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Reductive Polyheterocyclisation—New Method of Preparation of Polyheteroarylenes

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Reduction and cyclisation of *o*-nitro-substituted heterochain polymers provides a new method for obtaining polyheteroarylenes of cyclochain structure. A large number of reactions demonstrate synthetic possibilities and show its advantages over traditional methods. A list of 90 references is included.

CONTENTS

I. Introduction 1177
II. Reductive polyheterocyclisation 1177
III. Modified and combined reductive polyheterocyclisation 1180
IV. Conclusion 1183

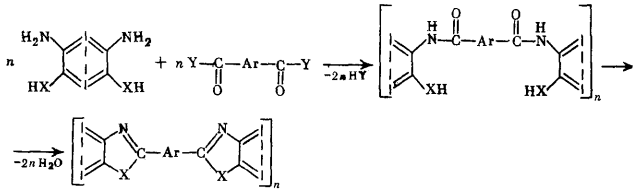
I. INTRODUCTION

The intense development of several modern industries—aviation, electronics, electrical technology, etc.—has made it necessary to produce polymeric materials combining high resistance to deformation with the ability to withstand prolonged operation at high temperatures. Solution of this problem is most directly related to the elaboration of new thermostable polymers, so that this has become a dominant trend in the development of the chemistry of macromolecular compounds during the past two decades[1-4].

The greatest progress in this field has been made in the development of polyheteroarylenes of cyclochain structure, compounds of high molecular weight containing in the main chains of the macromolecules alternating carbocyclic and heterocyclic aromatic ring systems[1-4]. Intense research on the synthesis of such polymers, undertaken in the USSR and abroad, has yielded a large number of products of this type, but only aromatic polyimides have become at all widely used[5,6], together with a few related systems made at present on an industrial or a semi-industrial scale. The overwhelming majority of polyheteroarylenes other than polyimides have not emerged beyond academic research or limited production on pilot plants. Yet many of these systems possess several important potential advantages over polyimides with respect to thermal and chemical stability, processability into articles, etc.

In most cases industrial exploitation of developments in the synthesis of polyheteroarylenes is difficult owing to the relative inaccessibility and inadequate stability of the initial monomers. A substantial obstacle is also the complexity of the technology involved in the principal methods for obtaining polyheteroarylenes, among which the most important are high-temperature polycyclocondensation in polyphosphoric acid[7-10], reaction in the melt followed by high-temperature solid-phase polycyclocondensation (Marvel's reaction),[11-13] and a multistage reaction involving a first stage under mild conditions, isolation of prepolymers, and their processing into articles followed by high-temperature cyclisation of the ready-made articles[1-6]. In the majority of cases the cyclisation stages are accomplished under severe conditions: the temperature usually exceeds 300 °C, which not only requires the use of special apparatus but also permits the occurrence of secondary processes—cross-linking, degradation, etc.—that have an unfavourable influence on the properties of the final products.

Typical examples of polyheteroarylenes are polybenzazoles[14-18]—a large family of thermostable polymers formed by reaction between *oo'*-disubstituted aromatic diamines and aromatic dicarboxylic acids or their derivatives:

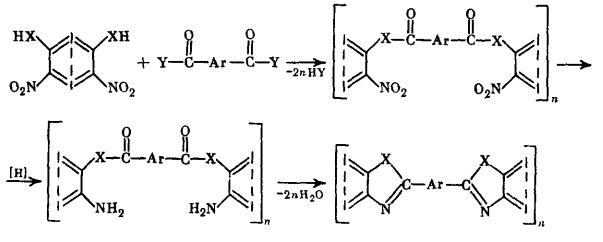


X = O, NR; Y = OH, OR', Cl; R = H, Alk, C_6H_5; R' = Alk, C_6H_5 . (1)

Replacement of the diamines by more accessible and stable monomers, and also elaboration of a technical method for synthesising these systems, may stimulate further development of the chemistry and technology of polybenzazoles. One solution to these problems is to synthesise them by reductive polyheterocyclisation.

II. REDUCTIVE POLYHETEROCYCLISATION

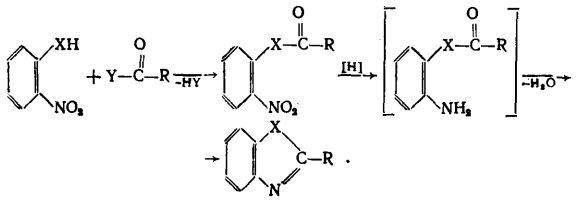
The synthesis of polybenzazoles by reductive polyheterocyclisation[19-28]



