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Reactions using nitro-containing monomers for the synthesis of aromatic polymers

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ABSTRACT. The progress made in the synthesis of aromatic polymers based on nitro-containing monomers is reviewed. It is shown that the main processes for the synthesis of aromatic polymers using nitro-containing monomers are nucleophilic aromatic polynitrosubstitution reactions, which are effectively used to obtain polymers containing ether groups in the main macromolecular chains. A group of novel reactions that includes thermal and chemical conversion of nitro-containing heterochain polymers is examined.

The bibliography includes 98 references.

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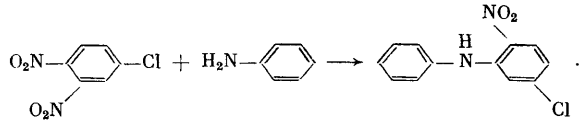
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I. Introduction

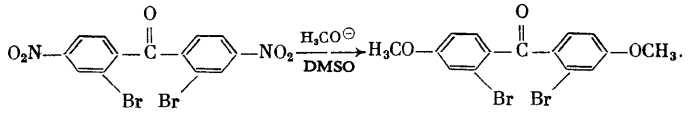
Research into novel functional groups used in polycondensation and the modification of condensation polymers is a topical question in the chemistry of high-molecular-weight compounds. Such groups should establish a sufficiently high reactivity of the monomers, without limiting their availability or increasing their toxicity. Up until recently nitro compounds, which are widespread in organic chemistry,[1,2] have not been used to any appreciable extent in polycondensation processes; however, developments that have occurred over the last 15 years have considerably changed the position in this area. The present review is devoted to an analysis of the principal advances made in the synthesis of condensation polymers based on nitro-containing monomers.

II. Nucleophilic aromatic polynitrosubstitution reactions

Reactions involving nucleophilic substitution of aromatic nitro groups have been known for a long time.[3] Thus, Laubenheimer[4,5] in 1876 described the replacement of the nitro group in 3,4-dinitrochlorobenzene by aniline to form 2-nitro-5-chlorodiphenylamine:



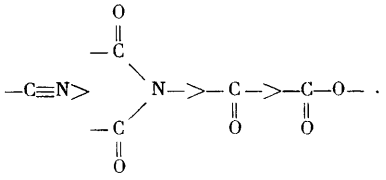
It is interesting to note that very little attention was subsequently given to the application of nitrosubstitution reactions until Gorvin[6] demonstrated the successful reaction between 2,2′-dibromo-5,5′-dinitrobenzophenone and methoxide ion:



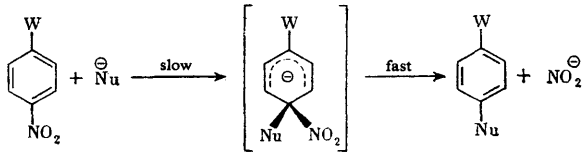
The reaction occurred almost quantitatively, indicating the higher reactivity of nitro groups compared to bromine atoms.

The successful achievement of this reaction was related to the use of a dipolar aprotic solvent. In general the use of dipolar solvents is a necessary condition for the preparation of products in high yield at moderate temperatures.

Subsequent studies[7–17] showed that nitrobenzene derivatives containing other electron-withdrawing groups undergo nitrosubstitution. The following series constitutes the rectivity of activating groups:

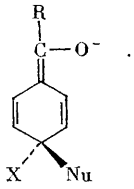


Nucleophilic substitution of a nitro group from an activated system usually occurs by a two-stage addition–elimination mechanism. The first stage is usually, but not always, limiting (determining the rate of the overall process).

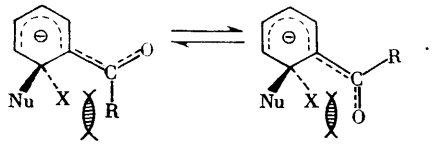


When strong electron-withdrawing substituents are present in the ring, nucleophilic substitution reactions occur under mild conditions. The presence of electron-withdrawing groups of the type $-\overset{\overset{O}{\|}}{C}-R$ at

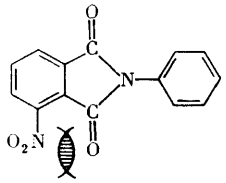
para positions relative to the leaving groups causes the substitution reactions to occur readily because of stabilisation of the Meisenheimer complex as a result of their acceptance of negative charge from the ring:



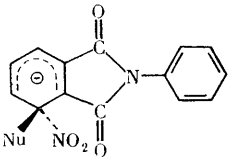
On the other hand, any electron-withdrawing groups situated at *ortho* positions cause a reduction in the rates of the substitution reactions as a result of the formation of high-energy conformers of a Meisenheimer complex:



Steric interactions in the Meisenheimer complexes are less clearly reflected in the case of activated systems containing condensed rings (nitro-substituted *N*-arylphthalimides) where the *ortho* isomers are much more reactive than *para* isomers as a result of the inductive effect, and also the relief of the *peri* interaction



and the absence of steric interaction in the Meisenheimer complex



Moreover, the formation of conformers of the Meisenheimer complex does not occur as a result of ring condensation.

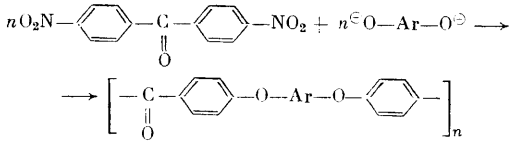
The higher rates of reaction found for nitro groups compared to chlorine groups are due to the greater electrophilicity of the carbon atoms on which substitution occurs, since the nitro group is a stronger electron acceptor than chlorine.

Substitution reactions obey second-order kinetics, being first-order with respect to both the aromatic substrate and the nucleophile.

In general the phenoxides used in nitrosubstitution reactions must be free of moisture. In the presence of the latter, derivatives containing ester and imide groups are readily deactivated as a result of hydrolysis and ring opening respectively. However, it should be noted that derivatives containing nitrile and ketone groups are less sensitive to the presence of small quantities of water. In these cases free phenols can be used in the presence of carbonates or alkali metal hydroxides. Under normal reaction conditions, alkali metal nitrites which are by-products of the reactions do not undergo undesirable conversions. Nevertheless, on increasing the time of the reactions—especially at higher temperatures—nitrite ions can attack other nucleophilic sites of the initial compounds or by-products.[17,18]

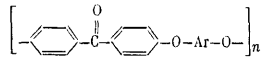
The efficiency of activation of the nitro groups by carbonyl "bridges" predetermined the theoretical possibility of using nucleophilic aromatic polysubstitution processes to obtain polyether containing carbonyl groups.[19,20]

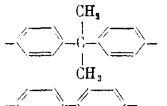
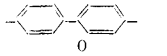
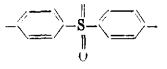
It was demonstrated for the first time by Radlmann et al.[21] and by Heath and Wirth[22] that nitrosubstitution reactions occur sufficiently productively to be able to extend them to the synthesis of high-molecular-weight aromatic polyethers. Reaction of 4,4′-dinitrobenzophenone with bisphenols gave different polyether-ketones,



whose individual properties are given in Table 1.

