarylenes over traditional heterocyclic systems in thermal stability and in heat, flame, radiation, and ablation resistance. Such superiority is due to highly stable heterocyclic groups in the macromolecules and also to close approach by the actual polymers to their ideal structures. The former factor is governed by the chemical structure of the polymers, whereas the latter largely depends on the method of synthesis of the polyheteroarylene.

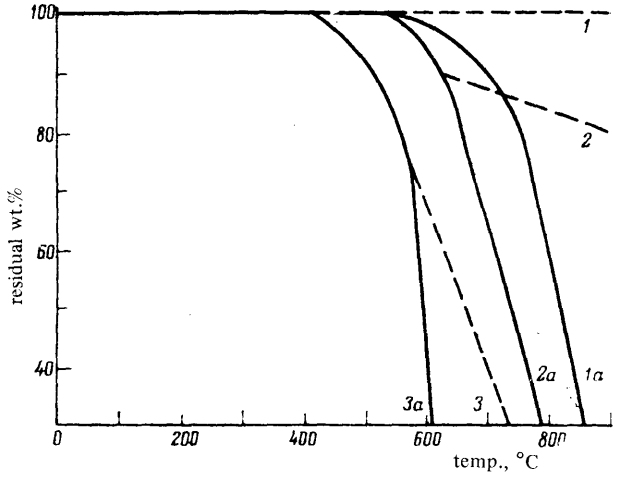
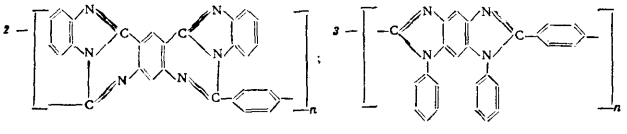


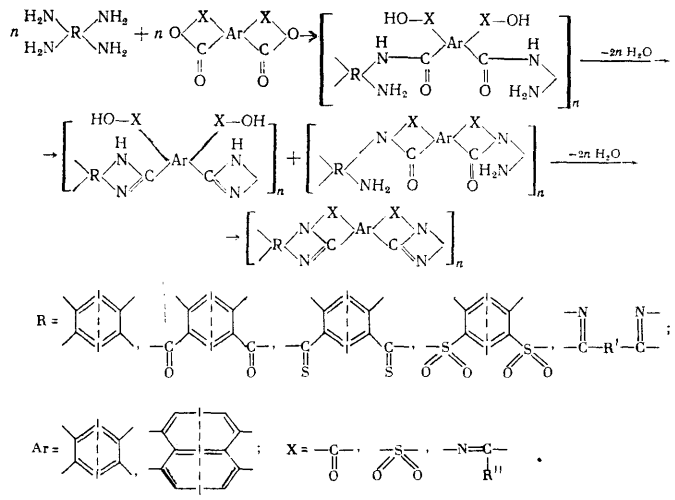

**Figure 4.** Dynamic thermogravimetric curves ($\Delta T$ = 5 deg min$^{-1}$) in: 1)–3) an inert atmosphere; 1*a*)–3*a*) air for: 1) graphite; 2) polybenzobispyrimidobenzimidazoles; 3) poly-*N*-phenylbenzimidazoles:



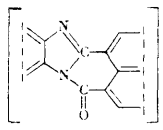
## III. PRINCIPAL METHODS OF SYNTHESIS

Most ladder polyheteroarylenes are obtained by multifunctional polycondensation, primarily by condensation polyheterocyclisation[72]. The synthetic reactions involved in this form of the process can be divided into three main groups[76]: (1) three-stage reactions of aromatic tetracarboxylic acids, their derivatives or analogues, with tetrafunctional nucleophilic reagents containing four amino-groups in the form of amine, amide, hydrazide, and other fragments[76]; (2) two-stage reactions of aromatic dicarboxylic acids or their derivatives with aromatic diamines containing in *ortho*-positions aromatic heterocycles with labile hydrogen atoms; and (3) two-stage homo- or co-polyheterocyclisations of tetrafunctional monomers containing the functional groups in pairs with *ortho*, *α*, or *peri* mutual orientation.

(1) The three-stage process is a logical continuation and development [76] of two-stage polyheterocyclisation yielding polyimides, which can be represented by the formalised and generalised scheme



Little has changed in this field since a recent detailed review of this process [76], and fundamental investigations confirming the earlier tendency [76] have been made on the synthesis and technology of polynaphthoylenebenzimidazoles of general formula



obtained by the polycyclocondensation of bis-*o*-phenylenediamines with bis-(naphthalic dianhydrides). Among these a noteworthy development is a method for synthesising polynaphthoylenebenzimidazoles of high molecular weight with high degrees of cyclisation by high-temperature catalytic polycyclocondensation in an organic solvent [144], which enables the polymers to be obtained as finely divided powders. Novel polynaphthoylenebenzimidazoles soluble in phenolic solvents have been obtained from bis-3,4-diaminophenylhexafluoropropane. [145] In addition, polynaphthoylenebenzimidazoles can be obtained from dianhydrides other than naphthalene-1,4,5,8-tetracarboxylic, namely, 4,4′-dinaphthalic anhydride [146] and 8,8′-biquinolyl-4,4′,5,5′-tetracarboxylic dianhydride [147]. Besides this synthetic work research has been aimed at improving traditional methods for obtaining polynaphthoylenebenzimidazoles in acidic solvents, by developing the method of synthesis without waste in Lewis acids [148] and by supercooling under special conditions to obtain polymers of large surface area [149]. Most probably pure and applied research on the manufacture of polynaphthoylenebenzimidazoles will remain in the near future the main lines of development of the three-stage method for the synthesis of ladder polyheteroarylenes.

(2) The first of the above two-stage processes was developed by Korshak and his coworkers [150,151] in the search for optimum methods of synthesising polybenzimidazoloquinazolines and poly-1,2,4-triazoloquinazolines, for which the three-stage method does not give satisfactory results [76]. The two-stage method [150,151] is a logical development of the general synthesis of polybenzazoles [44-46] based on the two-stage reaction of aromatic dicarboxylic acids or their derivatives with aromatic diamines containing simple substituents such as hydroxy, mercapto, amino, phenylamino, etc. *ortho* to the amino-groups. The first stage involves formation of aromatic polyamides containing these substituents *ortho* to the amide links. In the second stage these *ortho*-substituents react with the amide groups to form benzazole heterocycles.