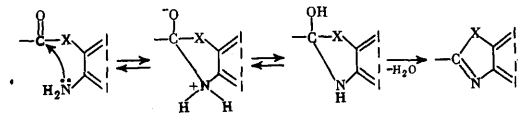
X = O, NR; Y = OR', Hal; R = H, C_6H_5, Alk; R' = Alk, C_6H_5 (2)

is based on well known reactions[29-31] in which benzazoles are formed by interaction of o-nitro-substituted amines and phenols with derivatives of carboxylic acids followed by

reduction and cyclisation of the products



Comparison of reductive polyheterocyclisation (2) with the traditional method (1) indicates that the former has several important advantages for the synthesis of polybenzazoles—(i) the use, instead of *oo'*-disubstituted aromatic diamines, of *oo'*-dinitro-substituted difunctional compounds, which are intermediates in the synthesis of the former[32], more accessible, cheaper, and more stable; (ii) the possibility of effecting the initial stages—synthesis of *o*-nitro-substituted heterochain polymers[19-28,33]—in the absence of competing reactions of acylation at two adjacent groups with branching and subsequent cross-linking of macromolecules[34,35], which permits the use as acylating agents of the most reactive derivatives of dicarboxylic acids, in particular their dichlorides; (iii) the possibility of using hydrogen chloride evolved as by-product in the early stages (when acid dichlorides are used as acylating agents) together with various metals, primarily activated iron[36], to reduce nitro to amino; and (iv) the possibility of using hydrogen chloride to catalyse polycyclisation[37,38], as a consequence of the increased electrophilic reactivity of the carbon atom in a protonated carbonyl group[39]

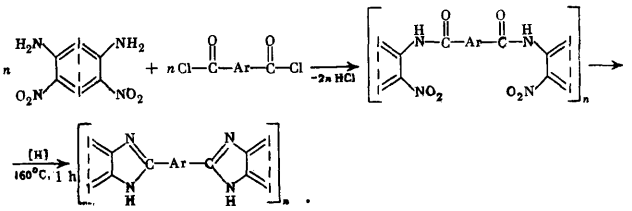


which enables the temperature of cyclisation to be lowered to 150–170 °C, with the possibility of ring-closure immediately after reduction of nitro to amino (which was responsible for the name *reductive polyheterocyclisation* for the whole process).

On the other hand, the process may be complicated by the possibility of incomplete reduction of nitro-groups and incomplete cyclisation of reduced and unreduced fragments, leading to an enhanced heterounit character of the polymers[39,40], which lowers the thermal stability, heat resistance, and chemical stability of the final products.

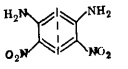
For maximum exploitation of the positive aspects of reductive polyheterocyclisation and elimination of inherent potential disadvantages it is advisable that all stages of the synthesis of polybenzazoles should be conducted as a continuous process in *N*-methylpyrrolid-2-one—an effective solvent for heterochain and heterocyclic polymers—with reduced iron and hydrogen chloride as reducing agents, the latter also catalysing cyclisation. Solubility of polymers at all stages of synthesis is especially important in reductive polyheterocyclisation, since polymers that separate out at any stage coat the iron and thus remove it from the sphere of reaction.

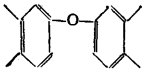
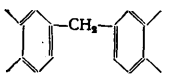
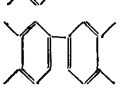
The presence in the monomers of nitro-groups, which are strongly electron-accepting substituents, has a decisive influence on the reactivity of fragments involved in polycondensation. In particular, the electronic and steric effects of *o*-nitro-substituents produce a sharp decrease in basicity and hence in nucleophilicity of diamines[20-22], and limit the possibility of using various bis-*o*-nitroanilines to obtain polybenzimidazoles by the reaction series



The highest (73 ± 3%) yields of dibenzimidazoles from bis-*o*-nitroanilines and benzoyl chloride are obtained[41] by the use as monomers of bis-*p*-amino-*m*-nitrophenyl ether and *mm'*-dinitrodiphenylmethane-*pp'*-diamine, which quantum-chemical calculations of potentiometric titration[21,22] show (Table 1) to be the most basic among the bis-*o*-nitroanilines used. The comparative basicity sequences of these latter compounds (Table 1) are identical with those of the structurally similar unsaturated aromatic diamines[42,43], among which the more basic are bis-*p*-aminophenyl ether and diphenylmethane-*pp'*-diamine. The comparatively high basicity of bis-*o*-nitroanilines containing ether and methylene bridging groups and also the high yields of dibenzimidazoles obtainable from them made it advisable to use such compounds for the synthesis of polybenzimidazoles. Another factor favouring their use in reductive polyheterocyclisation is the better solubility of the resulting polymers than of systems based on 3,3'-dinitrobenzidine and 4,6-dinitrophenylene-1,3-diamine, which enables the synthesis to be conducted in homogeneous solutions.

