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Phenyl-substituted Polyheteroarylenes

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The fundamental methods of synthesis of polyheteroarylenes containing phenyl substituents in the heterocycles, formed in the course of the polycyclocondensation process, are examined. The influence of the phenyl substituents on the principal characteristics of the polyheteroarylenes is analysed. The likely usefulness of the introduction of phenyl substituents into polyheteroarylenes, in the sense of increasing their solubility, thermoplasticity, and resistance to thermal oxidation, is demonstrated.
The bibliography includes 112 references.

CONTENTS

I. Introduction 459
II. Phenylated analogues of polyimides 459
III. Phenylated polybenzazoles, polytriazines, and polyquinoxalines 461
IV. Phenyl-substituted polyheteroarylenes obtained by the Friedlaender reaction 462
V. Phenyl-substituted polyheteroarylenes obtained by a modified reductive polyheterocyclisation reaction 463
VI. Phenylated ladder polyheteroarylenes 465

I. INTRODUCTION

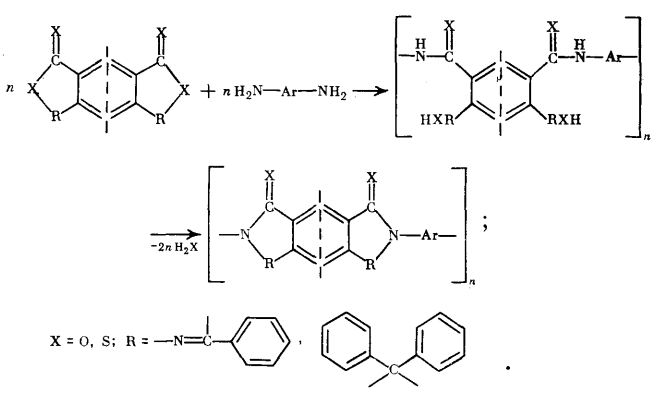
The development of a number of fields of modern technology has led to the necessity of synthesising thermostable polymeric materials and hence new thermostable polymers. Numerous studies designed to synthesise thermostable macromolecular compounds, both in the USSR and abroad, have resulted in the development of a series of organoelemental[1,2] and aromatic carbochain polymers[1,3-8], but aromatic polymers containing various heterocycles in the main macromolecular chains, namely polyheteroarylenes, have come to be most widely used[1,3,4,6,7,9,10-12].

One of the achievements in the chemistry of polyheteroarylenes has been the development of multistage methods of their synthesis in which the first stages are carried out under mild conditions, the resulting prepolymers are isolated and used to make the required articles, after which thermal cyclisation is carried out directly in the finished article[1,4,9]. This approach has been used widely and successfully in the synthesis of polyimides[13,14], polyazoles, and polybenzazoles[15-18] and also a series of other polyheteroarylenes. Together with unquestionable advantages, the multistage method of synthesis of polyheteroarylene suffers from a series of significant disadvantages, among which the main one is the instability of the prepolymers[13,14] and also the lack of technological procedures for the thermal cyclisation processes and the impossibility of secondary processing of the polyheteroarylenes. As a result, in the middle 1960s a tendency arose in the chemistry of polyheteroarylenes to impart to these systems solubility in organic solvents in the final stage. Solubility in inorganic solvents and hence improved capacity for being converted into articles can be imparted to polyheteroarylenes in various ways—by introducing "hinged" groups into the main chain of the macromolecules, by synthesising macromolecules with the most asymmetric structure possible[3,19], and by synthesising polymers with bulky side groups—the "card" polymers[20-22]. However, the approach involving the introduction of phenyl side groups into the polyheteroarylenes, i.e. the synthesis of phenyl-substituted polyheteroarylenes, has come to be most widely employed. Phenyl substituents can be introduced by using monomers containing phenyl groups either in fragments which do not change in the course of the polycyclisation reaction[23,24] or in functional groups or fragments involved in the formation of the heterocycle. Phenyl substituted polyheteroarylenes obtained by the second of the above two procedures will be examined in this review.

II. PHENYLATED ANALOGUES OF POLYIMIDES

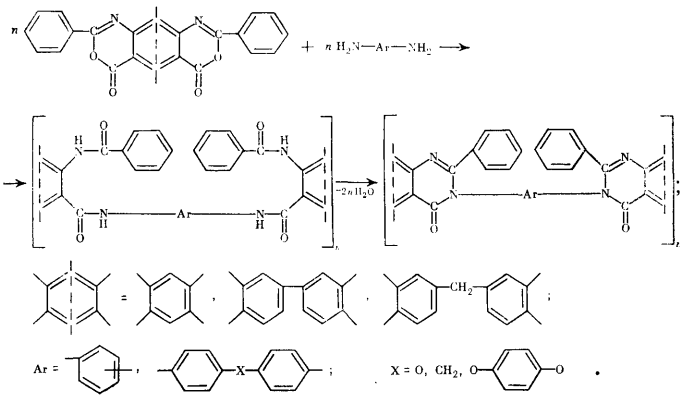
A large group of reactions involving the synthesis of phenyl-substituted polyheteroarylenes, obtained from monomers containing phenyl substituents in functional groups, can be represented by a general scheme similar to that for the synthesis of polyimides[13,14], i.e. involving the interaction of cyclic electrophilic monomers with diamines accompanied by ring opening and subsequent cyclodehydration of the resulting *o*-substituted polyamides (Scheme 1).

