polymer review

Reductive polyheterocyclization: A new approach to the synthesis of polyheteroarylenes

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A new general approach to the synthesis of polyheteroarylenes by reductive polyheterocyclization, based on the reduction and cyclization of *o*-nitrosubstituted heterochain polymers has been reviewed. The synthetic possibilities of the method are demonstrated with a wide range of reactions. The advantages of the reductive polyheterocyclization over conventional reactions of polyheteroarylene synthesis have been discussed.

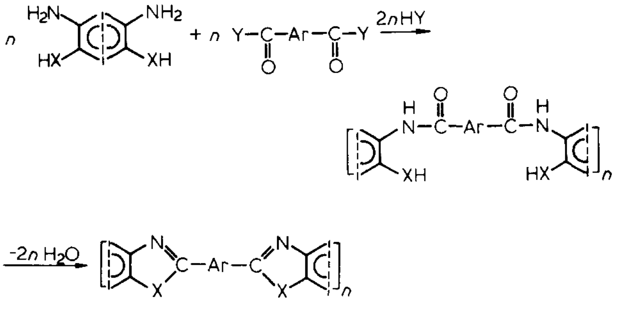
(Keywords: polyheterocyclization; polyheteroarylenes; polybenzazoles; dinitrosubstituted monomers; dinitrosubstituted heterochain polymers; thermostable polymers)

INTRODUCTION

Intense development of a number of modern branches of industry such as aircraft, electronics, electrical engineering and the like, has predetermined the necessity for the preparation of the polymeric materials combining high mechanical properties and capacity to perform long-term service at elevated temperatures. The solution of this problem is very closely connected with the development of new thermostable polymers, and just for this reason this subject area became one of the prevailing tendencies in development of high polymers chemistry in the past twenty years[1-4]. The most progress in this field is connected with the elaboration of polyheteroarylenes—high molecular weight compounds containing alternating aromatic carbo- and heterocycles in the main chains of the macromolecules[1-4]. Intense investigations in the field of polyheteroarylenes synthesis in the USSR and elsewhere resulted in a great number of polymers of this type, but only aromatic polyimides are widely used[5,6] and in addition some relative systems produced at present on an industrial or semi-industrial scale. The overwhelming majority of polyheteroarylenes differing from polyimides are not beyond the scope of academic investigation or limited production in a pilot plant. Nevertheless, many of these systems possess a number of essential potential advantages over polyimides in terms of their thermal and chemical stability. In most cases the industrial realization of the developments in the field of polyheteroarylenes synthesis is hampered by low availability and stability of the monomers. A serious handicap is also the poor technology involved in main methods of polyheteroarylene preparation, amongst which the most important are the high-temperature polycondensation in polyphosphoric acid (PPA)[7-10], the reaction in the melt followed by solid-state high-temperature polycyclocondensation, the so-called 'Marvel reaction'[11-13], and the stepwise reaction suggesting the mild conditions for the first step, the separation of prepolymers and their processing into articles followed by high-temperature cyclization of products obtained[1-6]. In most cases the cyclization stages of polyhetereoarylene synthesis are accomplished under extreme conditions (usually above 300°C), that not only require special apparatus, but also incur secondary processes such as 'crosslinking', degradation etc., adversely affecting the properties of the final systems.

Polybenzazoles[14-18] are also polyheteroarylenes and all the above-mentioned processes apply to them also. This is a large family of thermostable polymers, formed from the reaction of *o,o'*-disubstituted aromatic diamines with aromatic dicarboxylic acids or their derivatives as follows:

Scheme 1



X = —O—, —NR—, Y = —OH, —OR', —Cl;

R = H, —Alk, $-C_6H_5$; R' = —Alk, $-C_6H_5$

It is readily apparent that replacing of the *o,o'*-disubstituted aromatic diamines by more available and stable monomers, as well as developing a technological method of synthesizing these systems can stimulate further progress in chemistry and technology of polybenzazoles. One of the solutions to these problems consists in synthesizing polybenzazoles by reductive polyheterocyclization.

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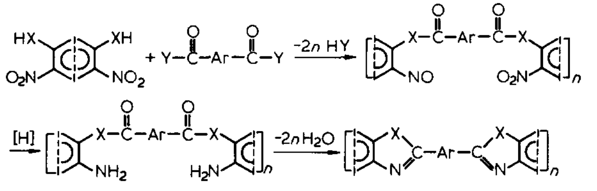
REDUCTIVE POLYHETEROCYCLIZATION

The synthesis of polybenzazoles by reductive polyheterocyclization[19-28] according to the scheme:

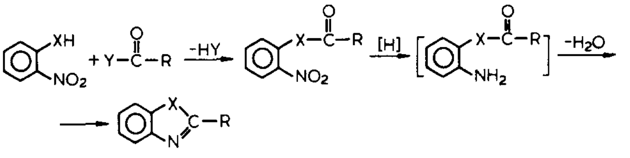
Scheme 2



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

is based on the known reactions[29-31] of benzazole synthesis by the interaction of *o*-nitrosubstituted amines and phenols with carboxylic acids derivatives and following reduction/cyclization of the reaction products:

Scheme 3



A comparison of the reaction schemes of polybenzazole synthesis by reductive polyheterocyclization (*Scheme 2*) and the conventional method (*Scheme 1*) shows some substantial advantages using the reductive polyheterocyclization, and these are as follows:

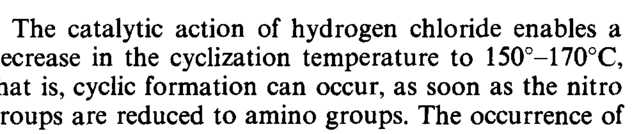
(1) The use of *o,o'*-dinitrosubstituted bifunctional compounds instead of *o,o'*-disubstituted aromatic diamines. Being intermediate products in the synthesis of the latter[32], the *o,o'*-dinitrosubstituted bifunctional compounds are readily available, cheaper and more stable than the disubstituted aromatic diamines.