Table 1. Polyetherketones obtained by nitrosubstitution.[21]



—Ar—	Temperature of polycondensation	Solvent	η_{int} in MP	mp of polymer, °C
	65	DMSO/C_6H_5Cl	1.32	195–220
	145	DMSO	1.18	236–255
	140	DMSO	1.07	201–228

Clendinning and Kwiatkovski[23] also used polynitrosubstitution reactions to obtain polyetherketones.

Because of the strong activation effect of the nitrile groups, the two nitro groups in 2,4- and 2,6-dinitrobenzonitriles readily undergo substitution. This make it possible to obtain high-molecular-weight polyethers containing nitrile substituents as a result of the reaction between dinitrobenzonitriles and salts of different bisphenols:[11]

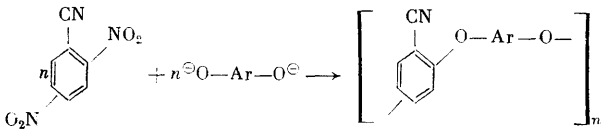
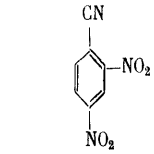
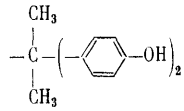
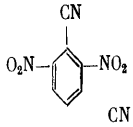
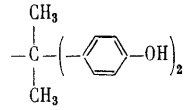
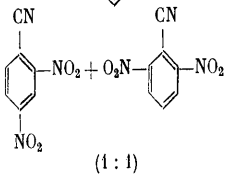
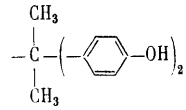
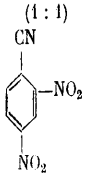
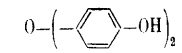
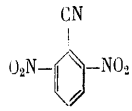
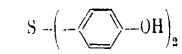
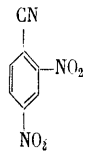
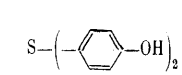
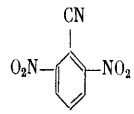
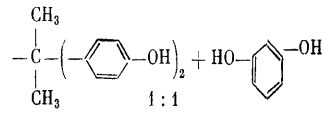
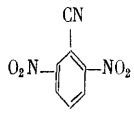
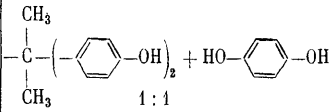
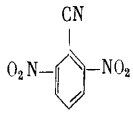
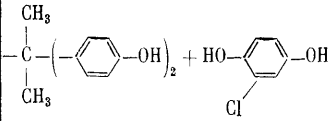
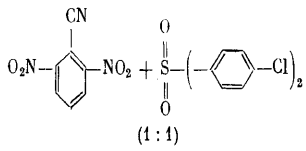
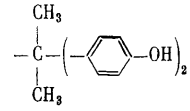


Table 2. Synthesis of polyethers by nitrosubstitution of dinitrobenzonitriles with bisphenol salts.[11]

Dinitro compounds	Bisphenols	Reaction conditions			Thermal properties of polymers		
		solvent/T, °C	yield, %	[η], dl g^{-1}	T_g, °C*	T_i, °C** air	T_i, °C** N_2
		DMSO/115	81	0,68	141	430	430
		DMSO/145	75	0,51	173	385	420
 (1 : 1)		DMSO/140	89	0.60	160	420	425
		DMSO/140	70	0.24	136	360	380
		DMSO/115	75	0.40	147	450	450
		DMSO/115	85	0.32	134	450	450
	 1 : 1	DMSO/115	75	0.34	155	390	400
	 1 : 1	DMSO/114	—	0.55	176	415	430
	 (1 : 1)	DMSO/115	88	0.50	174	430	410
 (1 : 1)		DMSO/150	91	0.38	178	430	420

* Glass-transition temperature as determined by differential scanning of calorimetry.

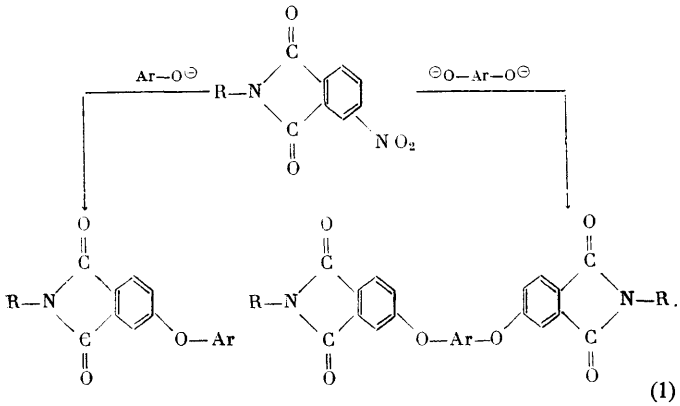
** Temperature of loss of 1% weight as determined by thermogravimetric analysis.

Some properties of the polyethers synthesised are given in Table 2.

The majority of the nitrile-substituted polyethers obtained are soluble in chlorinated solvents; strong and flexible films are obtained from their solutions. The high glass-transition and thermal-degradation temperatures are caused by the aromaticity of these polymers and the high polarity of the nitrile groups.

The second large family of polymers obtained with the use of polynitrosubstitution processes comprises aromatic polyetherimides.[19]

According to several studies,[10,24–27] nitro groups that are activated by two carbonyls undergo nucleophilic substitution. Activation of nitro groups by the two carbonyls contained in cyclic imides is particularly effective.[26,28] Thus, *N*-substituted 3- and 4-nitrophthalimides were converted to mono- and bis-etherimides by reaction with different mono- and bis-phenoxides by means of nitrosubstitution:

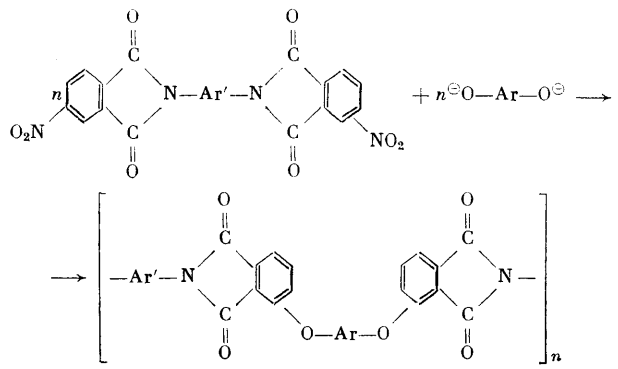


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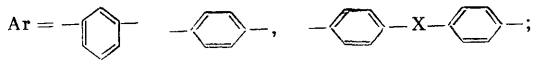
These nitrosubstitution reactions must be carried out in the complete absence of water, since *N*-substituted nitrophthalimides are readily deactivated as a result of hydrolysis and ring opening. Anhydrous solutions of phenoxide salts can be obtained from sodium hydride and the respective phenols or by azeotropic dehydration of aqueous phenoxide salts in DMSO–toluene in a similar manner to the techniques used in the synthesis of polysulphones.[29]