Scheme 1



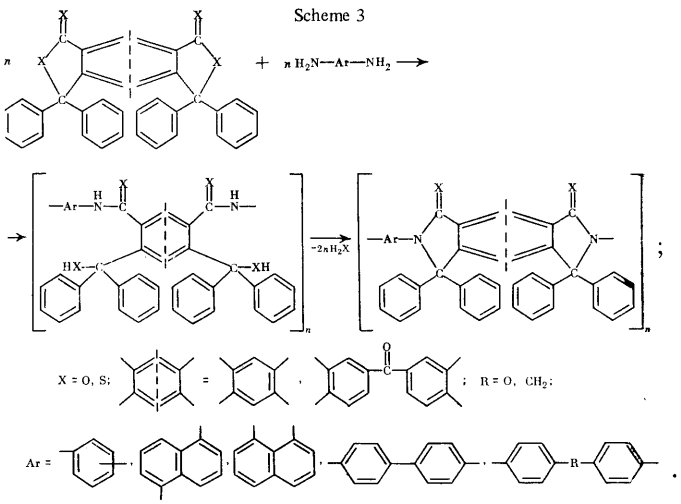
The first polyheteroarylenes obtained in accordance with Scheme 1 were phenyl-substituted polyquinazolinones, whose synthesis was achieved by the interaction of bis(2-phenylbenzoxazin-4-ones) with aromatic diamines[25–29] in accordance with Scheme 2.

Scheme 2



The reduced electrophilic reactivity of bis(2-phenylbenzoxazinones) compared with the dianhydrides of tetracarboxylic acids[30] necessitates the synthesis of phenyl-substituted polyquinazolinones under the conditions of high-temperature polycyclocondensation in polyphosphoric acid (PPA) or phenolic solvents[25–29]. The fact that the polycyclocondensation processes are carried out at 200° ± 20 °C combined with the ease of formation of six-membered heterocyclic systems makes it virtually impossible to isolate the intermediate poly(*o*-benzamido)amides and results in the occurrence of cyclisation reactions under the conditions of polymer chain propagation reactions. It is most useful to employ di(4-aminophenyl) ether and di(4-aminophenyl)methane as aromatic diamines. These substances are the most basic in the series of aromatic diamines[31]. Furthermore, the presence of "hinged" groups in these compounds determines the enhanced flexibility of the macromolecules obtained on their basis. Phenyl-substituted polyquinazolinones synthesised from these diamines are soluble in acid and phenolic solvents and are highly viscous, which makes it possible to prepare strong elastic films on their basis. Phenyl-substituted polyquinazolinones exhibit a comparatively high thermal stability—according to the results of dynamic thermogravimetric analysis (DTGA), the polymers do not undergo degradation in air up to 420 °C.

Scheme 3



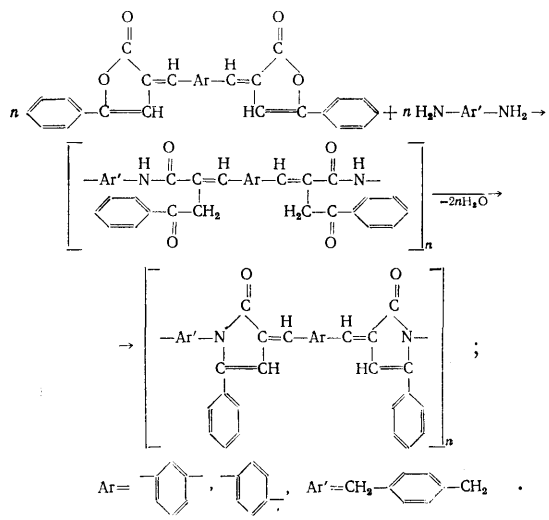
Phenylated polyimidines have been obtained by the reaction of phenylated phthalides[32–35] or their thio-analogues[33] with aromatic diamines in accordance with Scheme 3.

Like benzoxazinones, phthalides are comparatively weakly electrophilic[36,37] and react with amines, particularly aromatic amines, extremely slowly even in the presence of two phenyl substituents in the 3-position of the phthalide ring. For this reason, phenylated polyimidines are synthesised in accordance with Scheme 3 at high temperatures (180–350 °C), which precludes in its turn the isolation of the intermediate *o*-substituted polyamides and polythioamides. Regardless of whether the polyimidines were synthesised in the melt or in solvents, for example in PPA, nitrobenzene, biphenyl, dixylylethane, trichlorobenzene, or *m*-cresol, the polymers obtained have comparatively low viscosity characteristics (the maximum value of η_{log} of their solutions did not exceed 0.3 dl g^{-1}). At the same time the polyimidines were readily soluble in organic solvents—$CHCl_3$, dimethylformamide (DMF), and CCl_4—and exhibited a high thermal stability, losing 10% of the initial mass at 400–525 °C in air and at 450–560 °C in an inert medium[32–35]. These advantages of polyimidines are responsible for the interest in the synthesis of high-molecular-weight systems of this type. One of the possible ways of solving the problem of such synthesis consists in the employment as monomers of thio-analogues of phthalide compounds more reactive than the oxo-compounds[33].

Products similar in structure and properties to the polymers obtained in accordance with Scheme 3 were synthesised by the homocondensation of 6-amino-3,3-diphenylphthalide[38] and 3-(*p*-aminophenyl)-3-phenylphthalide[39] in PPA, nitrobenzene, trichlorobenzene, or dixylylethane.

The synthesis of phenylated polypyrrolinones by the reaction of 2,2-diphenyl-substituted bis(but-3-en-4-olides) with diamines[40] (Scheme 4) is fairly closely related to the reactions described in a general form by Scheme 1.

Scheme 4

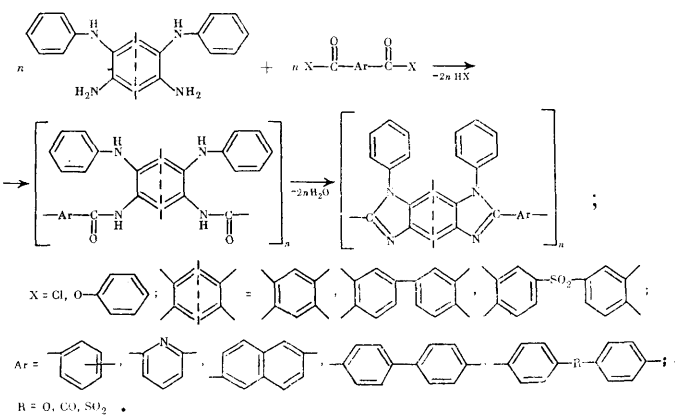


The first stage of the process at a low temperature in *m*-cresol led to the formation of polyamides with keto-side groups. When the process was carried out at 80 °C in the presence of acid catalysts (H_3BO_3, HCl, or CH_3COOH) or at 160 °C in the absence of catalysts, phenyl-substituted polypyrrolinones were obtained. Both polyamides with keto-substituents and phenylated polypyrrolinones are soluble in polar solvents (*m*-cresol, nitrobenzene, and DMF), but their viscosity characteristics are low (the maximum η_{log} of their solutions do not exceed 0.5 dl g^{-1}) and they have a low thermal stability, which makes these systems less interesting.