(2) The possibility of the first stages (the synthesis of *o*-nitrosubstituted heterochain polymers[19-28,33]) occurring without competitive acylation reactions of adjacent groups leading to gel formation[34-35], which allows the use of the most reactive dicarboxylic acid derivatives, and in particular, their dichlorides as acylating agents.

(3) The possibility of using hydrogen chloride liberated as a by-product in the early stages (when using dicarboxylic acid dichlorides as acetylating agents) in combination with various metals (mainly with activated iron[36]) to reduce nitro groups to amino groups.

(4) The possibility of using hydrogen chloride to catalyse polycyclization[37,38], caused by the increasing electrophylic reactivity of the carbon atom of the protonated carbonyl group[39]:

Scheme 4



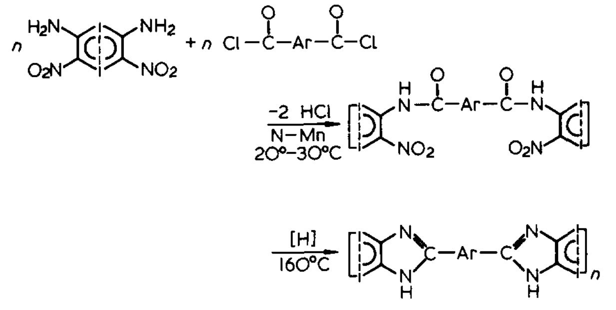
The catalytic action of hydrogen chloride enables a decrease in the cyclization temperature to 150°–170°C, that is, cyclic formation can occur, as soon as the nitro groups are reduced to amino groups. The occurrence of cyclization immediately after reduction accounts for the term reductive polyheterocyclization.

However, the reductive polyheterocyclization can be complicated by incomplete reduction of the nitrogroups and incomplete cyclization of the reduced and not fully reduced fragments increasing 'polymer raznozvennost' (chemical heterogeneity)[40] that decreases thermal, heat and chemical stability of the systems.

To make the best use of the positive aspects of reductive polyheterocyclization and to eliminate any disadvantages potentially inherent in it, it is advisable to carry out all reactions of polybenzazole synthesis as continuous processes in *N*-methyl-2-pyrrolidone (N-MP), an effective solvent for heterochain and heterocyclic polymers, using reduced (activated) iron and hydrogen chloride as reducing agents and hydrogen chloride as cyclization catalyst. Homogeneity of the reaction solutions is of particular importance in reductive polyheterocyclization, since the polymers formed at the various reaction stages envelop the iron and thereby remove it from the reaction zone.

The nitro groups, being strong electron-accepting substituents present in monomers used in reductive polyheterocyclization, are a deciding factor in the reactivity of the fragments participating in the polycondensation. In particular, electron and steric effects of the *o*-nitrosubstituents sharply decrease basicity and, consequently, nucleophylity of the diamines[20-22] and limit the use of various bis[(*o*-nitro)-anilines] to prepare polybenzimidazoles according to *Scheme 5*:

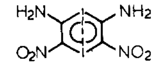
Scheme 5



An investigation of the model reactions (synthesis of bibenzimidazoles from bis[(*o*-nitro)-anilines] and benzoyl chloride[41]) showed that the highest yields of model compounds (73±3%) are achieved when using 3,3'-dinitro-4,4'-diaminodiphenyloxide and 3,3'-dinitro-4,4'-diaminodiphenylmethane as monomers. These monomers possessing, according to the potentiometric titration data and quantum-chemical calculations[21,22] (*Table 1*), the highest basicity among the bis[(*o*-nitro)-anilines] applied. It should be noted that the sequences of comparative basicity of bis[(*o*-nitro)-anilines] (*Table 1*) are identical to those of structurally similar unsubstituted aromatic diamines[42,43], 4,4'-diaminodiphenyloxide and 4,4'-diaminodiphenylmethane revealing the highest basicity. A comparative high basicity of bis[(*o*-nitro)-anilines] containing oxide and methylene 'bridge' groups and the possibility of preparing dibenzimidazoles in high yields determined the use of just these compounds for polybenzimidazoles synthesis. An additional factor determining the expedience of using just these monomers in reductive polyheterocyclization is the higher solubility of the polymers as compared with systems on the basis of 3,3'-dinitrobenzidine and 1,3-diamino-4,6-dinitrobenzene that provide a means for synthesizing polybenzimidazoles in homogeneous solutions.