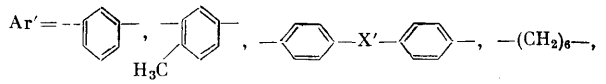
The synthesis of imidoethers is carried out under mild temperature conditions (25–60 °C), it occurs sufficiently rapidly (the reaction time varies from 5 min to several hours), and results in formation of the required products in high yield (>95%).[26]

The high yields of bis(etherimides) predetermined the possibility of extending the reactions depicted in Scheme (1) to the synthesis of polymers, namely, to the preparation of polyetherimides using nitrosubstitution processes[28,30–35]



where

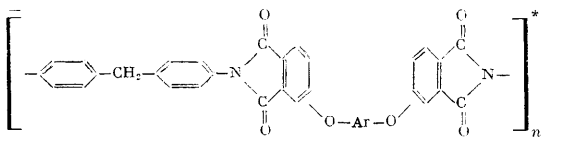




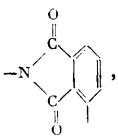
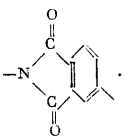
$X' = -CH_2-, -O-, -SO_2-$.

The synthesis of polyetherimides by means of polynitrosubstitution was carried out under modified conditions[29] in the complete absence of moisture.[31,32] The conditions for the synthesis of polyetherimides starting from the dinitrodiphthalimide derivative of 4,4′-diaminodiphenylmethane are given in Table 3 together with certain properties of the polyetherimides.

Table 3. Synthesis conditions and some properties of polyetherimides with the general formula[31,32]



Compound	—Ar—	Synthesis conditions			[η], dl g^{-1}	Yield, %
		solvent	*T*, °C	time, h		
1	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMSO	40	1.0	0.28	91 **
2	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMSO/toluene	40	1.0	0.39	91
3	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	"	40	22.0	0.56	–
4	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMF	50	2.0	0.43	–
5	*p*-C_6H_4–C_6H_4-*p*	DMSO	40	0.5	0.36	98 ***
6	*p*-C_6H_4–$C(CF_3)_2$–C_6H_4-*p*	DMSO	50	1.0	0.19	77
7	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMSO/toluene	60	17.0	0.42	89

* Compounds 1–6: , compound 7: .

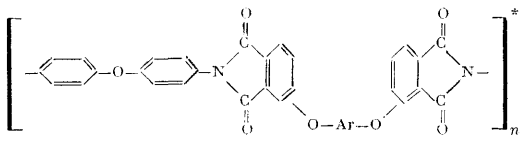
** T_g = 230 °C, T_{deg} = 380 °C.
*** T_{deg} = 400 °C.

Polyetherimides based on other dinitrophthalimides were obtained under similar or fairly similar conditions. Some properties of the polymers synthesised are given in Tables 4 and 5.

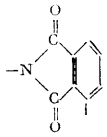
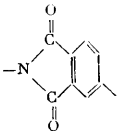
On the whole, polynitrosubstitution reactions occur rapidly even under comparatively mild conditions. When dipolar aprotic solvents or their mixtures with toluene are used, polymers with relatively high molecular weights are formed (M_w up to 123 × 10^3, M_n up to

23×10^3).[32] The most frequently used solvents are DMSO + toluene and DMF, the choice of solvent being determined by the method of obtaining the anhydrous bisphenoxide. The reactivity of dinitrophthalimides used is determined primarily by the position (3- or 4-) of the nitro groups rather than by the nature of the Ar residue. Monomers that contain nitro groups at the 3-position are more reactive than systems containing nitro groups at the 4-position.[26] Consequently, the synthesis of polyetherimides using dinitrophthalimides that contain nitro groups at the 4-position are carried out at higher temperatures and for a longer time. A factor that affects the rate of reaction is the rate of solution of the monomers; this gives rise to the possibility of polymers with relatively high molecular weight being formed when there is some departure from equimolarity of the monomers. The low solubility of bisphenoxides (and/or a low rate of their solution) can be compared with a slow feeding of these monomers into the reaction zone.

Table 4. Synthesis conditions and some properties of polyetherimides with the general formula[31,32]



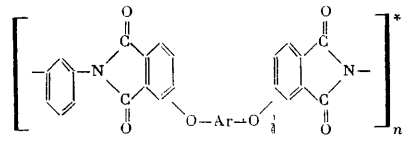
Compound	—Ar—	Synthesis conditions: solvent	T, °C	time, h	$[\eta]$, dl g^{-1}	Yield, %	T_g/T_{deg}
1	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMSO/toluene	45	0.25	0.61	97	–
2	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	"	40	17	0.33	89	226/385
3	*m*-C_6H_4–	DMF	60	1	0.18	100	226/–
4	*p*-C_6H_4–	DMSO	50	1	0.45	76	237/430
5	*p*-C_6H_4–S–C_6H_4-*p*	DMAA	60	1	0.37	100	234/–
6	*p*-C_6H_4–O–C_6H_4-*p*	DMF	60	1	0.80	100	239/400
7	*p*-C_6H_4–C_6H_4-*p*	DMSO	50	0.8	0.60	95	277/380
8	*p*-C_6H_4–$C(CH_3)_2$–C_6H_4-*p*	DMSO/toluene	55	14	0.41	94	196/420
9	*p*-C_6H_4–O–C_6H_4-*p*	DMF	60	1	0.44	96	215/–

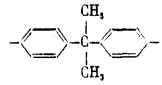
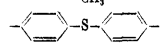
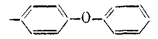
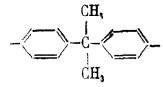
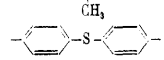
* Compounds 1–7: , compounds 8 and 9: 

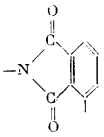
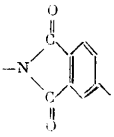
It is advisable to carry out the synthesis at elevated temperatures in order to increase the solubility of the monomers. However, it was found in a number of cases that an increase in temperature and duration of reaction resulted in the formation of products with a lower molecular weight.[32] It is possible that this occurs as a result of side reactions with nitrite ion,[26,28,36] which is eliminated during polynitrosubstitution. Consequently, the optimum temperature for reactions involving 3,3′-dinitrophthalimides is 50 °C, while for reactions involving 4,4′-dinitrophthalimides the optimum temperature is 10 °C higher.[32]