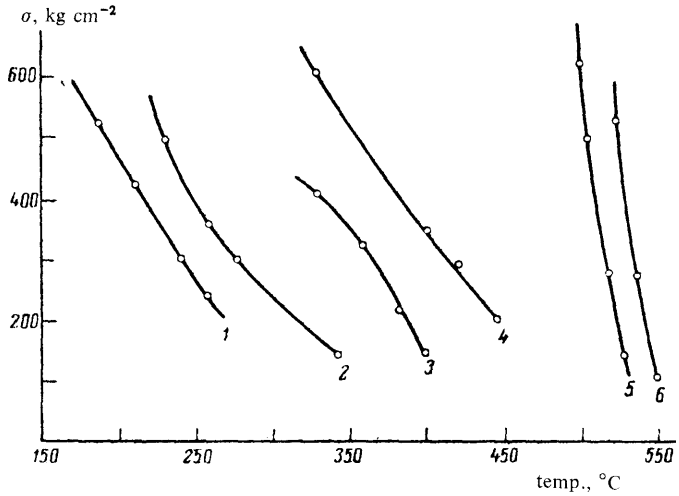
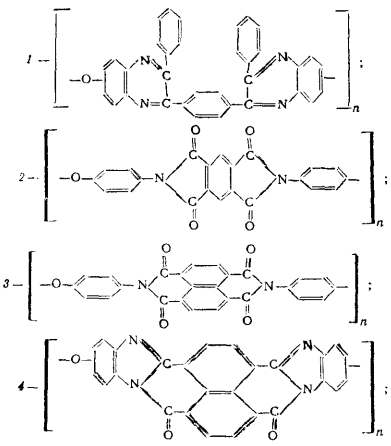
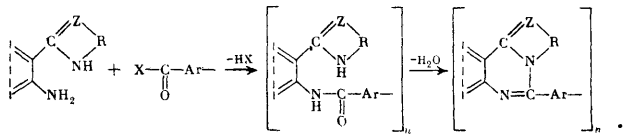



**Figure 5.** Working ranges of traditional polyheteroarylenes, ladder polyheteroarylenes, and glasses:

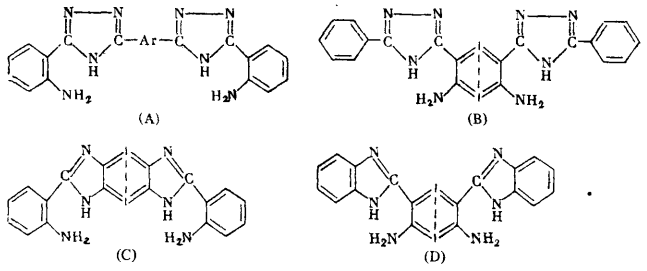


5) sodium silicate glass; 6) potassium silicate glass.

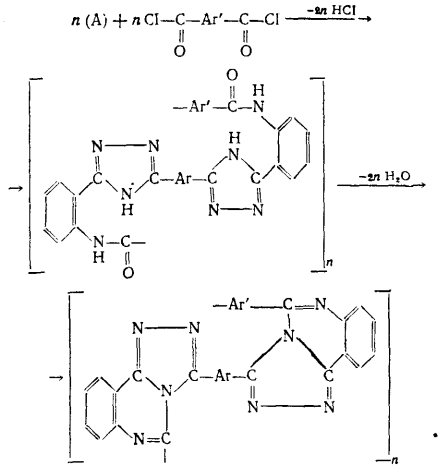
When diamines containing aromatic heterocycles in *ortho*-positions are used as monomers, the reactions follow a similar course, except that highly fused aromatic heterocycles are formed as a result of polycyclodehydration, and yield a partly ladder structure in the polyheteroarylenes obtained:



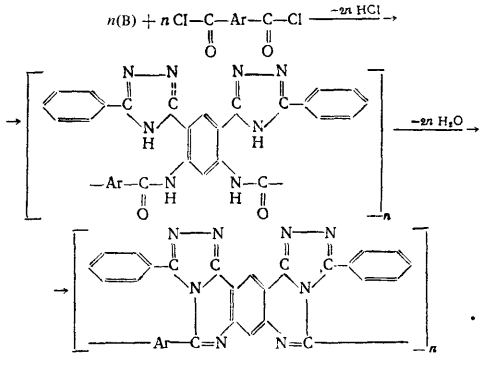
Among heterocycles that could potentially be used as *ortho*-substituents in the aromatic diamines the most widely used have been benzimidazole and 1,2,4-triazole rings:



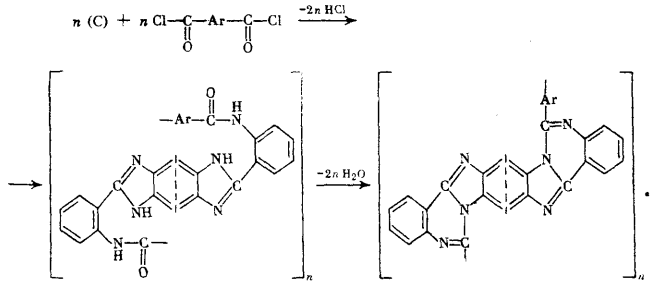
All four types of diamines have been used to obtain polyheteroarylenes of partly ladder structure. Diamines of type (A), bis-5-*o*-aminophenyl-1,2,4-triazol-3-ylarylenes, have given poly-1,2,4-triazoloquinazolines.[152-157] The most widely used synthesis of these polymers has been based on the two-stage method of mild interaction of the diamines with aromatic acid dichlorides in hexamethylphosphoramide followed by thermal cyclodehydration of the resulting poly-*o*-acylaminophenyltriazoles:



Under analogous conditions diamines of type (B), 4,6-di-(5-phenyl-1,2,4-triazol-3-yl)-1,3-phenylenediamines, have been treated with aromatic acid dichlorides to yield polybenzobistriazoloquinazolines of partly ladder structure[102,158,159]:



The same method of synthesis has been used to obtain partly ladder polyheteroarylenes from diamines of types (C) and (D). The action of acid dichlorides on 2,2′-di-*o*-aminophenylimidazolobenzimidazoles has given polybenzimidazoloquinazolines[150,151,160-166]:

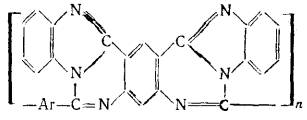


When diamines of type (D) are used as initial compounds, polybenzimidazoloquinazolines[160,167] and polybenzobispyrimidobenzimidazoles[102,158-160,168,169] are obtained.