The structure of the acid dichlorides does not greatly restrict their use in the preparation of polybenzimidazoles [the model compounds on the basis of all acid dichlorides have been obtained in high yields (80±6%)[41]]; preferred monomers are isophthalic and 4,4'-diphenyloxidedi-

Table 1 Basicity and electron density values for nitrogen atoms (PPP-method) of bis[(*o*-nitro)anilines] of general formula



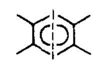
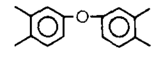
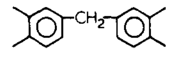
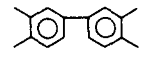
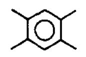
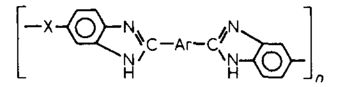
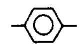
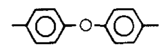
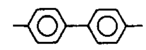
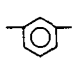
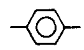
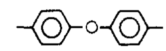
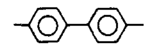
	pK_a (in DMF)			de_N	
	pK_{a_1}	pK_{a_2}	$\Delta pK_a = pK_{a_1} - pK_{a_2}$	1 Starting diamine	Mono-acylated diamine
	2.64 ± 0.20	1.81 ± 0.20	0.83	1.785	1.690
	2.57 ± 0.20	1.87 ± 0.20	0.70	1.782	–
	2.35 ± 0.20	1.59 ± 0.20	0.76	1.775	1.680
	2.17 ± 0.20	1.17 ± 0.20	1.00	1.751	1.61

Table 2 Some properties of polybenzimidazoles of general formula



–X–	–Ar–	$\eta_{red.}$* (dl/g)	Solubility†						Decomposition point‡
			N–MP	DMAA	TCE: phenol	HCOOH	CF_3COOH	H_2SO_4	
–O–		0.50	+	+	+	+	+	+	440
–O–		0.41	±	±	±	±	+	+	445
–O–		0.38	+	+	+	+	+	+	440
–O–		0.33	±	±	±	±	+	+	450
$–CH_2–$		0.57	+	+	+	±	+	+	420
$–CH_2–$		0.39	±	±	±	±	+	+	430
$–CH_2–$		0.53	+	+	+	+	+	+	425
$–CH_2–$		0.41	±	±	±	±	+	+	440

* Reduced viscosities of 0.5% solutions in H_2SO_4 at 30°C

† + soluble at room temperature, ± soluble when heated

‡ Temperature of a 5% loss of initial weight (t.g.a., T = 4.5°C/min in air)

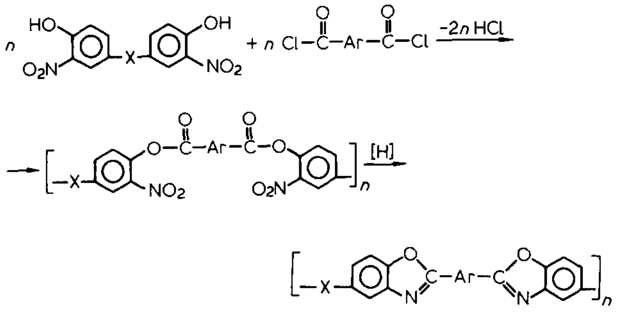
carboxylic acid dichlorides, since the polymers on their basis do not separate from solutions at all the synthesis stages. Moreover, the low electrophylicity of these compounds[44] is responsible for lowered positive charges on the carbon atoms of the amide carbonyl groups and, consequently, for their stability to hydrolysis and amidolysis in the reduction/cyclization processes.

Polybenzimidazole synthesis by reductive polyheterocyclization is a simple process which includes the addition of solid dicarboxylic acid dichloride to bis[(*o*-nitro)aniline] solution in N-MP, mixing of the reaction solution for 10–12 h, saturation with gaseous HCl, and heating in N_2 and HCl at 160°C for 1 h. The i.r. spectra of polybenzimidazoles obtained in this way, on the basis of isophthalic and 4,4′-diphenyloxidedicarboxylic acids with all synthesis stages under homogeneous conditions, do not contain any maxima indicative of incompletion of nitro group reduction or polycyclodehydration reactions. Some properties of polybenzimidazoles synthesized by reductive polyheterocyclization are given in *Table 2*.

High degrees of cyclization under very mild synthesis conditions (160°C, 1 h) are one of the most important advantages of reductive polyheterocyclization. Besides, the mild conditions suppressing all kinds of the reactions enable the preparation of polymers with a closed thermostability, but higher solubility in organic solvents (*Table 2*) and lower softening temperatures as compared with similar polymers synthesized by conventional methods. Thus, the catalytic polycyclization enables one not only to make the conditions essentially milder, but also to prepare polymers with principally new properties.

This concept seems to be applicable also for polybenzoxazole preparation according to the following scheme[23-28,33]:

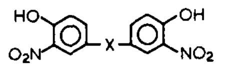
Scheme 6



The acidity of bis(*o*-nitro)phenols] used for polybenzoxazole synthesis, changes over a wide range (*Table 3*), but it is not a limiting factor in selecting the monomers. Thus, an investigation of model reactions showed that bisbenzoxazoles on the basis of all bis[(*o*-nitro)phenols] are obtained in high yields[45]. Consequently, primary consideration was given to the synthesis of polybenzoxazoles on the basis of the most available bis[(*o*-nitro)phenols] assuring homogeneity of the reaction solutions in reductive polyheterocyclization (3,3′-dinitro-4,4′-dihydroxydiphenylmethane and 2,2-bis(3-nitro-4-hydroxyphenyl)propane and also isophthalic and 4,4′-diphenyloxidedicarboxylic acid dichlorides).

The procedure of polybenzoxazole synthesis does not differ practically from the above-mentioned polybenzimidazole synthesis with the difference that the first stage of the process, synthesis of poly[(*o*-nitro)-esters], is carried out in the presence of triethylamine, and the process time does not exceed 30 min. The properties of polybenzoxazoles obtained under these conditions, and which are i.r. spectrally free from 'defective' units, are given in *Table 4*. Unlike the structurally similar polybenzoxazoles synthesized by the conventional methods[46,47], the resulting polymers are soluble in trifluororacetic acid and in a system containing isopropylidene groups and in a tetrachloroethane (TCE): phenol mixture (3:1). The high viscosity characteristics of polybenzoxazoles are indicative of the high molecular weights of these systems and are responsible for film-forming properties of these polymers (*Table 4*).