Increasing the concentration of the monomers generally assists the formation of polyetherimides with higher molecular weights, but on reaching very high concentrations (~50%) the rates of solution of the initial compounds decrease—as a result of saturation and an increase in viscosity—which also slows down polynitrosubstitution. The most frequently used concentration range is 20–25%.[32]

Table 5. Synthesis conditions and some properties of polyethermides with the general formula[31,32]



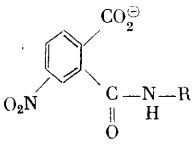
Compound	—Ar	Synthesis conditions: solvent	T, °C	time, h	$[\eta]$, dl g^{-1}	Yield, %	T, °C
1		DMSO/toluene	55	5.25	0.23	87	227
2		DMAA	60	1	0.16	100	209
3		DMAA	60	1	0.22	95	232
4		DMF	70	2.5	0.29	82	227
5		DMAA	60	1	0.1	80	–

*Compounds 1–3: , compounds 4 and 5: .

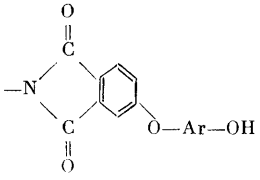
In a number of cases sodium phenoxide or sodium 4-methylphenoxide were introduced into the reaction mixtures after completion of the synthesis processes of polyetherimides in order to replace the terminal nitro groups and increase the thermal stability of the required polymers. At the same time careful control over the course of the reactions was necessary in order to decrease the contribution of exchange reactions between the phenols and the diarylether groups[26] which reduce the molecular weight of the polymers.

By analogy with the synthesis of mono- and bis-etherimides, reactions for the synthesis of polyetherimides by means of polynitrosubstitution are especially sensitive to the presence of moisture in the reaction system. The moisture remaining after formation of a bisphenol and also that contained in the reactants or solvents leads to poor reproducibility of results and to formation of low-molecular-weight polymers. The moisture remaining in the system is in equilibrium with the bisphenoxide, which gives rise to the presence of hydroxide ions in the reaction mixture. The latter

attack the imide rings[37] in the monomers and in the polymers formed. As a result of ring opening, an amino acid

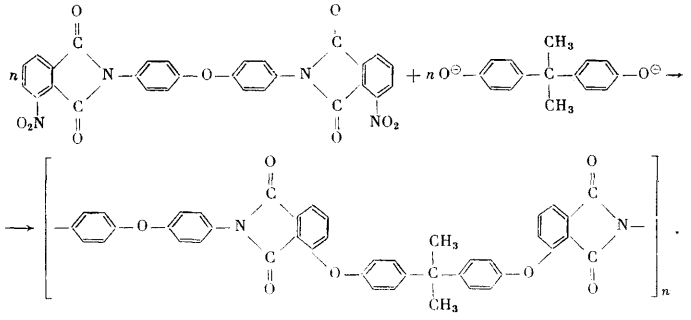


is formed, disrupting the stoichiometry during synthesis of the polymers and causing chain termination, since the nitro group in it is insufficiently activated to undergo substitution.[37] The presence of a hydroxide ion also opens up the possibility of formation of structures of the type



in which the hydroxyl group no longer behaves as a nucleophile.

The effect of moisture on the synthesis of a polyetherimide was demonstrated in the case of the synthesis of a polymer in accordance with the following scheme through the addition of a controlled amount of water to the system

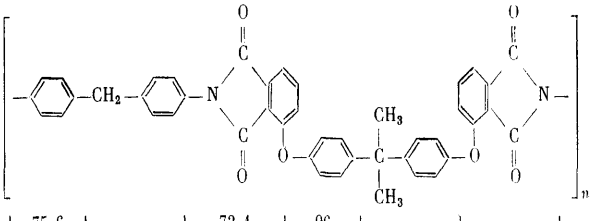
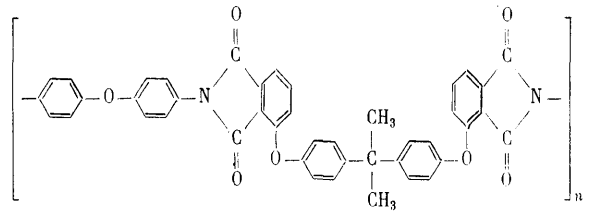
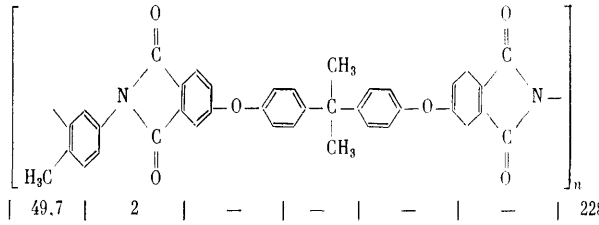


It transpired that when the process was carried out in the driest system in DMSO, a polymer with [η] of not less than 0.44 dl g^{-1} was formed, whereas addition of 0.03% water to the solvent (10 mol.% based on the reactants) assists the formation of a polymer with [η] = 0.25 dl g^{-1}, while addition of 0.09% water (30 mol.%) leads to the formation of a polymer with [η] = 0.18 dl g^{-1}.[32]

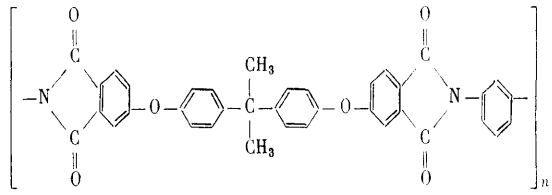
A study of polyetherimides using gel permeation chromatography showed that they have wide molecular weight ranges, which may also be due to the presence of water in the reaction mixtures. It is this factor that may determine the presence of "open" rings in chains and at the ends of the macromolecules, leading to the possibility of strong carboxylic acids being formed during processing.

Polyetherimides are amorphous in the majority of cases. This factor in combination with the asymmetry of their macromolecular structure and the presence of a considerable number of ether bonds in the latter governs the solubility of the polymers in solvents such as chlorinated hydrocarbons, phenols, and dipolar aprotic solvents. A further characteristic of polyetherimides, which is clearly illustrated in Tables 3–5, is the considerable difference between the glass-transition and degradation temperatures of these polymers, thus making it possible to process them into articles by moulding under pressure. Materials based on polyetherimides have high deformation strength characteristics. Some properties of polyetherimide films obtained from solutions and also those of moulding materials derived from them are given in Table 6.