Single-stage processes—polycyclocondensation in the melt with the use of diphenyl dicarboxylates[101,166,179,171] and high-temperature polycyclocondensation in polyphosphoric acid—can also be employed to obtain the above polymer systems. With triphenyl tricarboxylates as monomers "cross-linked" polybenzimidazoloquinazolines are obtained[101,171,172].

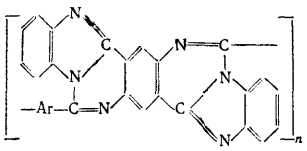
All the polyheteroarylenes obtained by the present method are closely similar in properties, both in the prepolymer stages and in the final stages. Depending on the specific structure of the prepolymers—copolyamidobenzimidazoles and copolyamido-1,2,4-triazoles, as well as polyamides containing *o*-benzimidazolyl and *o*-triazolyl substituents—they exhibit either limited solubility or complete insolubility in bipolar aprotic solvents. These polymers are characterised by comparatively low molecular weights (up to 30 000), probably because of the relatively weak nucleophilic character of the initial diamines containing bulky shielding substituents *ortho* to the amino-groups. The required partly ladder polymers are soluble only in strong acids such as sulphuric, trifluoroacetic, polyphosphoric, etc. These systems possess high heat resistance and thermal stability: under conditions of dynamic thermogravimetric analysis in air many of these polymers undergo no loss in weight right up to 500°C.

The greatest thermal stability is shown by polybenzobispyrimidobenzimidazoles

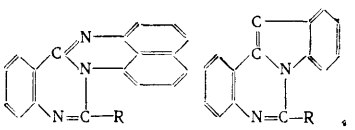


which are formed by the action of aromatic acid dichlorides on 4,6-bisbenzimidazol-2′-yl-1,3-phenylenediamine. The high thermal stability of these systems is probably due not only to stability of the heterocycles and high degrees of cyclisation of the polymers but also to absence of isomerism in the heterocycle, which according to Marvel[173] should influence favourably the thermal properties of polymers. For comparison we note that ladder polyheteroarylenes obtained by the three-stage method[76] contain a large quantity of structural isomers even in the ideal completely cyclised structures. Perhaps the thermal stability of polybenzobispyrimidobenzimidazoles

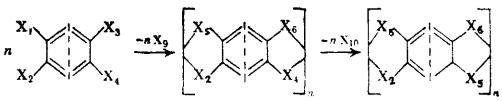
can be further enhanced by passing to more regular structures [173], e.g.



Diamines containing perimidine, indole, pyrrole, and other groups *ortho* to the amino-groups can also be used as monomers. This is supported by published results on the formation of the model compounds [174,175]

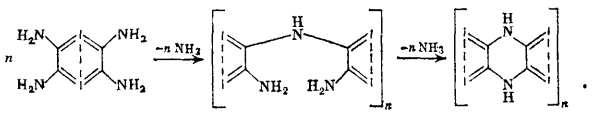


(3) The second of the above two-stage methods is the most widely used for the synthesis of partly or completely ladder polyheteroarylenes containing aromatic or hydroaromatic six-membered heterocycles. The general scheme of homocondensation can be written



where $X_1$–$X_4$ are the same or different functional groups, which differ from the groups $X_5$–$X_8$ by the molecules of the condensation by-products $X_9$ and $X_{10}$.

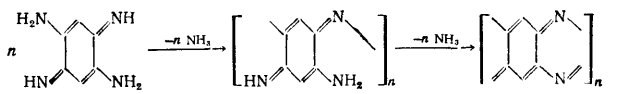
The simplest reactions of this type, in which $X_1 = X_2 = X_3 = X_4$, involve the homocondensation of bis-*o*-phenylenediamines [176–178] in polyphosphoric acid at 250–350°C:



The reaction products are polydihydrophenazines, which can undergo partial oxidation of quinoxaline fragments. The polymers obtained possess high thermal stability (that from bis-3,4-diaminophenyl ether loses only 14% of its initial weight when heated in nitrogen to 900°C). However, their thermo-oxidative stability is considerably lower (owing to the presence of the NH groups); they have limited solubility in sulphuric and methanesulphonic acids, and poor viscosity characteristics (specific viscosity 0.2–0.4 dl $g^{-1}$).

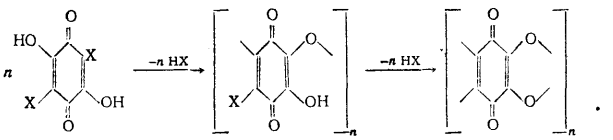
Polymers of closely similar structure have been synthesised by the homocondensation of 6,7-diaminoquinoxaline-2,3-diol in polyphosphoric acid [179]. The presence of imino-groups in the resulting polyquinoxalinodihydrophenazines is responsible for their relatively low resistance to thermal oxidation in comparison with the above polydihydrophenazines. An attempt at a fundamental improvement in the solubility and stability of the polymers by replacing hydrogen atoms in the dihydrophenazine rings with phenyl groups by using bis-*N*-phenyl-*o*-phenylenediamines as monomers did not yield the desired poly-*NN'*-diphenyldihydrophenazines [180].

A rather more successful attempt to use the homocondensation of tetrafunctional monomers to produce completely aromatic ladder polyheteroarylenes was made with 2,5-diamino-1,4-benzoquinonedi-imide in polyphosphoric acid [181]:



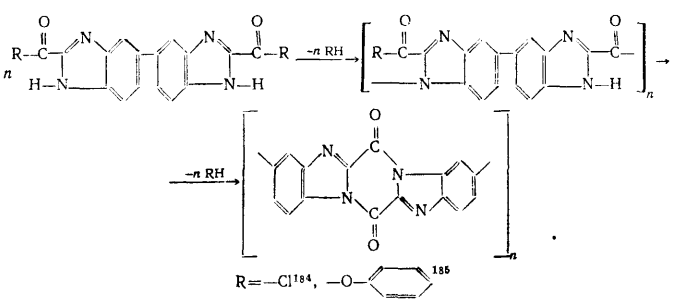
The resulting polymers have high thermal stability: weight losses associated with the start of degradation are observed at 450–480°C, while the most thermostable specimens lose 5% and 19% at 600 and 900°C respectively. Nevertheless, the products of homocondensation have only limited solubility in sulphuric acid and exhibit very poor viscosity characteristics (specific viscosity not exceeding 0.05 dl $g^{-1}$).