Table 3 Acidity of bis[(*o*-nitro)phenols] of general formula



$-X-$	pK_{a_1}	pK_{a_2}	ΔpK_a
$-SO_2-$	5.80	7.50	1.70
$-\overset{CF_3}{\underset{CF_3}{C}}-$	7.54	9.14	1.60
$-O-$	9.17	10.93	1.76
$-\overset{CH_3}{\underset{CH_3}{C}}-$	9.53	11.12	1.59
$-CH_2-$	9.73	11.22	1.69

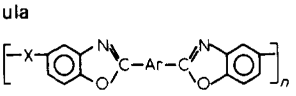
When the synthesis of high molecular weight *o*-nitro-substituted polymers or monomers essential to their preparation involves certain difficulties, these polymers can be obtained alternatively by nitration of the corresponding unsubstituted heterochain polymers. Thus, nitration of aromatic polyamides[22], polyesters[48] and polythioesters[49] gave high molecular weight poly[(*o*-nitro)amides], poly[(*o*-nitro)esters], and poly[(*o*-nitro)thioesters], the reductive polyheterocyclization led to polybenzimidazoles[22], polybenzoxazoles[48], and polybenzthiazoles[49]. Nevertheless, it should be noted that nitration of heterochain polymers can occur not only at the *o*-positions in the main macromolecular chains and this is connected with the formation of 'Raznozvenny polymers'[40], and besides, the viscosity characteristics substantially diminish during nitration of heterochain polymers. Thus, the reactions given in *Scheme 2* are the preferred processes for polyheteroarylene synthesis using reductive polyheterocyclization. Along with the above-mentioned disadvantages, these processes are characterized by a somewhat limited structural set of resulting systems and by the negative influence of the nitrogroups on the reactivity of fragments participating in polycondensation which are clearly shown when using bis[(*o*-nitro)anilines] as monomers. These disadvantages are absent to a large extent in modified and combined reductive polyheterocyclization processes developed in the course of the above-mentioned investigations.

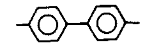
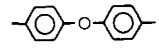
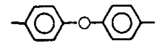
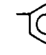
MODIFIED AND COMBINED REDUCTIVE POLYHETEROCYCLIZATION

The modified reductive polyheterocyclization differs from the foregoing processes[19-26] in that the cyclization processes are separated by one or several reactions (usually acylation) from the nitro-group to amino group reduction stage. As in the cases of the reactions considered earlier[19-26], the modified reductive polyheterocyclization processes were accomplished as continuous processes in N-MP using activated iron and hydrogen chloride as reducing agents and hydrogen chloride as cyclization catalyst. Proceeding from the above considerations, such processes occur completely, at all stages, as homogeneous reactions and primary emphasis was given to the synthesis of polyheteroarylenes with a higher solubility in organic solvents and particularly to that of phenyl-substituted polyheteroarylenes which exhibit excellent solubility in unsubstituted analogue, as exemplified by polybenzimidazoles[50,51], polyquinoxalines[52,53], polyquinazolones[54,55] and many other systems.

An illustrative example of modified reductive polyheterocyclization is the synthesis of C-phenylsubstituted polybenzimidazoles[27,28,56-64] by interaction of activated bis[(*o*-nitro)halogen]arylenes with aromatic diamines[27,28,56-62], reduction of the resulting poly[(*o*-nitro)imines] to poly[(*o*-amino)imines][27,28,56-60,63],

Table 4 Some properties of polybenzoxazoles of general formula



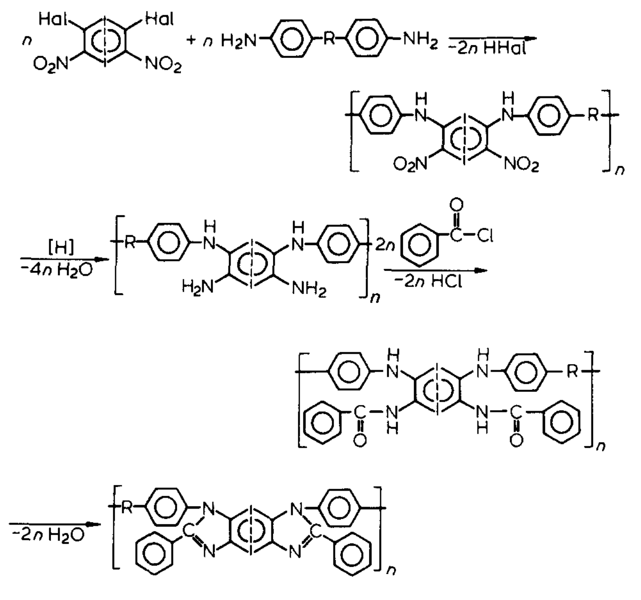
–X–	–Ar–	η_{red}* (dl/g)	T_{soft}, (°C)	T_{dec}, (°C)	Film properties	
					σ (kg cm^{-2})	ε (%)
$-C(CH_3)_2-$		1.5	270–290	400–420	900	2.6
$-C(CH_3)_2-$		1.9	280–300	430–450	1200	3.0
$-C(CH_3)_2-$		1.2	250–270	395–410	800	3.1
$-C(CH_3)_2-$		1.3	250–260	410–420	1030	3.2
$-CH_2-$		1.2	260–270	420–430	1150	3.8
$-CH_2-$		1.4	270–280	410–420	1050	2.5