III. PHENYLATED POLYBENZAZOLES, POLYTRIAZINES, AND POLYQUINOXALINES

Together with the synthesis of phenyl-substituted polyheteroarylenes by reactions analogous to those used in the synthesis of polyimides, the synthesis of phenyl-substituted polybenzazoles in accordance with the general scheme for the synthesis of these systems[16-18], has attracted the attention of investigators. In the series of phenyl-substituted polybenzazoles, the synthesis of poly(*N*-phenyl)benzimidazoles in accordance with Scheme 5 has attracted most attention[28,41-53].

Scheme 5

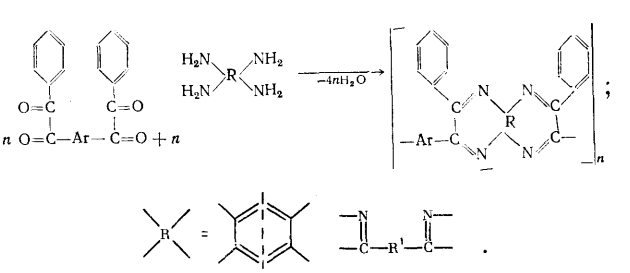


The first studies designed to obtain poly(*N*-phenyl)-benzimidazoles were associated with the reaction of bis(*N*-phenol-*o*-phenylenediamines) with the diphenyl esters of dicarboxylic acid; the process was carried out initially in the melt and was followed by the subsequent high-temperature additional cyclisation of the solid mass *in vacuo* (the Marvel reaction"[41-44]). The poly(*N*-phenyl)benzimidazoles obtained were distinguished by relatively low viscosity characteristics (the η_{int} of 0.5% solutions in HCOOH at 25 °C were in the range 0.64–0.86 dl g^{-1}),[44] which precluded the formation from them of articles with effective deformation-strength characteristics.

In order to increase the viscosity characteristics and hence the molecular weights of these polymers, attempts were made to synthesise poly(*N*-phenyl)benzimidazoles by a two-stage process. The first stage involved the interaction of bis(*N*-phenyl-*o*-phenylenediamines) with the dichlorides of dicarboxylic acids under the conditions of low-temperature polycondensation in dipolar aprotic solvents[28,42-52]. The second stage involved the cyclisation of poly(*o*-phenylamino)-amides under the conditions of thermal solid-phase polycyclisation[42-52]. When the synthesis of poly(*o*-aminophenyl)amides is carried out in amide solvents[28,45-49], high-molecular-weight systems, forming strong elastic films, are obtained; polymers with still higher molecular weights are formed when the polycondensation is carried out in sulpholan[51,52], which does not enter into side reactions with aromatic dicarboxylic acid dichlorides. The poly(*o*-aminophenyl)amides are usually cyclised to poly(*N*-phenyl)benzimidazoles by the solid-phase heat treatment of these systems[45-52]; this results in the formation of high-molecular-weight film-forming products which are soluble in acid and phenolic solvents. The cyclisation can also be achieved in PPA [45-47] or, more effectively, by adding hydrogen chloride or other acid catalysts to the reaction solutions of poly(*o*-aminophenyl)amides and then heating the latter at 160–170 °C.[28,45-47] Unfortunately the catalytic polycyclisation of poly(*o*-aminophenyl)amides has not come to be widely used, although there is no doubt about the likely usefulness of the method.

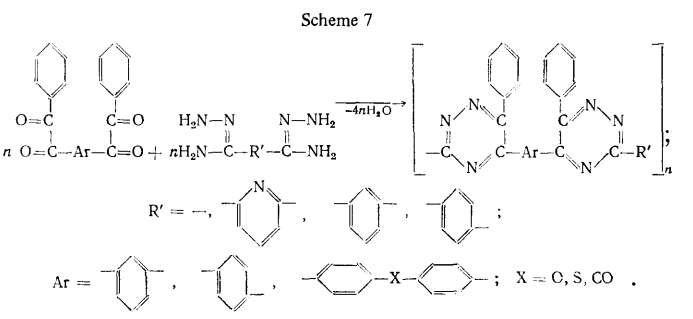
Detailed comparison of the properties of poly(*N*-phenyl)-benzimidazoles and unsubstituted polybenzimidazoles[42,53] showed that the introduction of phenyl substituents improves the solubility of the polymers and their resistance to thermo-oxidative degradation with the simultaneous decrease of their softening temperatures and thermal stability in an inert medium. The latter factor is due to the ease of abstraction of the phenyl substituents from the nitrogen atoms of the benzimidazole ring as a consequence of the lack of conjugation between the heterocycle and the substituent[53,54]. In the light of these data, the synthesis of polyheteroarylenes containing phenyl substituents at a carbon atom is preferable. A large family of such polymers has been obtained as a result of the reaction of tetrafunctional nucleophilic compounds (bis-*o*-phenylenediamines[55] and dicarboxylic acid bis-amidrazones[55,56]) with bisphenylglyoxalyl derivatives[55,57] in accordance with the general Scheme 6.

Scheme 6



The interaction of dicarboxylic acids bisamidrazones with bisphenylglyoxalyl derivatives in accordance with reaction (7) results in the formation of poly-*asym*-triazines[57-70].