Table 1. Basicity and electron densities on nitrogen atoms for initial and monoacylated d_N^0 and d_N^m bis-*o*-nitroanilines of general formula[22]

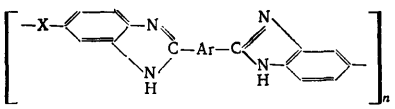


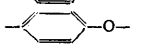
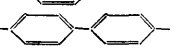
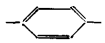
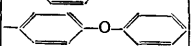
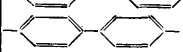
	pK_a (in dimethylformamide)			d_N^0	d_N^m
	pK_{a_1}	pK_{a_2}	ΔpK_a *		
	2.64±0.20	1.81±0.20	0.83	1.785	1.690
	2.57±0.20	1.87±0.20	0.70	1.782	—
	2.35±0.20	1.59±0.20	0.76	1.775	1.680
	2.17±0.20	1.17±0.20	1.00	1.751	1.61

*Here and subsequently $\Delta pK_a = pK_{a_1} - pK_{a_2}$.

The structure of the acid dichlorides imposes no severe restriction on their use to obtain polybenzimidazoles: model compounds are obtained in high (80 ± 6%) yields from all acid dichlorides[41], but isophthaloyl and oxy-*pp'*-dibenzoyl chlorides are preferred as monomers, since the resulting polymers remain in solution at all stages of the synthesis. Furthermore, the weak electrophilicity of these compounds[44] is responsible for the diminished positive charge on the amide carbon atoms and the consequent greater resistance to hydrolysis and amidolysis during reductive cyclisation.

Table 2. Some characteristics of polybenzimidazoles of general formula[22]

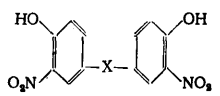


X	Ar	Solubility in *						Decomp. temp., °C**
		MP	DMA	$C_2H_2Cl_4$ + C_6H_5OH	HCOOH	CF_3COOH	H_2SO_4	
O		+	+	+	+	+	+	440
O		±	±	±	±	+	+	445
O		+	+	+	+	+	+	440
O		±	±	±	±	+	+	450
CH_2		+	+	+	±	+	+	420
CH_2		±	±	±	±	+	+	430
CH_2		+	+	+	+	+	+	425
CH_2		±	±	±	±	+	+	440

*MP = *N*-methylpyrrolid-2-one; DMA = dimethylacetamide; + = soluble at room temperature; ± = soluble on heating.

**Temperature at which 5% of initial weight has been lost (differential thermogravimetric analysis, ΔT = 4.5 deg min^{-1}, air).

Table 3. Acidity of bis-o-nitrophenols of general formula[26]

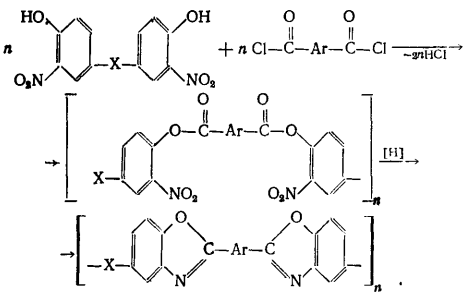


X	pK_{a_1}	pK_{a_2}	ΔpK_a
SO_2	5.80	7.50	1.70
$C(CF_3)_2$	7.54	9.14	1.60
O	9.17	10.93	1.76
$C(CH_3)_2$	9.53	11.11	1.59
$-CH_2-$	9.73	11.22	1.69

The synthesis of polyimidazoles by reductive polyheterocyclisation is a simple and technically efficient process involving addition of a solid acid dichloride to an *N*-methylpyrrolid-2-one solution of a bis-*o*-nitroaniline, stirring for 10–12 h, saturating the solution with gaseous hydrogen chloride, and heating in a stream of nitrogen and hydrogen chloride at 160 °C for 1 h. The infrared spectra of polybenzimidazoles obtained in this way from isophthaloyl and oxy-*pp'*-dibenzoyl chlorides, i.e. with all stages taking place in solution, contain no absorption maxima that would indicate incomplete reduction of nitro-groups or polycyclodehydration. Table 2 lists several characteristics of these polymers.

The attainment of high degrees of cyclisation under very mild conditions (160 °C for 1 h) is one of the most important merits of reductive polyheterocyclisation. Furthermore, such conditions tend to suppress any secondary reactions and yield polymers having the same thermal stability as those obtained by traditional methods, but better solubility in organic solvents (Table 2) and lower softening temperatures. Thus catalytic cyclisation not only permits substantial moderation of the conditions for obtaining polybenzimidazoles but also yields polymers having better properties.