* Reduced viscosity of 0.5% solutions in H_2SO_4 at 30°C

† Temperature of a 5% loss of initial weight (t.g.a., = 4.5°C/min in air)

benzoylation of the latter[27,28,56-60,63] and cyclization of the poly[(*o*-benzamido)imines][27,28,56-60,64] formed according to *Scheme 7*:

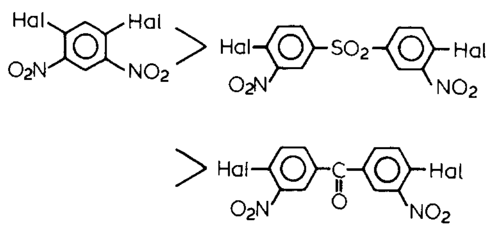
Scheme 7



1,3-Dihalogen-4,6-dinitrobenzenes and binuclear compounds with electron-accepting 'bridge' groups[65-71] -3,3′-dinitro-substituted 4,4′-dichloro- and 4,4′-difluoro-derivatives of diphenylsulphone and benzophenone can be utilized successfully as activated bis[(*o*-nitro)halogen]arylenes. From the above consideration, 4,4′-diaminodiphenylmethane, 4,4′-diaminophenyloxide and 4′,4″-diamino (hydroquinone diphenyl ether) were applied as aromatic diamines.

An investigation of the comparative electrophilicity of bis/(*o*-nitro)halogen]arylenes by means of Cl^{35} n.m.r., F^{19} n.m.r., ^{13}C n.m.r. and an analysis of the competitive amination data showed[60] that these compounds can be arranged in the following reactivity sequence:

Scheme 8

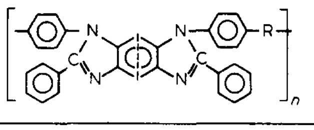


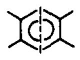
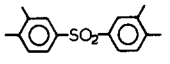
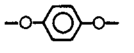
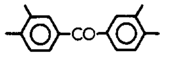
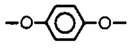
The fluorine-contained compounds are more reactive than the chloride-containing compounds. In spite of the higher activity of the 1,3-dihalogen-4,6-dinitrobenzenes, attention was paid mainly to the synthesis of polymers on the basis of diphenylsulphone- and benzophenone-containing monomers, as the 'hinged' groups within these monomers are responsible for the solubility of all intermediate and final polymeric systems in organic solvents and, correspondingly, the possibility of carrying out the polymer syntheses under homogeneous conditions.

Similar to the synthesis of polybenzazoles with the use of true reductive polyheterocyclization processes, the synthesis of C-phenylsubstituted polybenzimidazoles is a simple process proceeding under mild conditions. At none of the process stages does the temperature exceed 180°C. The C-phenylsubstituted polybenzimidazoles obtained under these conditions have no unreduced nitro groups and uncyclized fragments according to the i.r.-spectrum: their spectral characteristics are identical with the corresponding model compounds.

The mild conditions of cyclization, the presence of phenyl substituents and a large amount of 'hinged' groups in the main chains of polymers, determine the high solubility of polybenzimidazoles in dipolar aprotic and phenol solvents. The high viscosity characteristics of these systems (*Table 5*) offer the possibility of producing materials with high mechanical properties. Low 'raznozvennost'[40] of synthesized polymers determines their high degradation temperatures under conditions of dynamic (*Table 5*) and isothermal t.g.a. In particular, a comparison of thermostability of C-phenylsubstituted

Table 5 Some properties of C-phenylsubstituted polybenzimidazoles of general formula

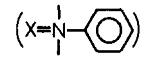


	–R–	η_{red},* (dl/g)	T_{soft}, (°C)	T_{dec},† (°C)	Film properties (25°C) σ (kg cm^{-2})	Film properties (25°C) ϵ (%)
	–O–	1.72	310–330	470	950	4
–"–	–CH$_2$–	2.34	335–350	490	1040	3–4
–"–		2.27	315–330	450	1050	4
	–O–	0.41	305–315	430	–	–
–"–	–CH$_2$–	0.32	320–325	430	–	–
–"–		1.75	300–320	420	990	5

* Reduced viscosity of 0.5% solutions in H_2SO_4 at 30°C

† Temperature of a 5% loss of initial weight (d.t.g.a., T = 4.5°C/min in air)

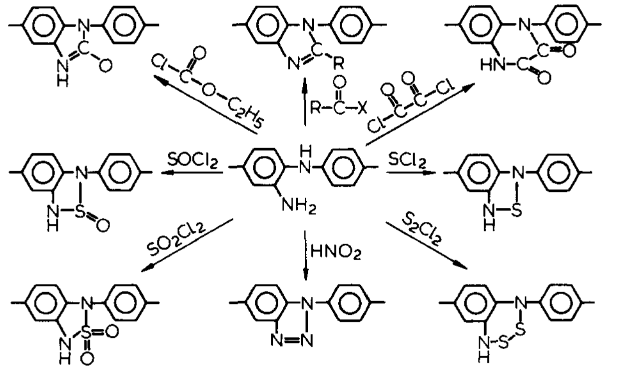
polybenzimidazoles obtained according to a scheme in ref. 7 and structurally approximating poly[(*N*-phenyl)benzimidazoles] obtained by a two-stage method[50] according to the scheme in ref. 1



showed that under the conditions of isothermal t.g.a. the polybenzimidazoles obtained by modified reduced polyheterocyclization are more thermally stable.