Other derivatives of *p*-benzoquinone have attracted the attention of research workers. In particular, Berlin et al. [182,183] accomplished the homocondensation of chloro- and bromo-anilic acids to polyquinonedioxins:



The synthesis of polyquinonedioxins in the melt [182] and in biphenyl, dimethylformamide, and *N*-methylpyrrolid-2-one [183] gives intensely coloured products of low molecular weight, characterised by sparing solubility and poor thermal stability. Thus these polymers lose up to 50% of their initial weight when heated in an inert atmosphere to 400°C for a few hours.

The homocondensation of derivatives of 5,5'-bibenzimidazolyl-2,2'-dicarboxylic acid [184,185] differs somewhat from the above reactions:

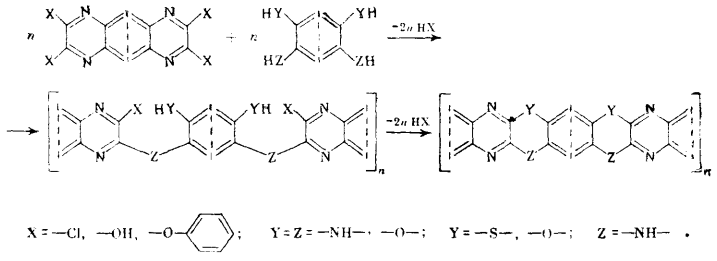


The mobile hydrogen atom of the benzimidazole ring acts as a functional group involved in polyheterocyclisation. Homocondensation of the acid dichloride was effected in thionyl chloride [184], and that of the diphenyl ester in the melt or in thiolan *S*-dioxide [185]. The resulting polybisbenzimidazopyrazinediones are partly soluble in sulphuric and methanesulphonic acids, have $[\eta] = 0.15$–$0.62$ dl $g^{-1}$, and according to thermogravimetric data begin to decompose in an inert atmosphere and in air at 465 and at 350–400°C respectively.

Inspection of the above results indicates that most ladder polyheteroarylenes obtained by the homocondensation of tetrafunctional monomers possess comparatively low molecular weights, limited solubility, and comparatively low (especially under conditions of thermal oxidation) temperatures at which degradation begins, which in combination present considerable difficulties to the use of

these polymers as foundations for thermostable materials. Another noteworthy feature is the limited range of tetrafunctional monomers used in homocondensation processes.

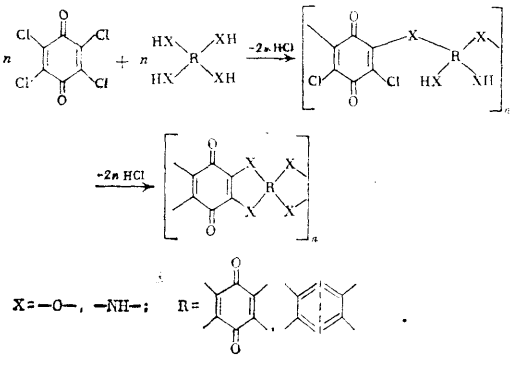
A considerably wider range of monomers can be used in the polycyclocondensation of two different tetrafunctional monomers. Marvel et al.[178,186-196] have made a comprehensive investigation of the reactions of tetrasubstituted bisquinoxalines and tetra-aza-anthracenes containing activated halogen, hydroxyl, and phenoxyl groups with bis-*o*-phenylenediamines, bis-*o*-aminophenols, bis-*o*-aminothiols, and tetraphenols. These processes can be represented by the general scheme



X = —Cl, —OH, —O—⟨benzene⟩; Y = Z = —NH—, —O—; Y = —S—, —O—; Z = —NH— .

The polymers can be synthesised in the melt or by high-temperature polycyclocondensation in an organic solvent of high boiling point or in polyphosphoric acid. They contain alternating quinoxaline and dihydrophenazine, oxazine, thiazine, and dioxin rings. They possess comparatively high thermal stability (dynamic thermogravimetric analysis indicates that their degradation begins at 450–550°C), but relatively low molecular weights and limited solubility, which presents considerable difficulties when they are processed into articles.

Although various groups can be used as functions in tetrasubstituted bisquinoxalines and tetra-aza-anthracenes, tetrachloro-derivatives have been most commonly employed, in which the chlorine atoms are highly reactive. Such derivatives have found the widest use also in another group of monomers—derivatives of *p*-benzoquinone—from which ladder polyheteroarylenes are obtained[197,198]. The general scheme of reaction of these compounds with tetrafunctional monomers can be represented

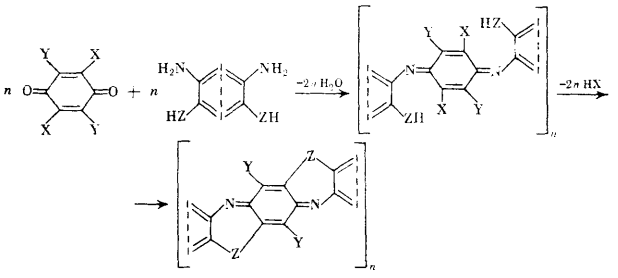


X = —O—, —NH—; R = ⟨quinone⟩ .

Polymers analogous in structure to products of the homocondensation of chloro- and bromo-anilic acids are obtained by reaction between chloranil and tetrahydroxy-*p*-benzoquinone[197]. The resulting polyquinonedioxins are intensely coloured substances of comparatively low molecular weight, identical in properties with products of the homocondensation of chloro- and bromo-anilic acids.

Polymers very similar in properties to polyquinonedioxins are obtained by the action of chloranilic acid or chloranil on bis-*o*-phenylenediamines[198].