These considerations apply also to the production of polybenzoxazoles by the reactions[23–28,33]



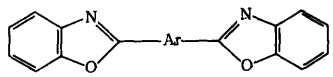
The acidity of the bis-o-nitrophenols used for the synthesis of polybenzoxazoles varies within wide limits (Table 3). but it is not the limiting factor in the choice of monomers. Thus model reactions show that high yields of bisbenzoxazoles are obtained from all bis-o-nitrophenols[45], so that attention has been concentrated on obtaining polybenzoxazoles from the most readily available 3,3'-dinitrodiphenylmethane-4,4'-diol and 2,2-bis-(4-hydroxy-3-nitrophenyl)propane, which furthermore ensure homogeneous solutions during reductive polyheterocyclisation, together with isophthaloyl and oxy-*pp'*-dibenzoyl dichlorides.

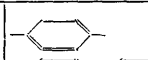
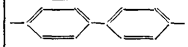
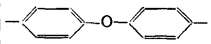
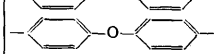
The procedure for obtaining polybenzoxazoles is essentially the same as that described above for polybenzimidazoles, except that the first stage—formation of poly-o-nitroesters—is accomplished in the presence of triethylamine, and the duration of the process does not exceed 30 min. The properties of the resulting polybenzoxazoles, shown by infrared spectroscopy to contain no "defective" monomer units, are given in Table 4. They differ from those obtained by traditional methods[46,47] in their solubility in trifluoroacetic acid, while systems containing isopropylidene groups are soluble in a 3:1 mixture of tetrachloroethane and phenol. The high viscosity characteristics of polybenzoxazoles, evidence of high molecular masses, are responsible for their film-forming properties.

When difficulties arise in obtaining o-nitro-substituted monomers or polymers, the required compounds can be produced by nitrating the corresponding unsubstituted heterochain polymers. Thus the nitration of aromatic polyamides[22], polyesters[48], and polythioesters[49] yields macromolecular poly-o-nitroamides, poly-o-nitroesters, and poly-o-nitrothioesters, reductive polyheterocyclisation

of which then gives polybenzimidazoles[22], polybenzoxazoles[48], and polybenzothiazoles[49]. However, the nitration of heterochain polymers may be ambiguous (i.e. it may not necessarily take place *ortho* to the main chains of the macromolecules), which leads to the formation of heterounit polymers[40], and furthermore such nitration is accompanied by a considerable decrease in viscosity.

Table 4. Some characteristics of polybenzoxazoles of general formula[26]



X	Ar	Softening temp., °C	Decomp. temp., °C	Film properties* σ_t, kg cm^{-2}	Film properties* ε, %
$C(CH_3)_2$		270—290	400—420	900	2.6
$C(CH_3)_2$		280—300	430—450	1200	3.0
$C(CH_3)_2$		250—270	395—410	800	3.1
$C(CH_3)_2$		250—260	410—420	1030	3.2
CH_2		260—260	420—430	1150	3.8
CH_2		270—280	410—420	1050	2.5

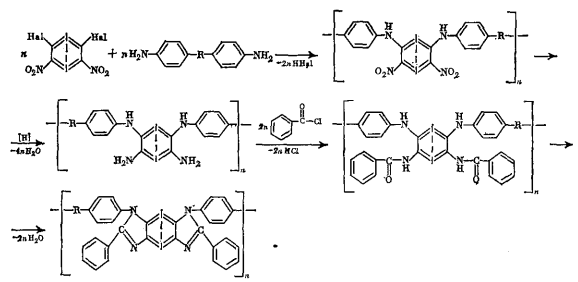
*Film parameters: σ_t = tensile strength; ε = elongation at break.

Thus the reactions represented by scheme (2) are preferred for the synthesis of polyheteroarylenes by reductive polyheterocyclisation. They not only have the disadvantages already mentioned but also somewhat restrict the set of structures obtainable; the nitro-groups have an adverse influence on the reactivity of fragments involved in polycondensation, which is especially marked when bis-*o*-nitroanilines are used as monomers. Processes of modified and combined reductive polyheterocyclisation are in considerable measure free from these defects.

III. MODIFIED AND COMBINED REDUCTIVE POLYHETEROCYCLISATION

Modified reductive polyheterocyclisation differs from the above processes[19–26] in the separation of cyclisation processes by one or more reactions (usually acylation) from nitro–amino reduction stages. As in the previous Section, the modified polymerisation has been conducted as continuous processes in *N*-methylpyrrolid-2-one with reduced iron and hydrogen chloride as reducing agents and the latter as cyclisation catalyst. Since such processes are most complete under homogeneous conditions, attention has been paid mainly to the synthesis of polyheteroarylenes having improved solubility in organic solvents, in particular of phenylated polyheteroarylenes considerably surpassing in solubility the unsubstituted analogues (as has been shown for polybenzimidazoles[50,51], polyquinoxalines[52,53], polyquinazolones[54,55], and several other systems).