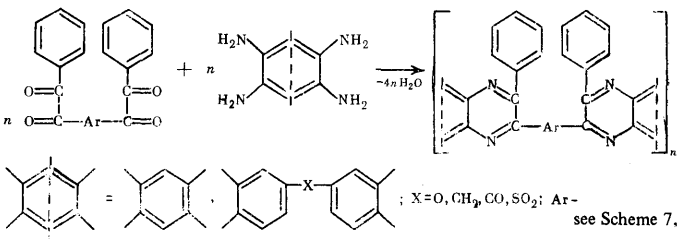
Scheme 7



The synthesis of poly-*asym*-triazines takes place smoothly in *m*-cresol and a number of other solvents even at room temperature. Fully aromatic phenylated poly-*asym*-triazines are characterised, depending on their structure, by a high or limited solubility in acid and phenolic solvents and also in chloroform, dimethyl sulphoxide (DMSO), dimethylacetamide (DMA), and other dipolar aprotic solvents. These polymers have high viscosities and hence high molecular weights which determine the possibility of preparing from them films, adhesives, and binders for glass plastics[63,66] capable of being used for a long time at 260 °C. Poly-*asym*-triazines soften at 270–330 °C and, in contast to unsubstituted poly-1,2,4-triazines, are characterised by a comparatively high resistance to isothermal thermal ageing in air, because the most thermostable representatives of this class of polyheteroarylenes lose 20–25% of the initial mass in 45 h at 290 °C. Polyphenylquinoxalines, which are the products of the interaction of bis(*o*-phenylenediamines) with bisphenylglyoxalyl

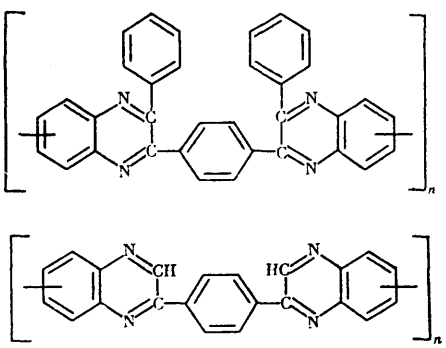
derivatives[57,71,72] in accordance with Scheme 8, are even more thermostable.

Scheme 8

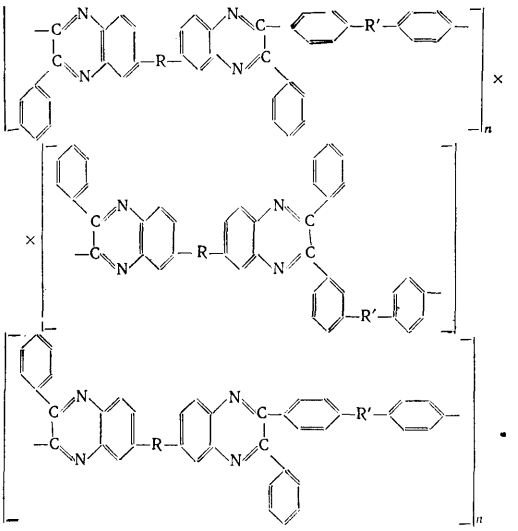


see Scheme 7.

In the series of phenylated polyheteroarylenes these polymers have attracted most attention. A number of careful reviews have been devoted to problems of their synthesis, their properties, and the materials based on them[57,71,72]. We shall therefore not analyse these data in detail. We shall only mention that, like polyphenyl-*asym*-triazines, polyphenylquinoxalines are obtained under very mild conditions. Thus, the polycyclocondensation is carried out at room temperature in phenolic solvents or in chlorinated hydrocarbons. The ease of formation of the quinoxaline ring is responsible for the almost complete absence of uncyclised fragments from these polymers, which, in combination with the high stability of individual heterocyclic compounds of this type, determines the high thermal and chemical stability of polyphenylquinoxalines. These properties of the above systems, combined with their high molecular weights and ready solubility in phenolic solvents, *N*-methyl-2-pyrrolidinone (NP), and chloroform, are responsible for the undoubted practical value of polyphenylquinoxalines, which can be used as binders in reinforced plastics[73,74], adhesives[73], films[72], fibres[72], and other polymeric materials capable of being employed for a long time at 320 °C. In full analogy with polyphenyl-*asym*-triazines, polyphenylquinoxalines also exhibit a higher resistance to thermal oxidation than their unsubstituted analogues. Thus comparison of the thermo-oxidative stabilities of polyphenylquinoxaline based on 3,3'-diaminobenzidine and 1,4-bis(phenylglyoxalyl)benzene and its non-phenylated analogue[75] showed that they lose respectively 6 and 50% of the initial mass at 400 °C in the course of 200 h.



The most significant disadvantage of polyphenylquinoxalines is their high thermoplasticity due to the "isomeric heterounit" structure of these systems: the macromolecules of polyphenylquinoxalines contain isomeric 2,2'-, 3,3'-, and 2,3'-substituted phenylquinoxaline fragments:



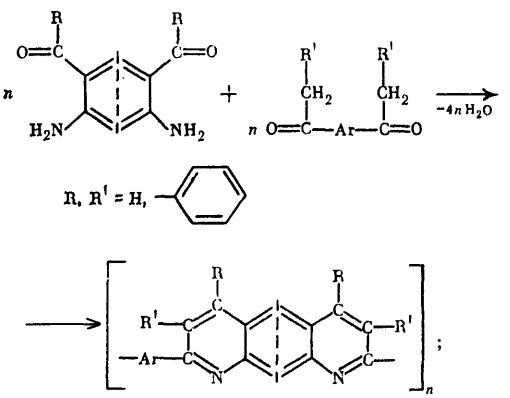
The relative amounts of these fragments in polyphenylquinoxaline macromolecules depend on the nature of the monomers employed. Despite the fact that the interaction of the most nucleophilic amino-groups of bis(*o*-phenylenediamines) with the most electrophilic carbonyl groups of bis(α-diketones) or the interaction of the least nuclephilic amino-groups of bis(*o*-phenylenediamines) with the least electrophilic groups of bis(α-diketones) is most likely, the "isomeric heterounit" structure is characteristic of all polyphenylquinoxalines without exception. As a result, all the known polyphenylquinoxalines proved to be amorphous and the attempts to synthesise ordered systems of this type were unsuccessful[72]. In the search for phenylated polyheteroarylenes free from "isomeric heterounit" structures, a number of investigators turned to polycyclocondensation reactions based on the Friedlaender reaction[76].