In the above syntheses of ladder polyheteroarylenes the carbonyl groups of *p*-benzoquinone are not involved in polycyclocondensation but remain in the final macromolecular structures. A somewhat different approach was made by Stille and by Marvel[108,109, 181,199-202], who achieved the polycyclocondensation of *p*-benzoquinone derivatives with various monomers in which the carbonyl groups of the former were involved in ring formation:



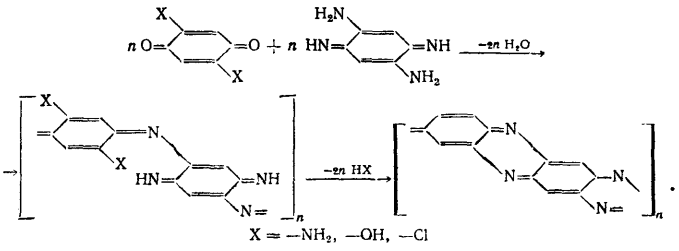
X = —OH, —O.CO.CH$_3$, —NH$_2$, —Cl; Y = —H, —Cl; Z = —O—, —NH—, —S— .

Thus polyphenoxazines of high molecular weight were obtained by reaction of bis-*o*-aminophenols with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone and with its diacetate[108,109]. The chief defects of these polymers are limited solubility in organic solvents and low thermal stability (in nitrogen a loss in weight was observed at 250–275°C), the latter due, as already noted, to the low thermal stability of the phenoxazine ring[108,109].

Polymers of great interest with respect to thermal stability have been obtained by the reaction of 2,5-dihydroxy-, 2,5-dichloro-, and 2,5-diamino-1,4-benzoquinones with bis-*o*-phenylenediamines[199-201]. In the case of the diol polycyclocondensation was accomplished in dimethylacetamide, hexamethylphosphoramide, and polyphosphoric acid; the polymers obtained in hexamethylphosphoramide were completely soluble in this solvent and possessed an intrinsic viscosity of 0.60–1.40 dl g$^{-1}$. Polydihydrophenazines obtained in dimethylacetamide and polyphosphoric acid are 50% and 30% soluble in hexamethylphosphoramide, and possess intrinsic viscosities of 0.57 and 1.45 dl g$^{-1}$ respectively. The polymers begin to decompose in air and in nitrogen at 525 and 535°C respectively.

Analogous polymers have been obtained with 2,5-diamino- and 2,5-dichloro-1,4-benzoquinones[199-201]. Marvel et al.[202] obtained a polytriphenodithiazine from the reaction of 2,5-dichloro-1,4-benzoquinone with the dihydrochloride of 4,4′-diaminobiphenyl-3,3′-dithiol. Continuing the reaction in dimethylacetamide at 150°C for 24 h gave a polymer of low molecular weight having a specific viscosity of 0.12 dl g$^{-1}$, soluble only in sulphuric acid. The same process in polyphosphoric acid gave a polymer that was partly soluble in sulphuric acid (specific viscosity 0.54 dl g$^{-1}$). Dynamic thermogravimetric analysis in helium indicates that the polymer loses 3% of its initial weight at 500°C.

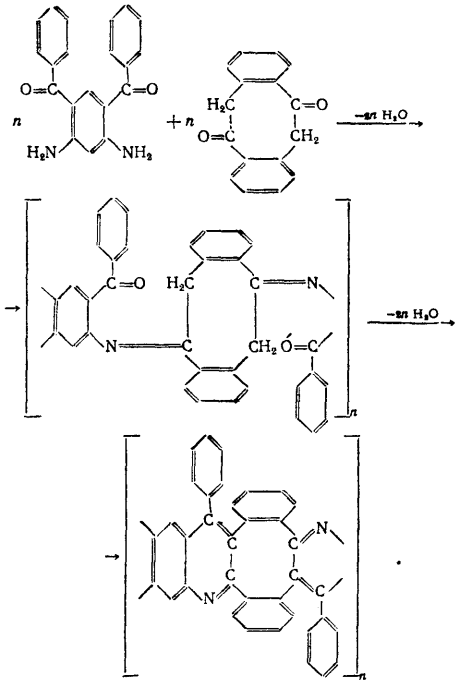
Polymers of completely ladder structure have been obtained by the reaction of 2,5-diamino-, 2,5-dihydroxy-, and 2,5-dichloro-1,4-benzoquinones with 2,5-diamino-1,4-benzoquinonedi-imide in polyphosphoric acid[181]:



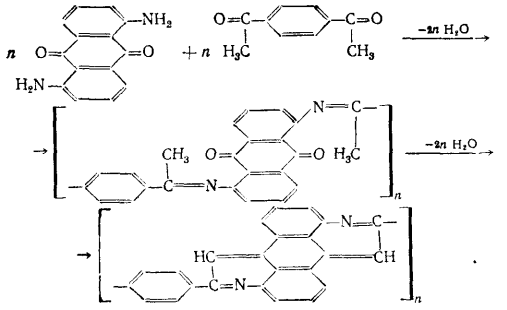
X = —NH$_2$, —OH, —Cl

Dynamic thermogravimetric analysis in nitrogen showed that the resulting polyphenazines possess comparatively high thermal stability, comparable with that of products of the homocondensation of 2,5-diamino-1,4-benzoquinone-di-imide. The ladder polyphenazines have the defects of poor solubility (they are only partly soluble in sulphuric acid) and comparatively low viscosity characteristics (specific viscosity $\leq 0.2$ dl g$^{-1}$).

Extending the Friedländer and related processes to the synthesis of macromolecular compounds is of considerable interest for the production of novel polyheteroarylenes of partly and completely ladder structure[203-205]. In particular, Stille et al.[204] have obtained a polymer of ladder structure from 4,6-dibenzoyl-1,3-phenylenediamine and a cyclic bisketomethylene compound—dibenzo[*a*,*e*]-cyclo-octene-5,11(6*H*, 12*H*)-dione:

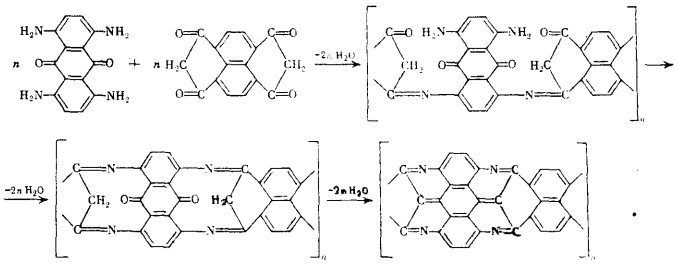


A process related to the Friedländer reaction has been used[206] to obtain a partly ladder polybenzodiquinoline from 1,5-diaminoanthraquinone and a series of diacetylated aromatic compounds. Most interesting results are obtained with *p*-diacetylbenzene[206]:



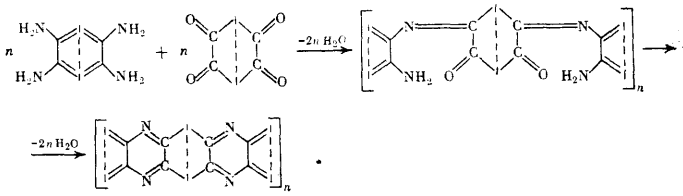
The first stage, effected in the melt at 240°C for 30 min, gives a polymeric Schiff base soluble in sulphuric and methanesulphonic acids, having a specific viscosity of 0.46 dl g$^{-1}$. The second stage occurs when the polymer is heated in polyphosphoric acid at 150°C for 5 h. Dynamic thermogravimetric analysis indicates that the resulting polybenzodiquinoline begins to decompose in air at 440°C, but in nitrogen it loses only 10% of its initial weight at 900°C.