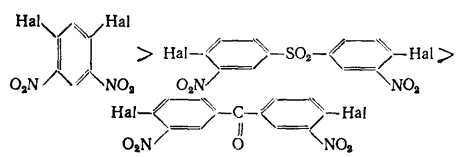
A typical example of modified reductive polyheterocyclisation is the synthesis of hitherto unreported *C*-phenylated polybenzimidazoles[27,28,56–64] by the action of aromatic diamines on activated di-(*o*-halogenonitro)arenes[27,28,56–62], reduction of the resulting poly-*o*-nitro-amines to poly-*o*-amino-amines[27,28,56–60,63], benzoylation of the latter[27,28,56–60,63], and cyclisation of the poly-*o*-benzamido-amines thus formed[27,28,56–60,64]:



(3)

Successful examples of the activated components are 1,3-dihalogeno-4,6-dinitrobenzenes and also dinuclear compounds having electron-accepting bridges[65–71], the 3,3'-dinitro-derivatives of 4,4'-dichloro- and 4,4'-difluorodiphenyl sulphone and -benzophenone; from the above considerations the diamines used have been diphenylmethane-*pp'*-diamine, bis-*p*-aminophenyl ether, and *p*-diphenoxybenzene-*p'p''*-diamine.

A comparative study of the electrophilicity of the di-*o*-halogenonitro-arenes by the application of chlorine-35 nuclear quadrupole and fluorine-19 and carbon-13 nuclear magnetic resonance spectroscopy, and also the results of competitive amination, have shown[60] that the above examples form the reactivity sequence



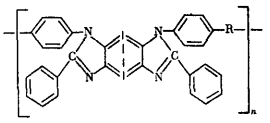
with fluorinated derivatives more reactive than the chlorinated compounds. Although 1,3-dihalogeno-4,6-dinitrobenzenes were the most reactive, attention was paid mainly to polymers from monomers based on diphenyl sulphone and benzophenone, since their "hinge" groups confer solubility in organic solvents on all intermediate and final polymer systems and hence the possibility of effecting synthesis under homogeneous conditions.

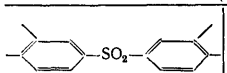
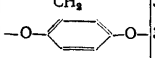
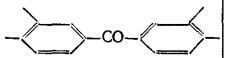
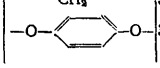
Like the synthesis of polybenzazoles by ordinary reductive polyheterocyclisation, that of *C*-phenylated polybenzimidazoles is an extremely simple process occurring under mild conditions: no stage of the process requires a temperature above 180 °C. The products are free from unreduced nitro-groups and uncyclised fragments (this was established by infrared spectroscopy);[60] their spectral characteristics are completely identical with those of corresponding model compounds.

The mild conditions of cyclisation, the presence of phenyl substituents, and the high content of "hinge" groups in the main chains are responsible for the good solubility of polybenzimidazoles in dipolar, aprotic, and phenolic solvents, while the high viscosity characteristics of these systems (Table 5) make it possible to obtain from them articles that are highly resistant to deformation. Because of the only slight heterounit character[40] the resulting polymers have high degradation temperatures under conditions of dynamic (Table 5) and isothermal thermogravimetric analysis: in

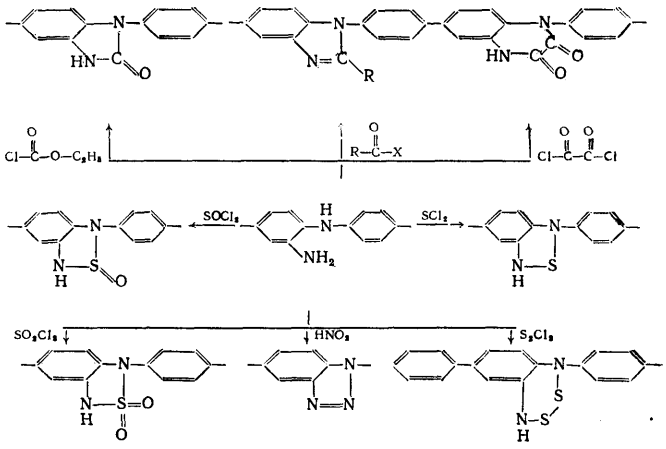
particular, polybenzimidazoles obtained by modified reductive polyheterocyclisation possess greater thermal stability in isothermal thermogravimetry than structurally similar poly-*N*-phenylbenzimidazoles obtained in two stages[50] [Scheme (1) with X = C_6H_5N].