IV. PHENYL-SUBSTITUTED POLYHETEROARYLENES OBTAINED BY THE FRIEDLAENDER REACTION

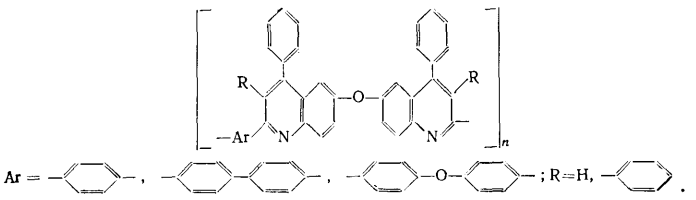
The classical version of this reaction consists in the condensation of *o*-aminocarbonyl compounds with ketomethylene products[76].

A number of phenyl-substituted polymers containing 2,6-quinoline and anthrazoline fragments in the main macromolecular chains have been synthesised by the reaction of diaminodicarbonyl compounds with aromatic diacetyl and diphenylacetyl compounds (Scheme 9).

Scheme 9



In particular the interaction of di(4-amino-3-benzoylphenyl)-ether with bis(α-ketomethylene) compounds in mixtures of *m*-cresol with PPA and P_2O_5 and 130–140 °C yielded a series of poly-2,6-quinolines[77–80] having the general formula

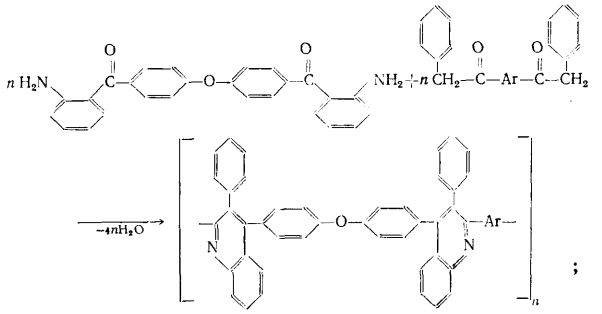


The polymers dissolve in *m*-cresol and chloroform and their intrinsic viscosities are in the range 0.6–4.1 dl g^{-1}. Their glass points are 260–350 °C and their melting points, corresponding to a ~20% degree of crystallinity, are in the range 450–480 °C. The temperatures of the onset of the degradation of poly(2,6-quinolines) are 530–545 °C in air and 530 ° to 570 °C in nitrogen according to DTGA data. Under the conditions of isothermal thermal ageing, polyquinoline based on di(4-acetylphenyl) ether, the least thermostable of the polymers synthesised, did not undergo degradation for 100 h at 300 °C, while after 100 h at 371 °C its mass diminished by 48%.[81]

In the series of polyanthrazolines obtained by the reaction of 4,6-diaminoisophthalaldehyde[80,82,83] and 4,6-dibenzoyl-1,3-phenylenediamine[84] with aromatic diacetyl and diphenacetyl compounds, the greatest interest attaches to systems based on 4,6-dibenzoyl-1,3-phenylenediamine—these are polymers soluble in *m*-cresol, HCOOH, and MP and having η_{log} up to 1.25 dl g^{-1}. According to DTGA data, these polyanthrazolines decompose at 500–550 °C in air and at 530–600 °C in an inert medium.

Poly(2,4-quinolines), which are isomeric with the poly(2,6-quinolines) described above, have been obtained by the reaction of di[4-(2-aminobenzoyl)phenyl] ether with diphenacetyl monomers[85] in accordance with Scheme 10.

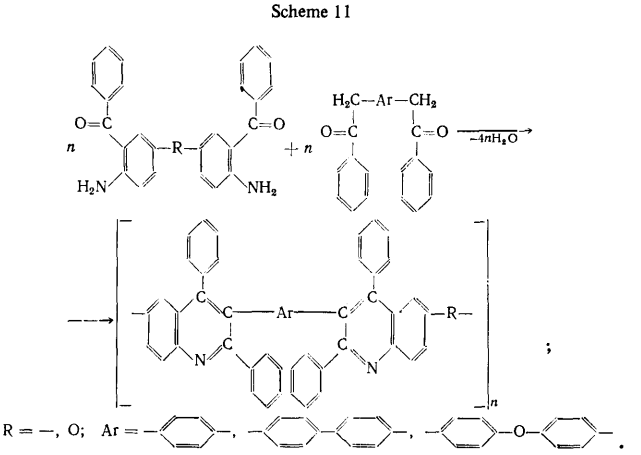
Scheme 10



They are soluble in *m*-cresol and have intrinsic viscosities of 0.26–0.57 in this solvent.

When aromatic diacetyl and diphenacetyl compounds are replaced by diphenacyl monomers of the type of 4,4'-diphenacylbiphenyl, di(4-phenacylphenyl) ether, and 1,4-diphenacylbenzene and on interaction of these products with di(4-amino-3-benzoylphenyl) ether and 4,4'-diamino-3,3'-dibenzoylbiphenyl, phenylated poly(3,6-quinolines) were obtained[86] (Scheme 11).

Scheme 11



Like the phenylated polyquinolines examined above, these polymers are soluble in *m*-cresol, chloroform, and tetrachloroethane and have intrinsic viscosities of 0.5–3.6. Their thermal characteristics are comparable to those of the polyquinolines considered above. Overall, phenyl-substituted polyquinolines and polyanthrazolines have higher softening temperature than polyphenylquinoxalines, but in this case the introduction of phenyl groups significantly increases the thermoplasticity of polyheteroarylenes.

Yet another group of reactions which lead to extensive possibilities for the synthesis of phenyl-substituted polyheteroarylenes consist of modified reductive polyheterocyclisation processes[87].