Further development of this line of attack led to the synthesis of a graphite-like polymer[207-209] from 1,4,5,8-tetra-aminoanthraquinone and 1,2,3,6,7,8-hexahydropyrene-1,3,6,8-tetraone. It would be more correct to regard this not as a two-stage polycyclocondensation of two tetrafunctional monomers but as a three-stage polycyclocondensation of two hexafunctional compounds:



Interaction of the initial compounds in polyphosphoric acid at 170°C for 20 h gave a polymeric Schiff base soluble in sulphuric acid, with specific viscosity 2.7 dl g$^{-1}$. Subsequent vacuum treatment at 340°C for 2–5 days yielded the required highly condensed system. Isothermal thermogravimetric analysis in circulating air indicated appreciable weight losses even at 300°C, probably largely owing to the low degree of cyclisation of the system. An interesting feature of the polymer is its high electrical conductivity of $2 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$.[210]

Examination of the literature indicates that the reaction most often used in the synthesis of ladder polyheteroarylenes is the condensation of amino and carbonyl groups. The same reaction forms the basis of the synthesis of ladder polyquinoxalines[89-91,107,204,211]:



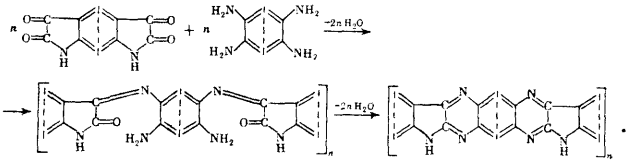
Using 3,3,6,6-tetramethylcyclohexane-1,2,4,5-tetraone as tetracarbonyl compound, Stille et al.[107] obtained polyquinoxalines of comparatively low thermal stability resulting from the ease of decomposition of the isopropylidene groups. In air the polymers began to break down at 200–290°C depending on their structure, but in an inert atmosphere at 400°C.

Completely aromatic ladder polyquinoxalines were obtained by the use of pyrene-1,2,6,7-tetraone and anthracene-1,2,6,7-tetraone as initial tetracarbonyl compounds, and of benzene-1,2,4,5-tetra-amine, naphthalene-1,2,5,6-tetra-amine, 1,2,5,6-tetra-aminoanthraquinone, and dibenzo-*p*-dioxin-2,3,6,7-tetra-amine as the initial bis-*o*-phenylenediamines[89-91].

Thus the reaction of benzenetetra-amine with pyrene- and anthracene-1,2,6,7-tetraones in hexamethylphosphoramide at 180°C for 120 h gave completely aromatic polyheteroarylenes, which would have been more correctly termed not polyquinoxalines but polytetra-aza-anthracenes[89]. These polymers did not dissolve in cold hexamethylphosphoramide, but were completely soluble in dichlorotetrafluoroacetone hydrate. The specific viscosities of the polymers reached 2.1 dl $g^{-1}$, corresponding to molecular weights of 7000–15 000. Still higher molecular weights were obtained by synthesising the polymers in polyphosphoric acid: the above polytetra-aza-anthracenes had specific viscosities up to 3.6 dl $g^{-1}$. Such polymers are characterised by *syn–anti* isomerism in the macromolecular chains, which enhances their solubility and processability into articles.

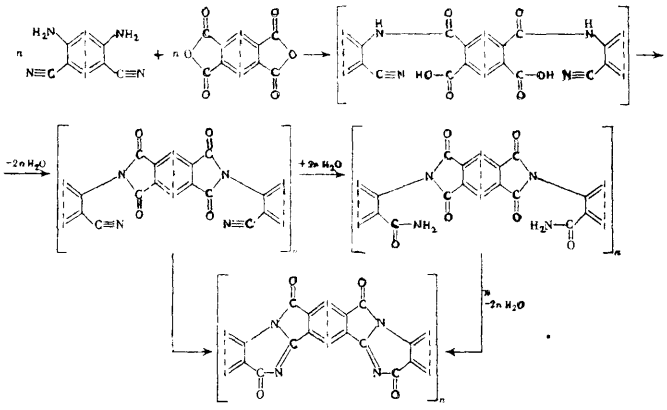
Several of the polymers possess film-forming properties. Dynamic thermogravimetric analysis indicates that the start of their degradation in air lies in the same temperature range as for linear polyquinoxalines (~550°C), but in an inert atmosphere the ladder systems exhibit considerably greater stability, beginning to decompose in the region of 700°C.

Bi-isatyls have also been used as tetraoxo-monomers: they react with bis-*o*-phenylenediamines to form polyindoloquinoxalines[212-219]:

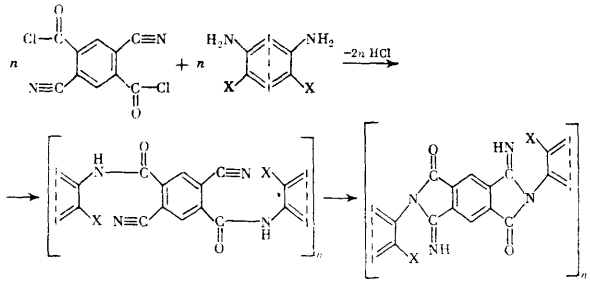


The synthesis of these polymers, like that of ladder polyquinoxalines, proceeds most smoothly in polyphosphoric acid, when the products are completely soluble in sulphuric and methanesulphonic acids with intrinsic viscosities up to 1 dl $g^{-1}$.[217-219] Dynamic thermogravimetric analysis indicates that these polymers begin to decompose at 460 and at 700°C in air and in nitrogen respectively[217-219].