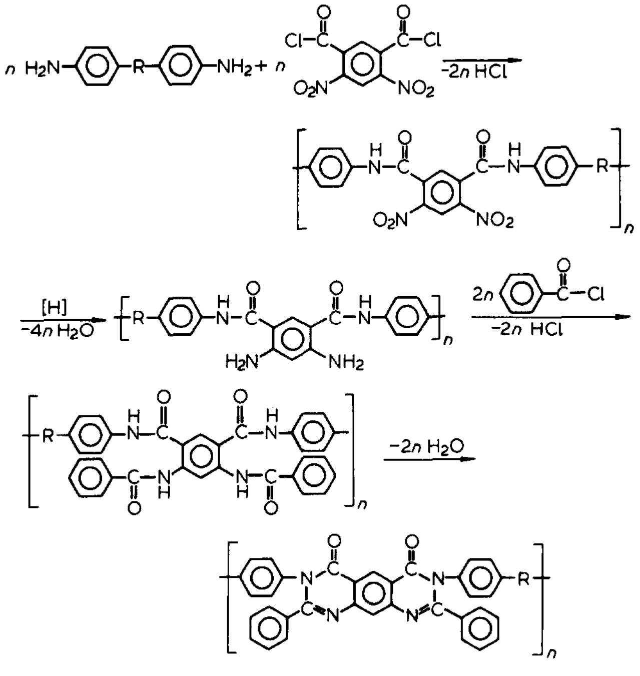
It should be noted that the poly[(*o*-amino)imines] formed at an intermediate stage of C-phenylsubstituted polybenzimidazole synthesis can be used for the preparation of a wide range of heterocyclic polymers[64]. In particular, when treated not with benzoylchloride but with ethylchlorocarbonate, oxalylchloride, thionylchloride, sulphurylchloride, sulphenylchloride, sulphur chloride, nitric acid and the like and by further cyclization of the reaction products they give polybenzimidazolones, polyquinoxalidinediones, polybenzthiazolidine-S-oxides, polybenzthiodiazolidine-S-dioxides, polybenzthiadiazolidine, polybenzdithiadiazines, polybenztriazoles and other such similar compounds:

Scheme 9



Another typical example of the modified reductive polyheterocyclization process is the synthesis of phenylsubstituted polyquinazolones[72,73] based on the interaction of aromatic diamines with 4,6-dinitroisophthalic acid dichloride[74] followed by reduction of the resulting poly[(*o*-nitro)amides] to poly[(*o*-amino)amides] and benzoylation of the latter at the free aminogroups and catalytic polycyclization of the resulting poly/(*o*-benzamido)amides]:

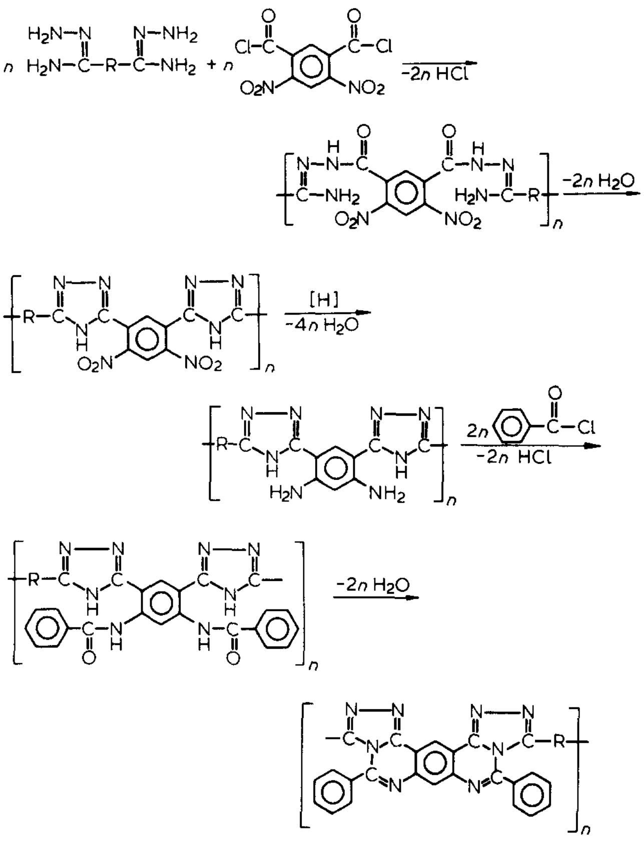
Scheme 10



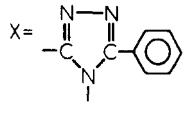
Like C-phenylsubstituted polybenzimidazoles, the i.r. spectra of the resulting poly[(2-phenyl)quinazolones] contain no maxima, a characteristic of unreduced nitro groups and uncyclized fragments that is confirmed by comparison of their spectra with those of model compounds. The synthesized polymers were soluble in strong acids, phenolic solvents (*Table 6*) and on heating in dipolar aprotic solvents. According to dynamic and isothermal t.g.a. data, the thermostability of these polymers is comparable with the thermal stability of identical systems obtained by known methods[54,55].

Higher solubility of polyheteroarylenes synthesized by modified reductive polyheterocyclization determined the use of this process in the synthesis of ladder polyheteroarylenes having high heat resistance and thermostability but resulted in unsatisfactory processing into finished materials[75-77]. Phenylated poly{benz[di(s-triazolopyrimidines)]} were obtained by using dicarboxylic acids bisamidrazones[78] as comonomers of 4,6-dinitroisophthalic acid dichloride[79,80]:

Scheme 11



These polymers are isomeric to known earlier systems[81,82] prepared by two-stage processes according to the *Scheme (1)*



The i.r. spectra show that the resulting polyheteroarylenes do not contain unreduced nitrogroups and uncyclized fragments. The presence of phenyl side groups and mild conditions of polycyclization processes explain the solubility of the resulting systems in acidic solvents (H_2SO_4, CF_3COOH), in a TCE–phenol (3 :1) mixture and a partial solubility in hot N-MP (*Table 7*).