Table 6. Mechanical properties of materials based on polyetherimides obtained by polynitrosubstitution.[32]

[η], dl g^{-1}	Yield point, MPa	Elongation at yield, %	Break point, MPa	Elongation at break, %	Ultimate flexural strength, MPa	Flexural modulus, MPa	Thermal stability, °C
							
0.42	75.6	—	72.1	96	—	—	—
0.49	78.4	5.5	—	—	—	—	223
0.70	93.7	6.8	—	—	147.7	3080	217
							
0.38	93.7	7	86.1	65	—	—	204
							
0.36	49.7	2	—	—	—	—	228

Of polyetherimides that have been synthesised, the polyetherimide which corresponds to the structural formula



is of the greatest interest in terms of the availability of the starting compounds, processability, and deformation-strength and thermal properties of materials based on it. This polyetherimide, for which 4-nitrophthalic anhydride, *m*-phenylenediamine, and bisphenol A are

the starting compounds, is manufactured by General Electric (USA) under the name Ultem®.[10,34,38–47] Some properties of this polyetherimide are given in Table 7.

Table 7. Properties of Ultem® polyetherimide.[11]

Mechanical properties	
Stress at yield point (yield point)	105 MPa
Modulus of elasticity	3000 MPa
Elongation at break	60–80%
Ultimate flexural strength	145 MPa
Flexural modulus	3300 MPa
Ultimate compressive strength	140 MPa
Compressive modulus	2900 MPa
Gardner impact strength	36 N m
Izod impact strength	
notched sample	50 J m^{-1}
unnotched sample	1300 J m^{-1}
Thermal properties	
Glass-transition temperature	217 °C
Heat-deflection temperature under load	
1.85 MPa	200 °C
0.46 MPa	210 °C
Oxygen index	47
Inflammability by UL-94 method (vertical sample)	V–O at 0.64 mm Hg
Smoke evolution by NBS (National Bureau of Standards) method	
D_s after 4 min	0.7
D_{max} after 20 min	30

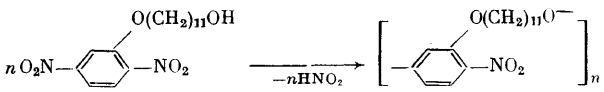
Ultem® is one of the best engineering thermoplastics known at the present time.[40–47] Its distinctive merits are good processability on standard equipment,[43–47] high tensile strength and modulus of elasticity,[34,38,40–43,46,47] good preservation of mechanical properties at elevated temperatures,[38,40,41,43,46,47] valuable electrical properties that remain stable over wide temperature and frequency ranges.[34,38,40,41,43,46,47] The material is distinguished by its high heat resistance and low smoke density. With regard to the latter property it is superior to all known unfilled thermoplastics.[38,40,41,43,44,46,47] The polyetherimide is stable towards solvents[41,45,47] and has high chemical stability.[38,46,47]

Because of the unique properties of Ultem®, in particular the possibility of using it to obtain articles with a complex configuration, it can be successfully used as a construction material in electrical engineering, electronics, the aerospace industry, ship building, and transportation, including the manufacture of components in the car industry.[38,41,46–48] Moreover, Ultem® and other polyetherimides can be used as heat-resistant adhesives,[50] layers and films for the electronics industry,[51] and foamed plastics for use in heat insultion and vibrational absorption.[52]

Mixtures of polyetherimides with other heterochain and heterocyclic polymers are of considerable interest. Thus, composites based on aromatic polyamides and polyetherimides were obtained with improved impact strength and stability towards chlorinated solvents.[53] Attempts have been made to produce mixtures of polyetherimides and polybenzimidazoles.[54]

On the whole polyetherimides have attracted the attention of consumers, and according to several studies[3,13,38–49] constitute a significant achievement in the chemistry and technology of condensation polymers.

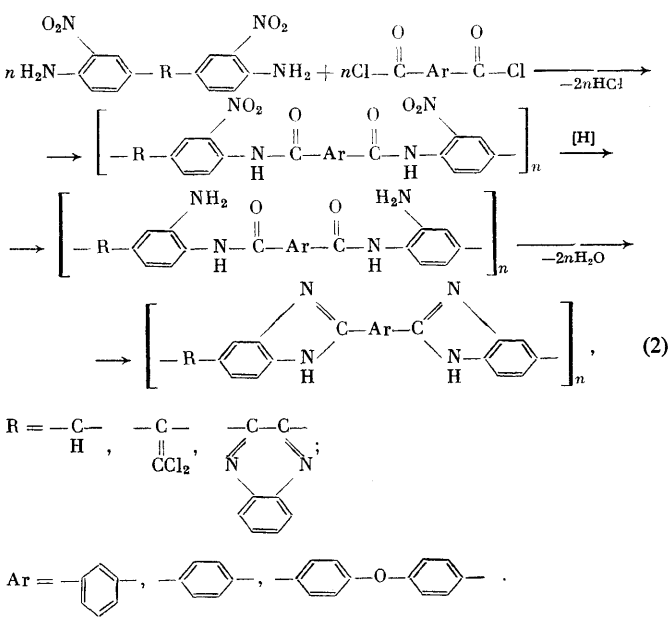
It was shown by Schaeffer in recent studies[55,56] that not only phenol groups but also aliphatic hydroxyl groups can be used in nitrosubstitution reactions. Thus, polycondensation of 1,4-dinitro-2-(n-hydroxyundecyloxy)benzene in a mixture of THF : DMSO (3 : 1) using phase-transfer catalysts gave polyethers with molecular weights of up to 32 000.



III. Reductive polyheterocyclisation reactions

In contrast to nucleophilic aromatic polynitrosubstitution processes, reductive polyheterocyclisation reactions[57–60] do not assume substitution of nitro groups contained in the monomers used. The nitro groups are retained as *o*-substituents in heterochain polymers, but after their reduction to primary amine groups they participate in processes for the formation of the required aromatic heterocycles.

The evolution of reductive polyheterocyclisation processes in recent years has been due primarily to the development of novel polybenzimidazoles. Novel unsubstituted poybenzimidazoles have been obtained[61–65] from novel bis(*o*-nitroanilines) that are derivatives of chloral and DDT [66–68] by a route that had been proposed previously[57–60,69–71] and which involves the mild reaction between bis(*o*-nitroanilines) and aromatic dicarboxylic acid dichlorides in NMP followed by reduction/cyclisation of the poly(*o*-nitroamides):



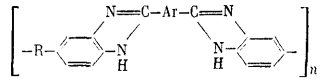
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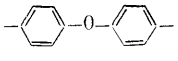
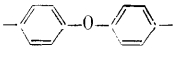
Some properties of the unsubstituted polybenzimidazoles synthesised, which are soluble in MP, DMF, DMAA, and DMSO, are given in Table 8.