V. PHENYL-SUBSTITUTED POLYHETEROARYLENES OBTAINED BY A MODIFIED REDUCTIVE POLYHETEROCYCLISATION REACTION

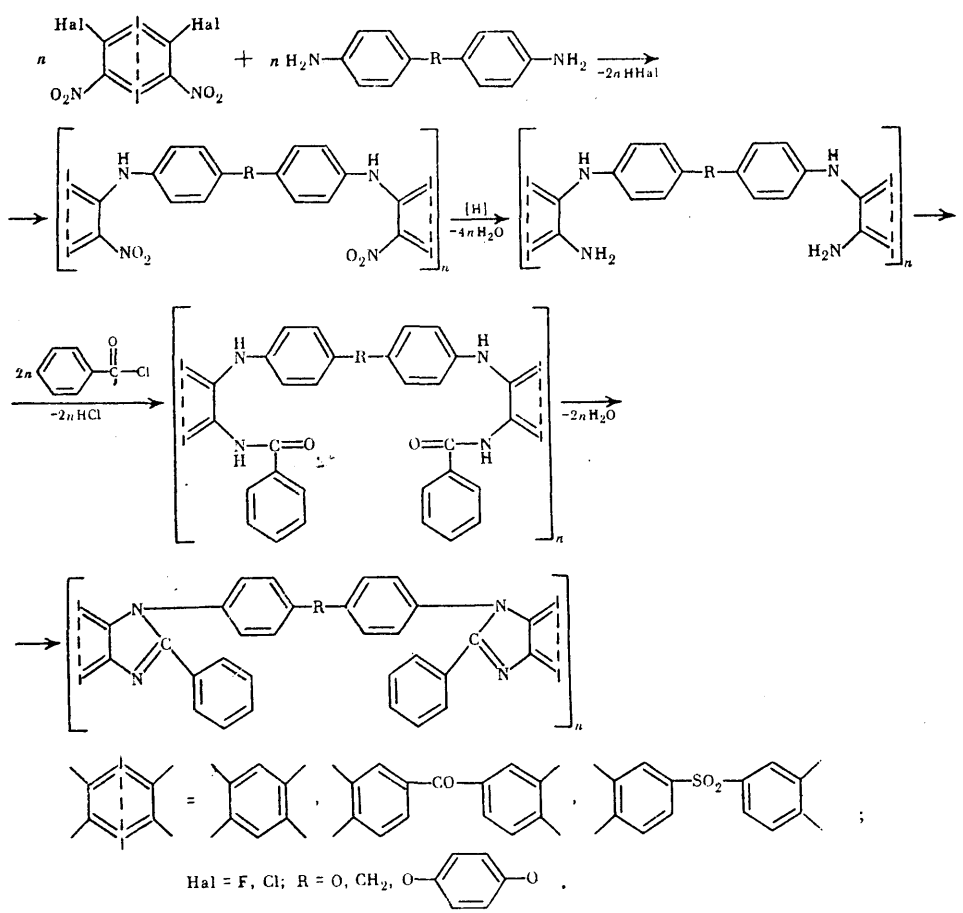
These processes were used successfully for the first time to synthesise *C*-phenyl-substituted polybenzimidazoles, including the interaction of activated bis(*o*-nitro)halogenoarylenes with reactive aromatic diamines[88–94], the reduction of the nitro-groups in the resulting poly(*o*-nitro)amines to the amino-groups[88–92,95], the benzoylation of the latter[88–92,95], and catalytic polycyclisation of the poly(*o*-benzamido)amines formed to poly(*C*-phenyl)benzimidazoles[88–92,96] (Scheme 12).

Such polyphenylbenzimidazole are most usefully synthesised in a single-stage process, i.e. without isolation of the intermediate polymeric structures[88–92], in MP and using as a source of hydrogen and as a polycyclisation catalyst the hydrogen halide evolved as a side product in combination with metals. The employment of a catalyst makes it possible to carry out this process at relatively low temperatures (160–170 °C), eliminating thereby the risk of all possible secondary cross-linking degradation, etc. reactions.

In the series of poly(*C*-phenyl)benzimidazoles, polymers based on di(4-chloro-3-nitrophenyl) sulphone and di(4-aminophenyl) ether or di(4-aminophenyl)methane—readily available and at the same time reactive compounds— are of greatest interest. These polymers have high viscosities, are readily soluble in phenols and amide solvents, and have higher thermal stabilities than the poly(*N*-phenyl)benzimidazoles, which are similar to them in structure (see above).

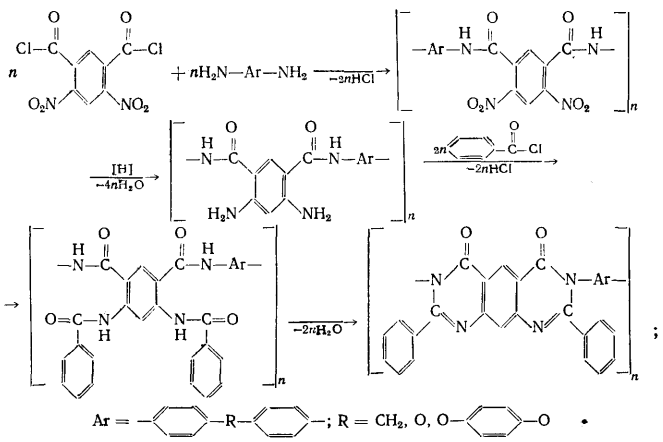
High quality carbon plastics, capable of being used for a long time at 250–300 °C, have been obtained from these polymers[87]. A significant disadvantage of these systems is their low softening temperatures (300–320 °C), which are responsible for their thermoplasticity at elevated temperatures.

Scheme 12



Somewhat higher softening temperatures are characteristic of phenylated polyquinazolinones obtained by the method of modified reductive polyheterocyclisation[97,98], involving the interaction of the dichloride of 4,6-dinitroisophthalic acid with activated aromatic diamines, the reduction of the *o*-nitro-substituents in the resulting polyamides to the amino-groups, benzoylation of the latter, and catalytic cyclisation of the poly(*o*-benzimido)amides formed (Scheme 13).