Table 5. Some characteristics of *C*-phenylated polybenzimidazoles of general formula[60]

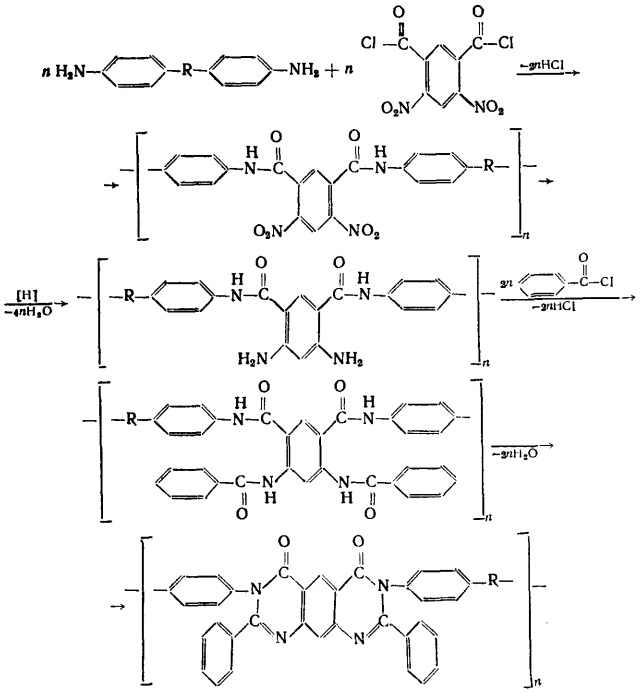


	R	Softening temp., °C	Decomp. temp., °C	Film properties at 25 °C σ_t, kg cm^{-2}	Film properties at 25 °C ε, %
	O	310—330	470	950	4
	CH_2	335—350	490	1040	3—4
		315—330	450	1050	4
	O	305—315	430	—	—
	CH_2	320—325	430	—	—
		300—320	420	990	5

The intermediate poly-*o*-amino-amides formed in the synthesis of *C*-phenylated polybenzimidazoles can be used to obtain a wide range of heterocyclic polymers[64]. In particular, if they are treated not with benzoyl chloride but with ethyl chlorocarbonate, oxalyl, thionyl, sulphuryl, sulphenyl, and sulphur chlorides, nitric acid, etc., subsequent cyclisation of the reaction products yields polybenzimidazolones, polyquinoxalidinediones, polybenzothiazolidine *S*-oxides, polybenzothiadiazolidine *S*-dioxides, polybenzothiadiazolidines, polybenzodithiadiazines, polybenzotriazoles, etc.:

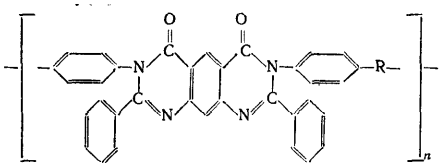


Another typical example of modified reductive polyheterocyclisation is the synthesis of phenylated polyquinazolones[72,73] by reaction between aromatic diamines and 4,6-dinitroisophthaloyl dichloride[74] followed by reduction of the resulting poly-o-nitro-amides to poly-o-amino-amides, benzoylation of the latter at the free amino-groups, and catalytic polycyclisation of the poly-o-benzamido-amines formed:



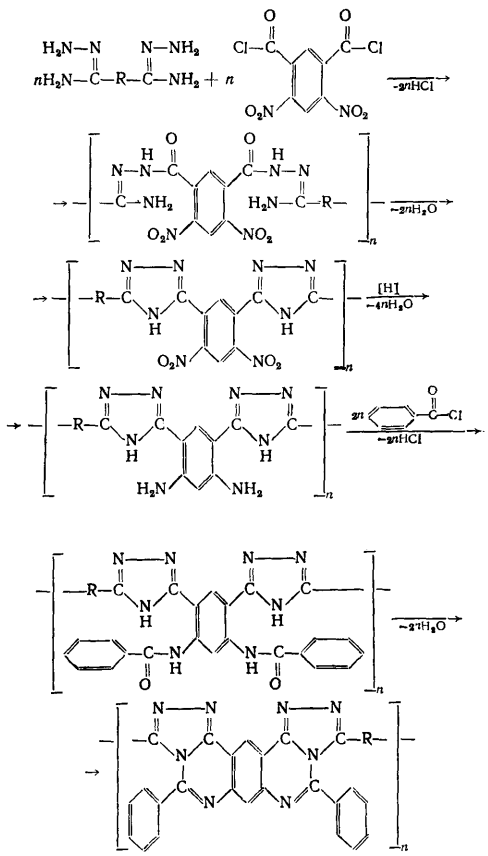
Like *C*-phenylated polybenzimidazoles, poly-2-phenylquinazolones obtained in the same way are free from unreduced nitro-groups and uncyclised fragments, as has been confirmed in particular by the identity of their spectra with those of model compounds[73]. The resulting polymers dissolved in strong acids, in phenolic solvents (Table 6), and on heating in aprotic dipolar solvents. Dynamic and isothermal thermogravimetry indicates that their thermal stability is comparable with that of identical systems obtained by earlier methods[54,55].