It is evident from the properties listed that the majority of the unsubstituted polybenzimidazoles are non-softening polymers with relatively low values of the temperatures of loss of 10% of initial

weight (T_{10}) during differential thermogravimetric analysis (air, ΔT = 5 °C min^{-1}). The unusual series of thermal stability of the polybenzimidazoles in relation to the dicarboxylic acid residue may be due to incomplete reduction of the nitro groups and the subsequent ring-closure reactions of (*o*-nitro)amide residues at high temperatures (see below).

Table 8. Some properties of unsubstituted polybenzimidazoles with the general formula[61,65]



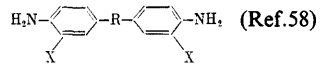
—R—	—Ar—	η_{int} in NMP, dl g^{-1}	T_{soft}, °C	T_{10}, °C
—C(=O)—		0.44	–	360
—C(=O)—		0.30	–	350
—C(=O)—		0.28	300	410
—C(=CCl$_2$)—		0.28	–	380
—C(=CCl$_2$)—		0.46	–	360
—C(=CCl$_2$)—		0.30	–	410
		0.28*	–	475
		0.10*	–	425

*Viscosities determined in *m*-cresol.

Another characteristic feature of unsubstituted polybenzimidazoles synthesised by means of reductive polyheterocyclisation is provided by their low viscosities and hence molecular-weight characteristics, caused by the lower basicity (Table 9) and correspondingly lower nucleophilicity of bis(*o*-nitroanilines) compared to unsubstituted diamines containing the same "bridging" groups.

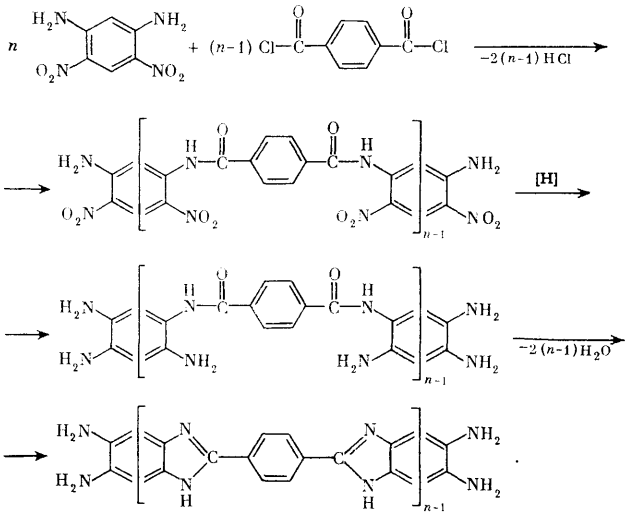
The outcome of this situation is evident in the use of reductive polyheterocyclisation processes for the synthesis of oligomeric benzimidazoles rather than polymeric forms,[72] for which it is most suitable to carry out polycondensation with a certain excess of bis(*o*-nitroanilines).

Table 9. Ionisation constants of bis(*o*-nitroanilines) and unsubstituted diamines with a corresponding structure, having the general formula

 (Ref.58)

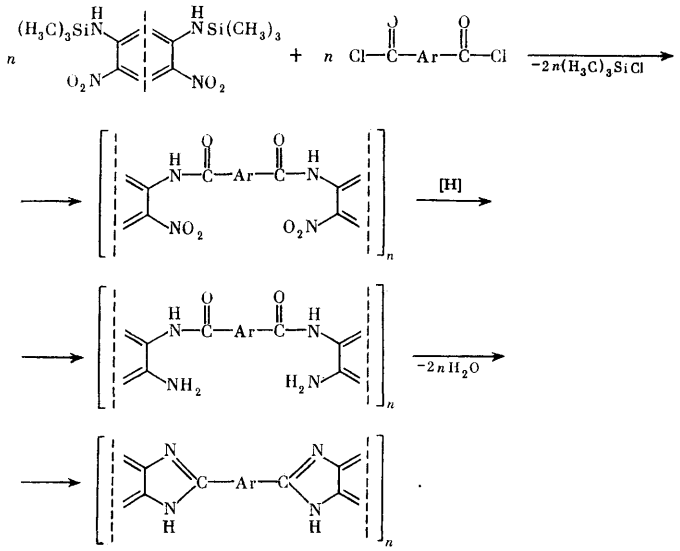
—R—	—X	pK_{a1} (DMF)	pK_{a2} (DMF)	ΔpK_a
—C(=CCl$_2$)—	–H	3.65	3.20	0.45
—C(=CCl$_2$)—	–NO$_2$	2.75	2.50	0.25
—C(=O)—	–H	3.02	2.72	0.30
—C(=O)—	–NO$_2$	2.75	2.45	0.30
	–H	2.95	2.62	0.33
	–NO$_2$	1.88	1.76	0.12

Such an approach is of particular interest in relation to the synthesis of rod-like oligobenzimidazoles starting from 1,3-dinitro-4,6-diaminobenzene and terephthalyl chloride:[72]

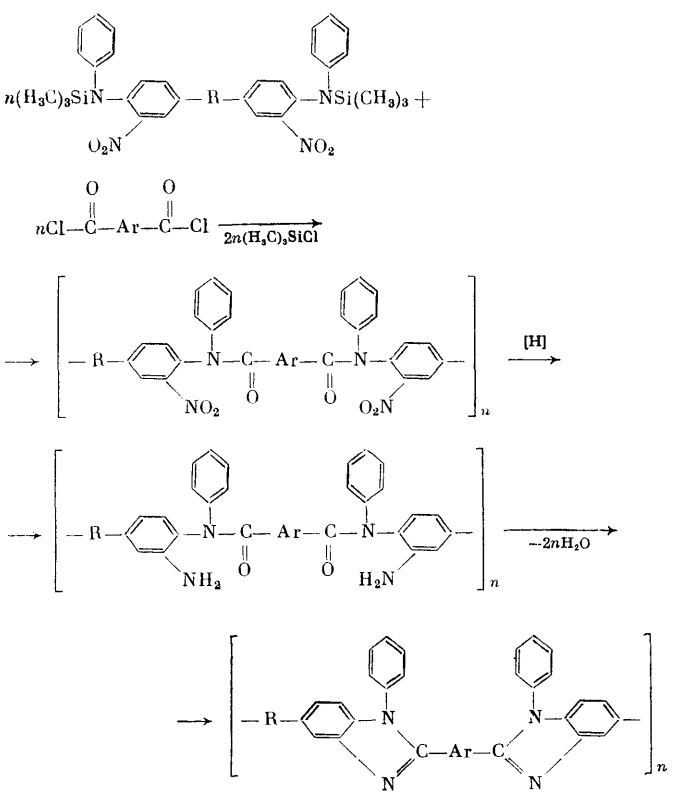


Rod-like oligobenzimidazoles containing *o*-phenylenediamine terminal groups can be used, according to Gordon et al.[73–76] to obtain molecular composites, which have stimulated considerable interest amongst research workers recently.[77–80]