A comparative study of thermostability of poly{benz[di(s-trizolopyrimidines)]} synthesized by modified reductive polyheterocyclization and a two-stage method[81,82] using dynamic (*Table 7*) and isothermal t.g.a. showed that these systems are comparable.

The synthesis of polyquinazolinoquinazolones[83] can also be realized using the modified reductive polyheterocyclization:

Scheme 12

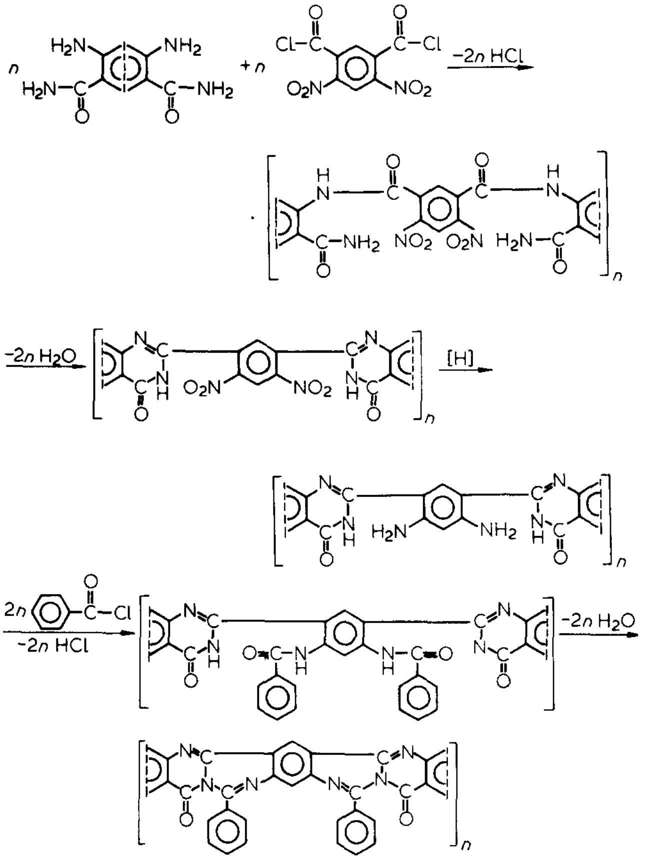
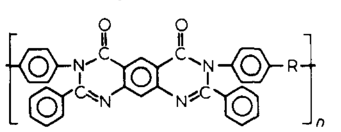
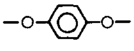


Table 6 Some properties of poly[(2-phenyl)quinazolones] of general formula

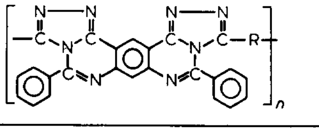


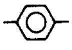
–R–	η_{red}* (dl/g)	T_{soft}, (°C)	T_{dec},† (°C)	Film properties (25°C)	
				σ (kg cm^{-2})	ε (%)
–O–	1.21	380–385	450	1200	8
$-CH_2-$	1.02	375–380	430	1100	8
	1.15	350–360	440	1100	12

* Reduced viscosity of 0.5% solutions in H_2SO_4 at 30°C

† Temperature of a 5% loss of initial weight (d.t.g.a., T = 4.5°C/min in air)

Table 7 Some properties of poly[benz(di(S-triazolopyrimidines))] of general formula



–R–	η_{red}* (dl/g)	T_{dec}† (°C)	Solubility			
			H_2SO_4	CF_3COOH	TCE:phenol	N–MP
–	0.68	500	+	+	+	±
	0.86	505	+	+	+	+
	1.04	520	+	+	+	±
	0.92	475	+	+	+	+

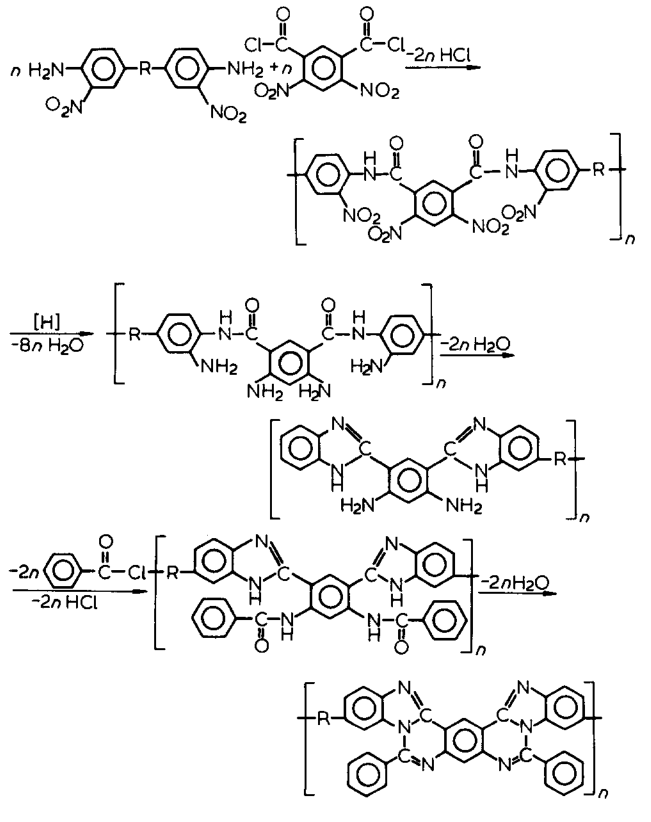
* Reduced viscosity of 0.5% solutions in a TCE:phenol mixture (3:1) at 25°C