Table 6. Some characteristics of poly-2-phenylquinazolones of general formula[72]

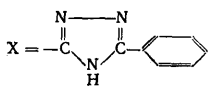


R	Softening temp., °C	Decomp. temp., °C	Film properties at 25 °C σ_t, kg cm^{-2}	Film properties at 25 °C ε, %
O	380—385	450	1200	8
CH_2	375—380	430	1100	8
	350—360	440	1100	12

The enhanced solubility of polyheteroarylenes synthesised by modified reductive polyheterocyclisation made it useful to extend this process to the production of ladder polyheteroarylenes, which are characterised by high heat resistance and thermal stability but unsatisfactory processability into articles[75–77]. With 4,6-dinitroisophthaloyl dichloride and a bisamidrazone of a dicarboxylic acid[78] as comonomers phenylated polybenzodi-sym-triazolopyrimidines were obtained[79,80]:

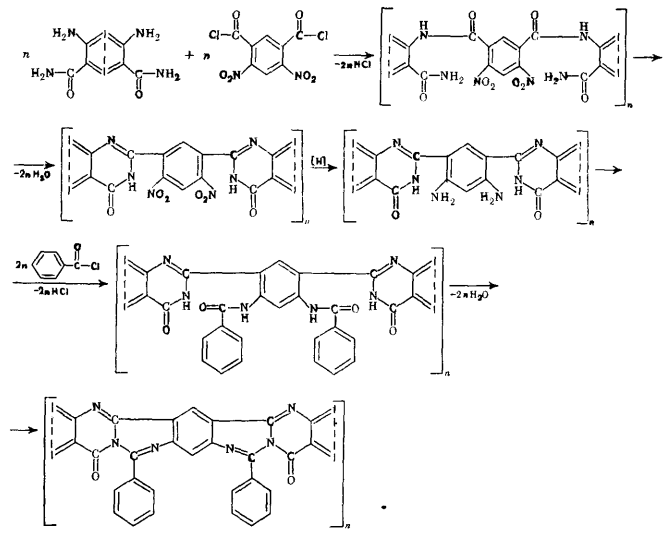


the products being isomeric with previously known systems[81,82] obtained by two-stage processes—scheme (1) with



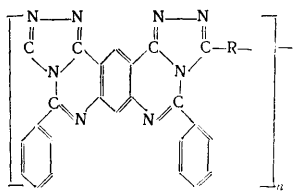
Infrared spectra indicate that polyheteroarylenes obtained in this way are free from unreduced nitro-groups and uncyclised fragments. The presence of phenyl side-groups and the mild conditions of polycyclisation are responsible for the solubility of the resulting systems in acid solvents (sulphuric and trifluoroacetic acids) and a 3:1 tetrachloroethane–phenol mixture, and for their partial solubility in hot *N*-methylpyrrolid-2-one (Table 7). A dynamic (Table 7) and isothermal thermogravimetric study has shown the comparable thermal stabilities of polybenzobis-sym-triazolopyrimidines prepared by modified reductive polyheterocyclisation and by the two-stage method[81,82].

Another example of modified reductive polyheterocyclisation is the synthesis of polyquinazolinoquinazolones[83]:



The resulting polymers are soluble in acids, phenolic solvents, and hot *N*-methylpyrrolidone and dimethyl sulphoxide. Solutions in a 3:1 mixture of tetrachloroethane and phenol have viscosities $\eta = 0.96–1.30$ dl g^{-1}. At 25 °C films based on these polymers possess tensile strengths $\sigma_t = 850–950$ kg cm^{-2} and elongations at break $\varepsilon = 2–10\%$.[38]

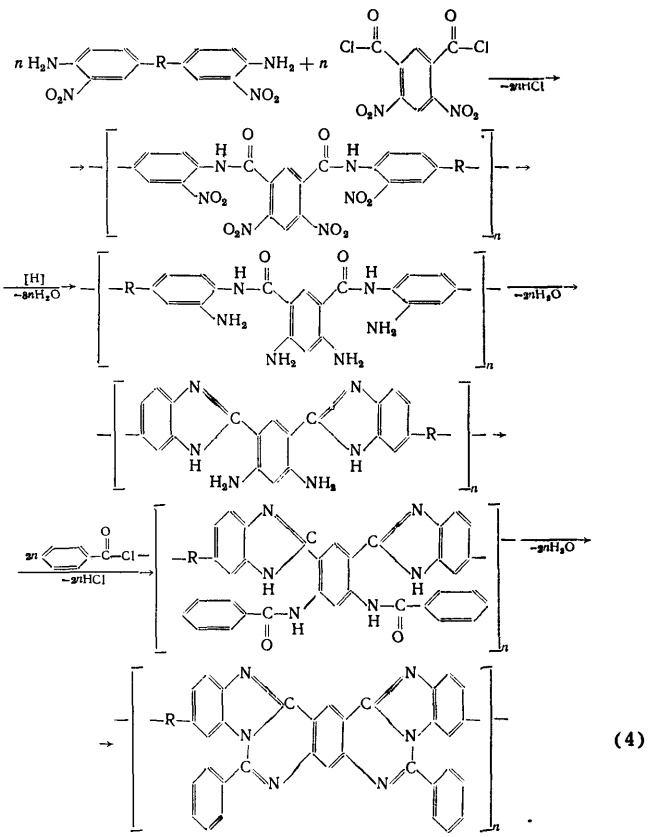
Table 7. Some characteristics of polybenzobis-sym-triazolopyrimidines of general formula[79]