An alternative approach to the use of bis(*o*-nitroanilines) to obtain benzimidazole-containing systems involves increasing the basicity of the amino groups of these monomers by trimethylsilylating them:[81,82]

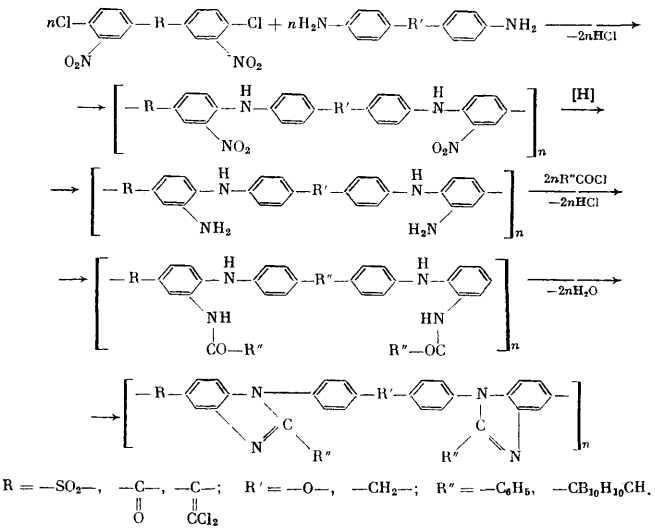


According to Rusanov and Tugushi,[72] a similar approach can yield relatively high-molecular-weight polybenzimidazoles containing phenyl substituents on the nitrogen atom in the benzimidazole rings, which are synthesised from very weakly basic bis(*o*-nitrodiphenylamines):



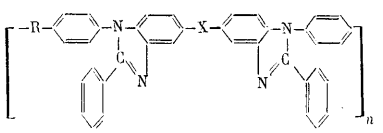
R = $-SO_2-$, $-\overset{\overset{O}{\|}}{C}-$, $-\overset{\overset{CCl_2}{\|}}{C}-$.

Novel poly(*C*-substituted) benzimidazoles[83–86] were obtained by means of modified reductive polyheterocyclisation processes. According to Rusanov et al.,[87,88] these involved the reaction of activated bis(*o*-nitrohalo)arylenes with aromatic diamines, reduction of the nitro groups in the resulting poly(*o*-nitro)imines to amino groups, acylation of the latter, and catalytic cyclisation of polyimines containing *o*-acylamine substituents:



R = $-SO_2-$, $-\overset{\overset{O}{\|}}{C}-$, $-\overset{\overset{CCl_2}{\|}}{C}-$; R′ = $-O-$, $-CH_2-$; R″ = $-C_6H_5$, $-CB_{10}H_{10}CH-$.

Table 10. Fundamental properties of poly(*C*-phenyl)benzimidazoles with the general formula[83–85]



—R—	—X—	η_{int}, dl g^{-1}	T_{soft},** °C	T_{10}^{*}, °C
$-\overset{\overset{CCl_2}{\|}}{C}-$	—O—	1.30	360	450
$-\overset{\overset{CCl_2}{\|}}{C}-$	$-CH_2-$	1.00	330	410
$-\overset{\overset{O}{\|}}{C}-$	—O—	1.50	310	510
$-\overset{\overset{O}{\|}}{C}-$	$-CH_2-$	1.20	280	470

* Determined from thermomechanical curves.
** Differential thermogravimetric analysis, air, ΔT = 4.5 °C min^{-1}.

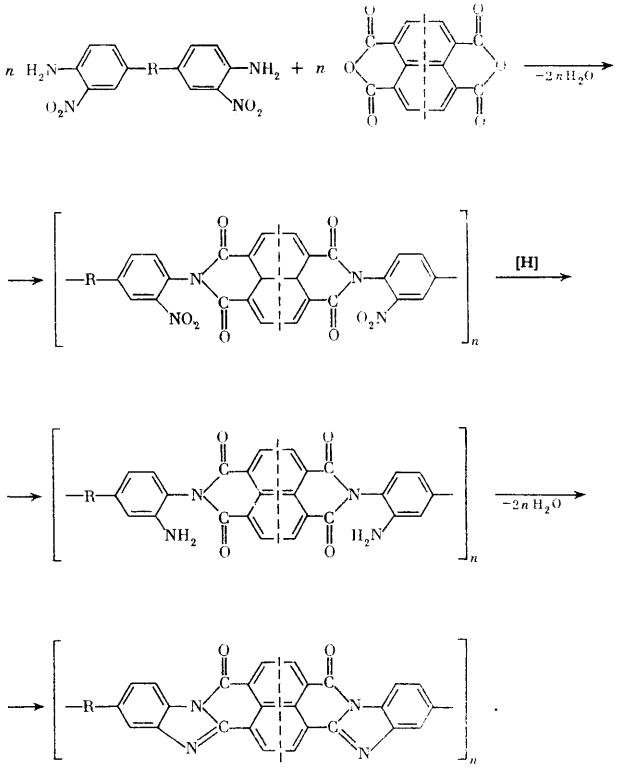
C-phenyl-substituted polybenzimidazoles that combine high viscosity and thermal properties with solubility in phenolic solvents, MP, and DMF have been obtained using 3,3′-dinitro-4,4′-dichloro-

benzophenone and 1,1-dichloro-2,2-bis(3-nitro-4-chlorophenyl)-ethylene,[83–85] which are derivatives of chloral and DDT,[66–68] as activated bis(*o*-nitrohalo)arylenes. Some properties of these polymers are given in Table 10.

C-Carborane-substituted polybenzimidazoles were obtained[86] by reaction of 3,3′-dinitro-4,4′-dichlorodiphenylsulphone with 4,4′-diaminodiphenyl oxide, reduction of the nitro groups in the resulting poly(*o*-nitro)imine to amino groups, acylation of the latter with *m*-carborane-1-carboxylic acid chloride, and catalytic cyclisation of the systems obtained to the required polybenzimidazoles. It is interesting to note that the carborane-containing polybenzimidazoles obtained in this manner are superior in terms of their viscosity and thermal properties as well as the strength of their films to poly(*C*-phenyl)benzimidazoles obtained from *m*-carborane-dicarboxylic acid dichloride.[86]

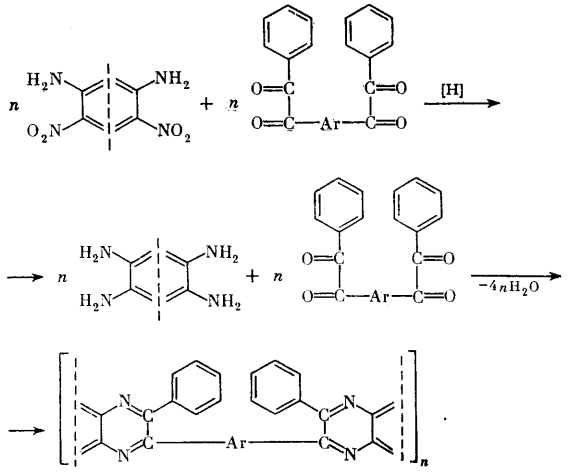
As well as increasing the range of polybenzimdazoles obtained by means of reductive polyheterocyclisation, the attention of research workers in recent years has been focussed on the possibility of using this process to obtain classes of polyheteroarylenes such as polynaphthoylenebenzimidazoles and polyphenylquinoxalines.