Scheme 13



The poly(2-phenyl)quinazolinones obtained in this way do not contain unreduced nitro-groups and uncyclised fragments according to the infrared spectroscopic data for the polymers and model compounds. The polymers synthesised are soluble at room temperature in strong acids and phenols and on heating in dipolar and aprotic solvents. The viscosities η_{int} of poly(2-phenyl)quinazolinones are 1.02–1.21 dl g^{-1}, which makes it possible to obtain from these systems strong ($\sigma \leq 1200$ kg cm^{-2}) and fairly elastic ($\varepsilon \geq 12\%$) films. According to DTGA data and the results of isothermal thermogravimetric analysis (ITGA), the thermal stability of these polymers is comparable to that of identical systems obtained by the usual (see above) method[26].

The properties of phenylated and unsubstituted polyheteroarylenes have been by no means compared in all the systems examined above. However, analysis of the available data and systematic arrangement of the results scattered throughout the literature show that in the vast majority of cases the introduction of phenyl substituents into polyheteroarylenes leads to the following results:

1) the improvement of the solubility of polyheteroarylenes in organic solvents;

2) an increase of the resistance of polyheteroarylenes to thermo-oxidative degradation;

3) a decrease of the softening temperatures and hence an increase of the thermoplasticity of polyheteroarylenes.

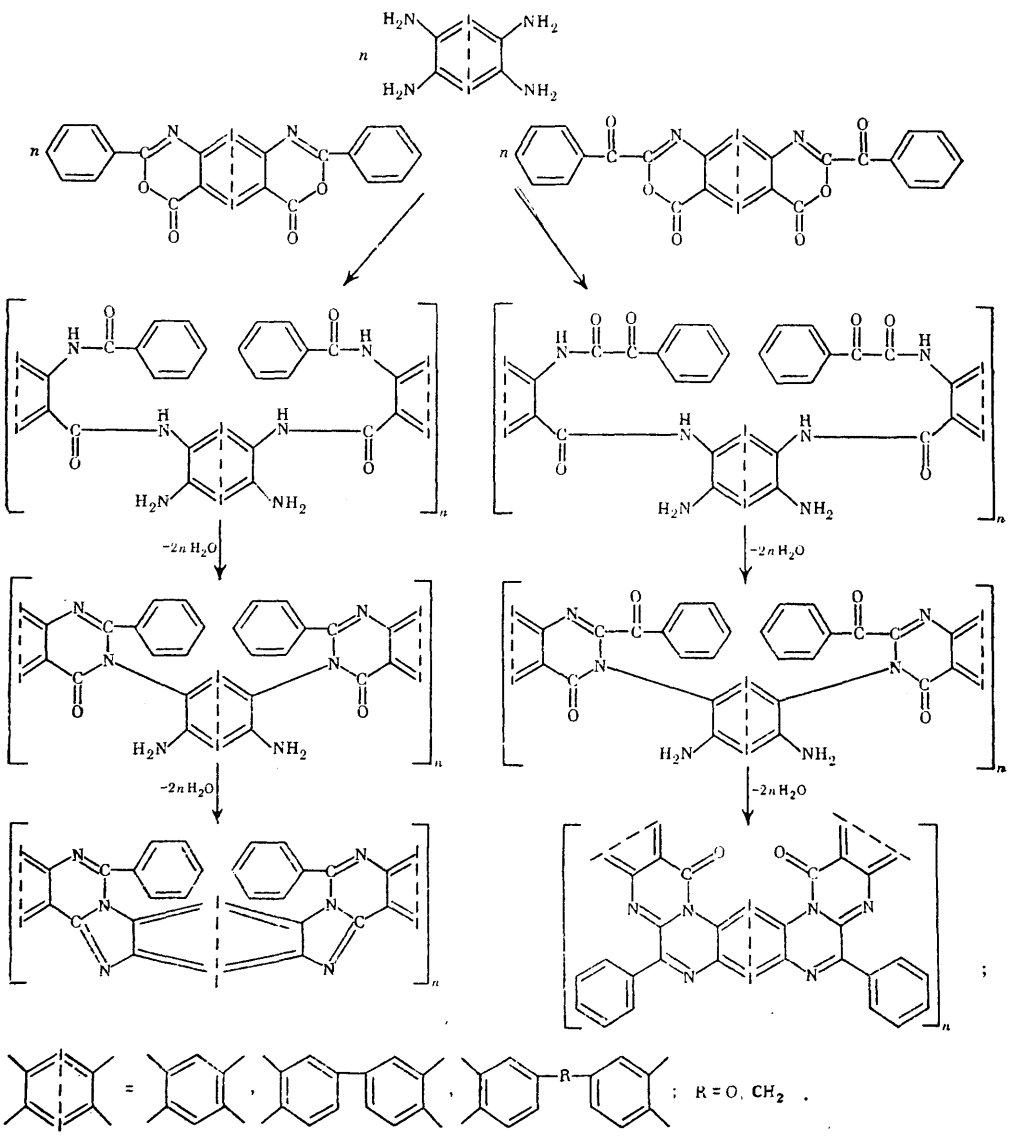
The latter factor facilitates the conversion of polyheteroarylenes into articles, but it limits the temperature ranges in which materials based on polyheteroarylenes can be used. As

a result, the synthesis of phenylated ladder polyheteroarylenes, i.e. systems containing highly condensed aromatic heterocycles in the main chains of the macromolecules, have become one of the most vigorously developing fields in the chemistry of phenyl-substituted polyheteroarylenes[99-101].

VI. PHENYLATED LADDER POLYHETEROARYLENES

The use by Hedberg et al. of aromatic tetra-amines with condensed rings, namely 2,3,7,8-tetra-aminodibenzofuran, 2,3,7,8-tetra-aminophenazine, 1,2,5,6-tetraminoanthraquinone, 2,3,11,12-tetra-aminodiquinoxalino[2,3-*e*: 2',3'-1]pyrene, and 2,3,8,9-tetra-aminodiquinoxalino[2,3-*e*: 2',3'-1]cyclopentanepentone for the synthesis of polyphenylquinoxalines[102] led to the formation of polymers soluble in *m*-cresol and at the same time having glass points exceeding 400 °C. Other examples of the synthesis of phenylated ladder polyheteroarylenes are reactions involving the formation of polyphenylquinoxalinoquinazolines[103] and polyphenylbenzimidazoquinazolines[104-106] by the reaction of aromatic bis(o-phenylenediamines) with bis(2-phenylbenzoxazin-4-ones) and 6,6'-(2-benzoylbenzoxazin-4-one) in accordance with Scheme 14.