R	Softening temp., °C	Solubility in			
		H_2SO_4	CF_3COOH	$C_2H_2Cl_4 + C_6H_5OH$	MP
	500	+	+	+	±
	505	+	+	+	+
	520	+	+	+	±
	475	+	+	+	+

Syntheses of ladder polyheteroarylenes have been effected also by combined processes involving true reductive polyheterocyclisation at one stage. A typical example is the synthesis of polybenzodi(pyrimidobenzimidazoles) from

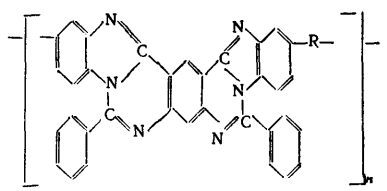
bis-*o*-nitroanilines and 4,6-dinitroisophthaloyl dichloride[84,85]:



(4)

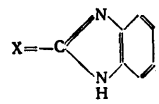
It is evident from (4) that the formation of poly-*o*-aminophenylbenzimidazoles is true reductive polyheterocyclisation, whereas that of the final structure is a modified reductive polyheterocyclisation.

Table 8. Some characteristics of polybenzodi(pyrimidobenzimidazoles) of general formula[84]



R	Softening temp., °C	Solubility in			
		H_2SO_4	CF_3COOH	$C_2H_2Cl_4 + C_6H_5OH$	MP
O	530	+	+	+	±
CH_2	520	+	+	+	±
—O—⟨⟩—O—	500	+	+	+	±

Like all the systems discussed already, polybenzodi(pyrimidobenzimidazoles) obtained by combined reductive polyheterocyclisation are, according to infrared spectral data, free from unreduced nitro-groups and uncyclised fragments. Those obtained by scheme (4) differ from corresponding polymers obtained in two stages[81,82], by scheme (1) with



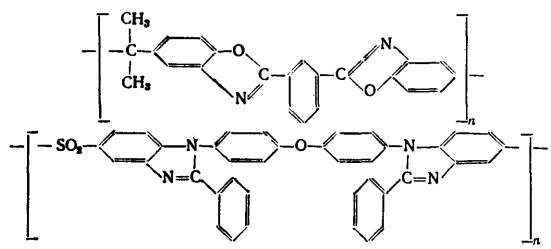
as X, in containing phenyl substituents, which together with the mild conditions of polycyclisation confer solubility in a 3:1 tetrachloroethane–phenol mixture, sulphuric acid, or trifluoroacetic acid (Table 8). Polybenzodi(pyrimidobenzimidazoles) surpass in thermal stability other polyheteroarylenes obtained by modified reductive polyheterocyclisation (Tables 2–8) and are comparable under conditions of isothermal thermogravimetry with polymers obtained in two stages[81,82].

The above syntheses of polyheteroarylenes do not exhaust all the possibilities of modified and combined reductive polyheterocyclisation. Nevertheless, the results surveyed indicate the undoubted promise of such approaches to obtaining comparatively simple and more complicated polymer systems.

IV. CONCLUSION

Thus research during the past five years has developed a new method for synthesising polyheteroarylenes using as intermediates compounds employed in traditional methods. It involves also catalytic cyclisation, with consequent moderation of the reaction conditions and also improvement in the solubility of the resulting systems and their processability into articles.

Among the polymers that have been synthesised the greatest industrial promise is shown by polybenzoxazoles and *C*-phenylated polybenzimidazoles. In particular, those having the structural formula



are of considerable interest. The first system is obtained from 2,2-bis-(4-hydroxy-3-nitrophenyl)propane[86]—a product of the direct nitration of bisphenol A, the latter used in chemical industry to obtain polycarbonates[87] and polysulphones[4]—and isophthaloyl chloride, which finds employment in industry for the production of polyamides[88]. Synthesis of the second system is based on bis-4-chloro-3-nitrophenyl sulphone[89]—formed by the direct nitration of di-p-chlorophenyl sulphone, which is used in industry to obtain polysulphones[4]—and di-*p*-aminophenyl ether, employed in the manufacture of polyimides[5,6]. The combination in these systems of good solubility with high viscosity characteristics of the polymers makes it possible to obtain from them various materials—films, carbon plastics, gas-separating membranes[22,26,60]—suitable for operation at 250–300 °C. There have been indications

of the practical utilisation of other systems[90] obtained by reductive polyheterocyclisation.

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