The synthesis of polynaphthoylenebenzimidazoles was carried out in accordance with following scheme:[89]



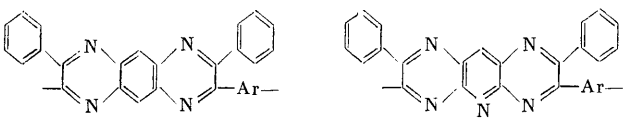
An advantage of this approach to the synthesis of polynaphthoylenebenzimidazoles, in addition to those already known,[57–60] is the possibility of decreasing the number of isomers of the required structures by means of acylation reactions exclusively on the amino groups at the early stages of the reactions. In turn, a decrease in the number of isomers opens up a route to the creation of more regularly formed systems, which have correspondingly higher thermal properties.

The synthesis of polyphenylquinoxalines was carried out in accordance with the following scheme:[90]



This process differs from the previously developed reductive polyheterocyclisation reactions[57–60] in that the stage involving the formation of linear nitro-containing polymers is absent — bis(*o*-nitroanilines) do not react with bis(α-diketones) even under very severe conditions. In actual fact this process essentially involves the reduction of bis(*o*-nitroanilines) to bis(*o*-phenylenediamines) in the presence of bis(α-diketones) and, owing to the specific nature of the reactions leading to polyphenylquinoxalines,[91–94] a polycondensation reaction *in situ* of the resulting bis(*o*-phenylenediamines).

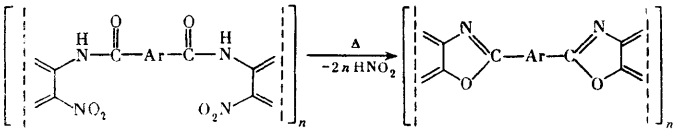
The scheme put forward is attractive as it opens up the possibility of obtaining polyphenylquinoxalines with high heat stability (T_{soft} ~ 400 °C) containing condensed heterocycles starting from 1,3-dinitro-4,6-diaminobenzene instead of the unstable 1,2,4,5-tetraaminobenzene and 3,5-dinitro-2,6-diaminopyridine instead of the unstable 2,3,5,6-tetraaminopyridine.

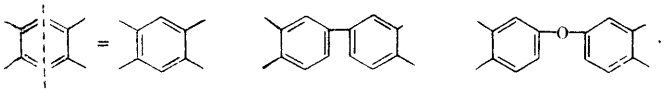


It was reported by Korshak et al.[90] that when processes involving the catalytic reduction with hydrogen over Raney nickel or the reduction with activated iron mixed with HCl were used, only low-molecular-weight polymers ($\eta_{init} \leqslant 0.2$ dl g^{-1}) were obtained. It would appear that under these conditions either the selectivity of reduction is disrupted, i.e., not only is bis(*o*-nitroaniline) reduced but also the bis(α-diketone) is partially reduced, or the reduction of bis(*o*-nitroaniline) to bis(*o*-phenylenediamine) is not quantitative. Further research into the optimum process conditions will most likely lead to considerable progress in the synthesis of polyphenylquinoxalines.

IV. Thermal polyheterocyclisation reactions of poly(*o*-nitroamides)

Poly(*o*-nitroamides) obtained in accordance with Scheme (2) can, according to Kim and Pearce,[95] be regarded as prepolymers for the preparation of polybenzoxazoles:





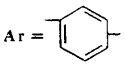
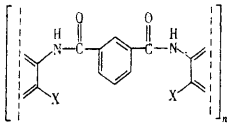
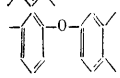
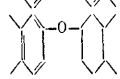
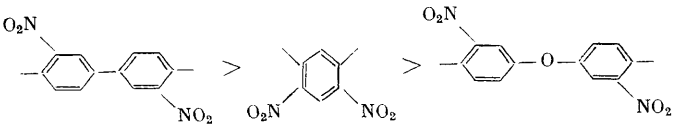


Table 11. Thermal stability and yield of carbon of aromatic polyamides with the general formula:[95]

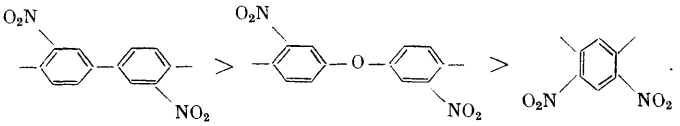


	–X	T_{sd}, °C	$T_{mr}I$, °C	$T_{mr}II$, °C	Yield of carbon, %
	–H	425	460	–	42
	$-NO_2$	336	351 373	650	35
	–H	440	470	588	37
	$-NO_2$	291	325 390	592	45
	–H	505	542	–	38
	$-NO_2$	386	405	660	52

The series of thermal stability of poly(*o*-nitroamides) in relation to the bis(*o*-nitroaniline) residue takes the following form:



while the yield of carbon is given by the series:



The respective temperatures of start of degradation (T_{sd}), temperatures of maximum rate of weight loss (T_{mr}), and yields of carbon of poly(*o*-nitroamides) and unsaturated polyamides are given in Table 11.

An analysis of the data listed in Table 11 indicates that the temperatures of start of thermal degradation for poly(*o*-nitroamides) are lower than for unsubstituted polyamides in all cases. At the same time, the yield of carbon in the majority of cases is higher for poly(*o*-nitroamides), which confirms that reactions leading to more stable systems occur in poly(*o*-nitroamides).

The occurence of two maxima for the rate of weight loss is a conspicuous feature. In the opinion of Kim and Pearce[95] it is due to the differing ease of elimination of the first and second nitro groups from each fundamental unit of the polymer.

The formation of polybenzoxazoles from poly(*o*-nitroamides) occurs more readily than from the corresponding poly(*o*-chlorophenyl)amides[96–98] and may be regarded as a promising method for the synthesis of these polyheteroarylenes.

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