All the aoove processes involve condensation polyheterocyclisation: i.e. they are accompanied by the evolution of volatile products of low molecular weight, which makes it difficult to obtain massive articles free from defects (pores, cracks, etc.). As a consequence, isomerisation cyclisation, which does not involve the formation of volatile products, is of considerable interest for the production of ladder polyheteroarylenes, as of heterocyclic polymers as a whole[220-224]. Ladder polyheteroarylenes have been most commonly synthesised from prepolymers containing nitrile groups, although by no means all the processes considered below involve purely isomerisation polycyclisation. Thus reaction between tetracarboxylic dianhydrides and bis-*o*-amino-nitriles forms poly-*o*-carboxy-*o'*-cyano-amides, cyclodehydration of which yields polyimides containing *o*-nitrile substituents; cyclisation of these polyimides in turn leads to poly-isoindoloquinazolinediones[225-227]:

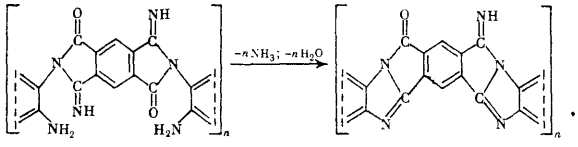


Several ladder polyheteroarylenes are obtained by thermal cyclisations of *ortho*-substituted poly-imino-imides[228]:



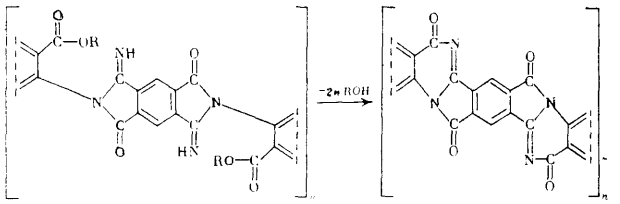
X = —$NH_2$, —COOR, —C≡N .

In some cases only intermediate *ortho*-substituted poly-iminoimides are formed by the isomerisation mechanism, and the concluding stage is accompanied by the evolution of simple products. Thus the reaction of hydrochlorides of aromatic tetra-amines with 2,5-dicyanoterephthaloyl chloride gives rise to poly-*o*-amino-*o'*-cyano-amides, heat-treatment of which at 150°C is accompanied by isomerisation cyclisation giving poly-*o*-amino-imino-imides. Heating these polymers at 250–350°C leads to the formation of polybenzoylenebenzimidazoles and their imino-analogues with the liberation of water or ammonia[229]:



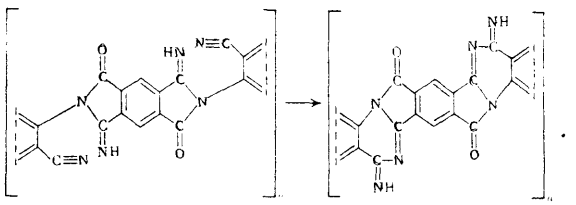
The resulting polymers are soluble in sulphuric acid, possess specific viscosities of ~0.5 dl $g^{-1}$, and according to thermogravimetric analysis lose 5% of their initial weight in air at 400°C. The comparatively low thermal stability is not surprising in view of the great activity of the 1,2-benzoylenebenzimidazole ring[76], also containing an exocyclic imino-group, which is undoubtedly the "weak spot" in these systems.

The action of 2,5-dicyanoterephthaloyl chloride on bisaniline-*o*-carboxylic acids or their methyl esters forms polyamides containing nitrile and carboxyl or methoxycarbonyl *ortho*-substituents. Isomerisation cyclisation of these systems at 130–150°C results in poly-iminoimides containing *o*-carboxyl or *o*-methoxycarbonyl groups and undergoing at 200–250°C cyclocondensation with the liberation of water or methanol and formation of polyisoindoloquinazolinediones [230]:



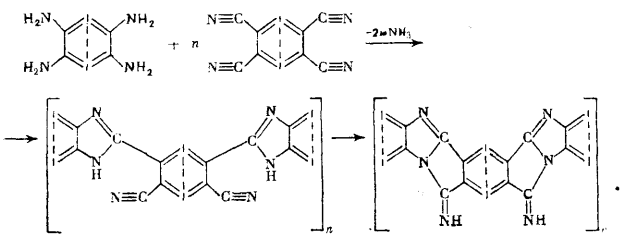
The resulting polymers are soluble only in sulphuric acid, possess specific viscosities up to 0.8 dl $g^{-1}$, and begin to undergo extensive degradation at 500°C.

Polyheteroarylenes of partly or completely ladder structure, which undergo cyclisation solely by an isomerisation mechansim, are obtained by reaction between 2,5-dicyanoterephthaloyl chloride and bis-*o*-aminonitriles followed by heat-treatment of the resulting poly-*oo'*-dicyano-amides with the temperature raised step by step to 300°C [231,232]:

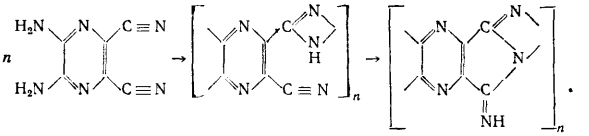


The poly-*oo'*-dicyano-amides formed in the first stage are readily soluble in polar organic solvents and possess sufficiently high molecular weights to form strong and flexible films. The final polyiminoisoindoloquinazolinediones begin to decompose at 400–450°C according to thermogravimetric data. Since the second stage of isomerisation cyclisation does not involve the separation of simple products, the resulting polymers can be processed into monolithic articles of considerable thickness or used as binders for glassfibre-reinforced plastics and for adhesives.