Scheme 14

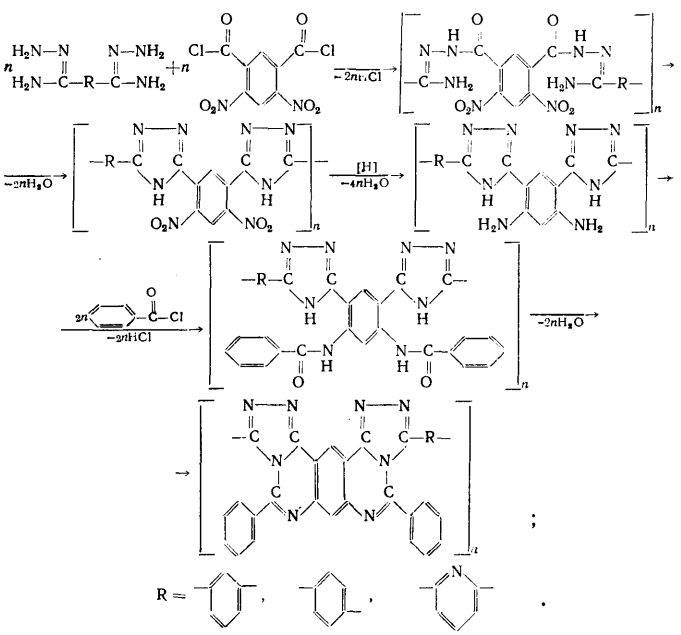


These reactions have been carried out in the melt, in phenolic solvents, or in PPA at elevated temperatures and led directly to the required polymeric structures without the isolation of intermediate systems. The polymers were soluble in acid and phenolic solvents and had a comparatively high thermal stability and heat resistance, but their viscosities (η_{int} up to 0.85) were insufficient to permit the preparation on their basis of materials with acceptable deformation-strength properties.

A number of phenylated ladder polyheteroarylenes have been obtained by the methods of modified and combined reductive polyheterocyclisation[87].

Phenylated polybenzo[di(*S*-triazolopyrimidines)], isomeric with previously known polymers, were obtained in the reaction of the dichloride of 4,6-dinitroisophthalic acid with the bisamidrazones of dicarboxylic acids and in the subsequent reactions of the resulting poly(*o*-nitro)aroylamidrazones[107, 108,109,110] (Scheme 15).

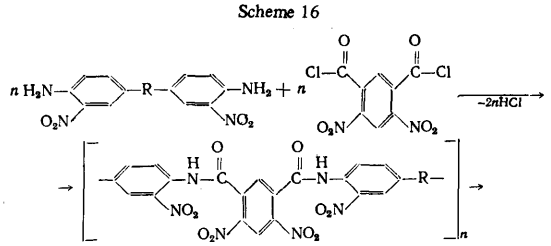
Scheme 15

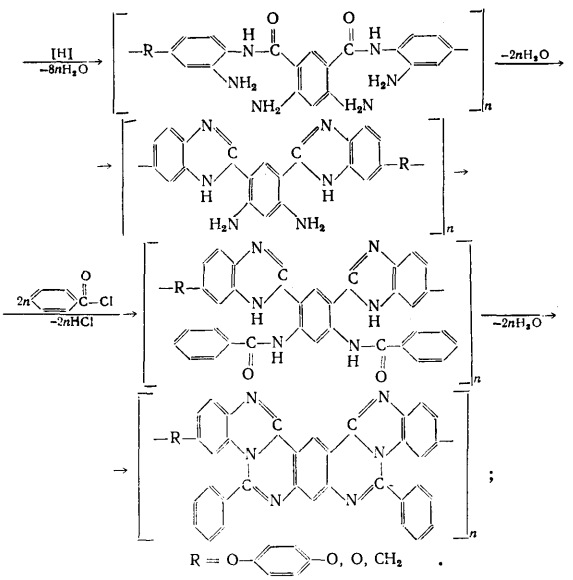


The presence of phenyl side groups and the relatively mild conditions of the polycyclisation processes are responsible for the solubility of the resulting polymers in acid solvents (H_2SO_4 and CF_3COOH) and the 3 : 1 trichloroethane (TCE)–phenol mixture and for their partial solubility in hot MP. A comparative study of the thermal stabilities of polybenzo[di-(*S*-triazolopyrimidines)], synthesised by modified reductive polyheterocyclisation and by the two-stage method[109,110], showed that these systems are comparable.

When various bis(*o*-nitroanilines) were used as the comonomers of the dichloride of 4,6-dinitroisophthalic acid, phenyl-substituted polybenzo[di(pyrimidinobenzimidazoles)] were obtained[111,112] (Scheme 16).

Scheme 16





Phenyl substituents combined with mild conditions of the polycyclisation processes are responsible for the solubility of the polymers in the 3 : 1 TCE–phenol mixture, H_2SO_4, and CF_3COOH. The thermal stabilities of polybenzo[di(pyrimidinobenzimidazoles)] obtained by reductive polyheterocyclisation are comparable under ITGA conditions with those of polymers obtained by the two-stage method[109,110].

The softening temperature of polybenzo[di(*S*-triazolopyrimidines)] and polybenzo[di(pyrimidinobenzimidazoles)] are in the range 350–420 °C, depending on the structure of the polymers.

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The introduction of phenyl substituents into polyheteroarylenes constitutes a reliable and effective method of increasing the solubility of the polymers and their overall capacity for being converted into articles. By varying the structure of the main macromolecular chains, it is possible to obtain phenyl-substituted polyheteroarylenes with softening temperatures from 250° to 400 °C and to generate a wide assortment of polymers of interest for the preparation of thermostable polymeric materials.

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