† Temperature of a 5% loss of initial weight (d.t.g.a., T = 4.5°C/min in air)

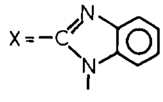
The resulting polymers are soluble in acids, phenolic solvents and partially in hot N-MP and DMSO, $\eta_{red.}$ of their solutions in the TCE–phenol mixture (3:1) is 0.96–1.30 dl g^{-1}. The polyquinazolinoquinazolone films have a tensile strength of 850–950 kg cm^{-1} at 250°C and an elongation of 2–10%.

Along with the above modified reductive polyheterocyclization processes, in synthesis of ladder polyheteroarylenes we used the processes of combined reductive polyheterocyclization, some of the stages of which belong to the true reductive polyheterocyclization and others to the modified reductive polyheterocyclization. The synthesis of poly{benzo[di(pyrimidobenzimidazoles)] on the basis of bis[(*o*-nitro)-anilines] and 4,6-dinitroisophthalic acid dichloride is a typical example of combined reductive polyheterocyclization[84,85]:

Scheme 13



As can be seen from the scheme[13], the poly[(*o*-amino)-phenyl]benzimidazole formation stage can be regarded as a true reductive polyheterocyclization, while the formation of the aimed poly{benz[di(pyrimidobenzimidazole)]} structure belongs to the processes of modified reductive polyheterocyclization. Like all the systems considered above, the poly{benz[di(pyrimidobenzimidazoles)]} obtained by the combined reductive polyheterocyclization reveal in the i.r. spectra no unreduced nitrogroups and no uncyclized fragments. Unlike the polymers obtained by the two-stage method[81,82], according to *Scheme 1*, the poly{benz[di(pyrimidobenzimidazoles)]} prepared according to *Scheme 13* contain phenyl substituents that, in combination with the mild conditions of polycyclization processes, make the polymers soluble in a TCE–phenol mixture (3:1), H_2SO_4 and CF_3COOH (*Table 8*). The poly{benz[di(pyramidobenzimidazoles)]} have higher thermostability than the other polyheteroarylenes prepared by the modified reductive polyheterocyclization (compare *Tables 2–8*) and are comparable under the isothermal t.g.a. conditions with polymers obtained by the two-stage method[81,82].

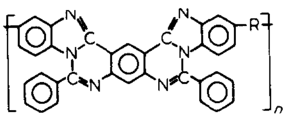


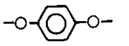
The potentialities for the foregoing reactions of polyheteroarylenes synthesis inherent in the modified and combined reductive polyheterocyclization have not yet been exhausted, but nevertheless, they undoubtedly point to promising developments of such approaches to the preparation of comparatively simple and complicated polymeric systems.

CONCLUSIONS

As a result of investigations during the last seven years we developed a new general method of polyheteroarylene synthesis suggesting the use of intermediate products of compounds applied in the conventional synthesis of the same polymers, as well as the use of a catalytic cyclization process which not only makes the conditions of the

Table 8 Some properties of poly{benz[di(pyrimidobenzimidazoles)]} of general formula



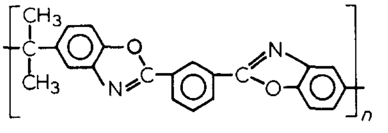
–R–	η_{red}* (°C)	T_{dec}† (°C)	Solubility			
			H_2SO_4	CF_3COOH	TCE:phenol	N–MP
–O–	0.83	530	+	+	+	±
$-CH_2-$	0.69	520	+	+	+	±
	0.63	500	+	+	+	±

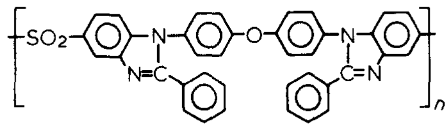
* Reduced viscosity of 0.5% solutions in a TCE:phenol mixture (3:1) at 25°C

† Temperature of a 5% loss of initial weight (d.t.g.a., $T = 4.5$°C/min in air)

processes milder, but also imparts higher solubility and better processing to the desired systems.

Nowadays, polybenzoxazoles and C-phenylsubstituted polybenzimidazoles are, from the practical point of view, among the most synthesized polymers; in particular, of significant interest are the synthesized polymers with the following structural formulae:





The former is based on 2,2-bis-(3-nitro-4-hydroxyphenyl)propane[86], a product of the direct nitration of bisphenol A used in the chemical industry in the production of polycarbonates[87] and polysulphones[4] and on isophthaloyl chloride used in the synthesis of polyamides[88]. The latter is based on 3,3′-dinitro-4,4′-dichlorodiphenylsulphone a product of the direct nitration of 4,4′-dichlordiphenylsulphone[89] and 4,4′-diaminodiphenyloxide used in the synthesis of polyimides[5,6]. The combination of high solubility with high molecular weights of polymers in these systems makes it possible to prepare various materials such as films, reinforced plastics, gas-separating membranes[22,26,60], which can operate at 250°–300°C. There are also some indications of practical use of other systems[90] obtained by the method of reductive polyheterocyclization and thus displaying undoubted practical significance of this research trend.

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