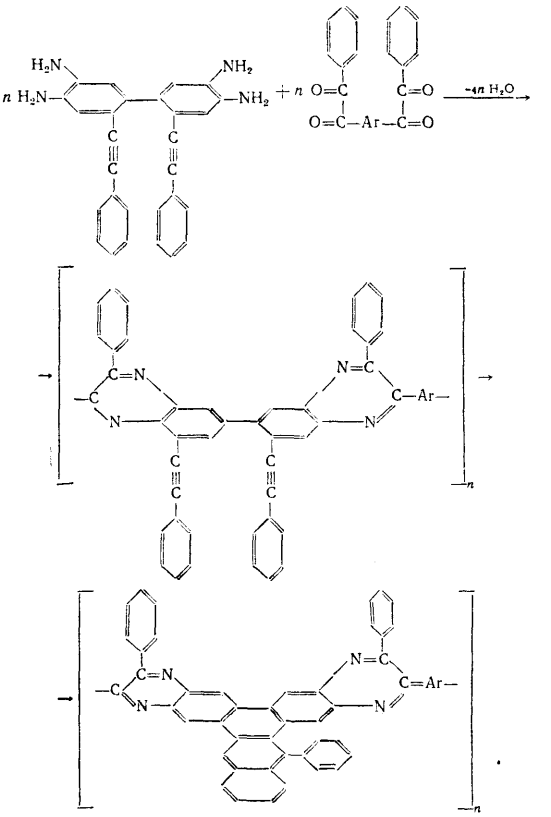
Polybenzimidazoles containing *ortho*-nitrile substituents can also undergo isomerisation cyclisation [233,234]. Thus the condensation of equimolecular quantities of tetranitriles with bis-*o*-phenylenediamines in boiling 2-methoxyethanol containing sodium 2-methoxyethoxide gives insoluble black polymers [233]:



Thermogravimetric analysis indicates that the polymer formed from biphenyl-3,3'-4,4'-tetra-amine and the tetranitrile of pyromellitic acid is the most thermostable, losing 10% of its weight respectively at 500 and 700°C in air and in argon. Still better thermal characteristics are attributed to the product of the homocondensation of 2,3-diamino-5,6-dicyanopyrazine [234]



Isomerisation cyclisation can be applied also to polymers containing ethynyl side-chains. A typical example of such intramolecular processes is the formation of condensed systems by the heat-treatment of polyphenylquinoxalines obtained from 6,6'-diphenylethynyl-biphenyl-3,3',4,4'-tetra-amine and various tetraones [235-238]:



The resulting phenylated polyanthrabisquinoxalines have high glass points combined with high degradation temperatures (respectively > 360 and ~450°C).

On the whole ladder polyheteroarylenes obtained by isomerisation cyclisation do not possess especially good thermal characteristics, but the advantages of the cyclisation process open up wide prospects before isomerisation cyclisation.

## IV. PRACTICAL APPLICATION—ACHIEVEMENTS AND PROSPECTS

The most considerable achievement in the practical application of ladder polyheteroarylenes is the development of polynaphthoylenebenzimidazole fibres, obtained

by spinning sulphuric-acid solutions of these polymers[239-245]. After being stretched 80–120% at 525–600°C these fibres possess at room temperature a tensile strength of 5 g denier$^{-1}$ and an extension at break of 5%. In air the fibres retain 55–60% of their strength after 1 min at 660°C and after 30 h at 360°C; they resist the action of moisture and ultraviolet radiation[243]. At the present day they are the most thermostable among organic fibres. Not only fibres but also thermostable films[246], composition materials[247-249], and several other materials have been obtained from polynaphthoylenebenzimidazoles.

Polybenzimidazoloquinazolines can form the basis for carbon plastics that retain good strength characteristics (bending strength 1080 kg cm$^{-2}$) at temperatures around 370°C,[101,170-172] and also for adhesives which maintain a high strength after being aged in air at 400°C.[250]

Ladder polyquinoxalines have been used as binders for glassfibre-reinforced plastics[252], but only fragmentary attention has been paid to the properties of these materials. Practical utilisation of ladder polyheteroarylenes—even the most heat-resistant and thermostable—is governed primarily by their poor processability into articles: the great rigidity of these ladder polymers is responsible for their high softening points, which often lie even above the temperatures at which decomposition begins. The same factor also causes the limited solubility of ladder polyheteroarylenes, most of which are soluble only in strong acids. Several approaches are now envisaged towards overcoming the poor processability of ladder polyheteroarylenes.

Among purely synthetic approaches an important place will probably be occupied by the above trend to diminish the rigidity of the macromolecules[145-147,254] by using new monomers containing single carbon–carbon bonds or "hinge" groups. However, this requires the development of novel monomers and careful selection of the most readily available among them. In this connection it seems more promising to prepare copolymers and make polymer mixtures[255]. In particular, considerable interest attaches to the production of random and block copolymers containing fragments of ladder polyheteroarylenes and no less thermostable polymers that appreciably surpass the former in processability, among which polyphenylquinoxalines present the greatest interest[256-258]. On the other hand, such production of copolymers of polyphenylquinoxalines and ladder polyheteroarylenes can be regarded as a method of enhancing the thermal stability of the former, an urgent problem in the chemistry of polyphenylquinoxalines[256-258]. Mixtures of traditional polymers with ladder polyheteroarylenes are still more promising, provided, of course, that the components show good compatibility. Small additions of ladder polyheteroarylenes to traditional polymers may lead to stabilisation[259] and "alloying"[260] of the latter, whereas the introduction of considerable quantities of ladder polyheteroarylenes can probably raise the temperature of prolonged operation of the polymeric materials to 300–350°C. The search for optimum forms of such mixtures of polymers is an extremely promising approach, since it may lead to relatively cheap thermostable polymeric materials.

## V. CONCLUSION

The present survey enables us to assess the present situation in the chemistry of ladder polyheteroarylenes. Greater resistance to various types of degradation can be expected from partly and completely ladder polyheteroarylenes than from traditional polyheteroarylenes, provided that the heterocycles in the main chains are very stable and the polymers as highly cyclised. At the present time this potential advantage of ladder polyheteroarylenes has been realised only with a comparatively small number of systems—ladder polyquinoxalines, polynaphthoylenebenzimidazoles, polybenzimidazoloquinazolines, polybenzobispyrimidobenzimidazoles, and a few others—which meet both requirements formulated above.

A low degree of cyclisation is not adherent in all ladder polyheteroarylenes: high degrees can be achieved in such systems, but careful choice both of the reactions themselves and of the reaction conditions is necessary. The latter requirement is quite understandable, for the synthesis of ladder polyheteroarylenes (especially the three-stage process[76]) may involve the formation of various intermediate structures and lead to a wide range of end-products. As a consequence, processes that in the chemistry of individual (model) compounds give maximum yields of the required systems are to be preferred. There is no doubt that more careful selection of the processes involved in synthesis of ladder systems and careful selection of reaction conditions can lead to the appearance of novel polymers possessing enhanced stability to various types of degradation.

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