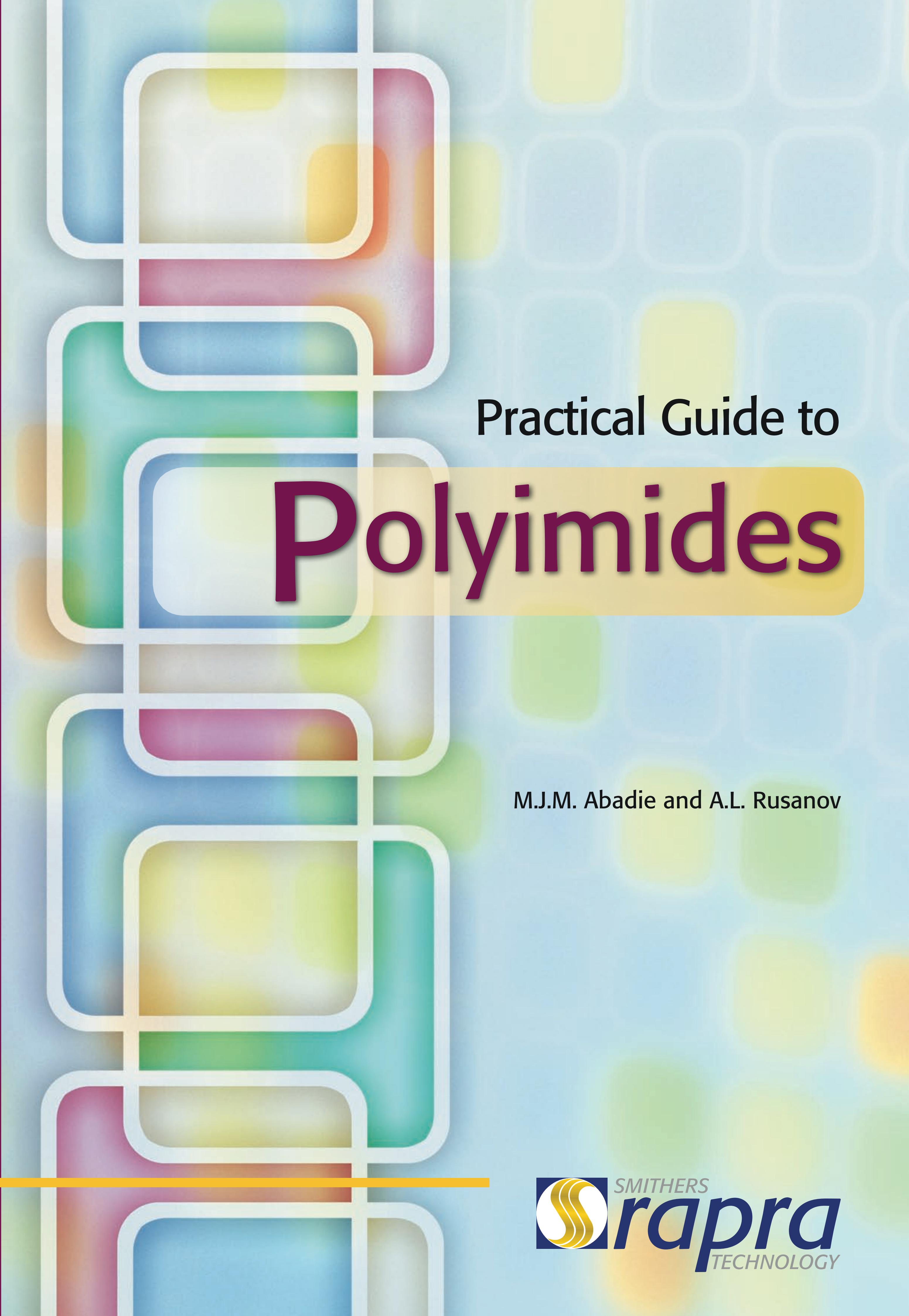

Practical Guide to Polyimides

M.J.M. Abadie and A.L. Rusanov

SMITHERS RAPRA TECHNOLOGY

Practical Guide to Polyimides

Processable Aromatic Polyimides Based on Non-traditional Raw Materials

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First Published in 2007 by

Smithers Rapra Technology Limited
Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK

A catalogue record for this book is available from the British Library.

ISBN: 978-1-84735-058-9

Typeset by Smithers Rapra Technology Limited
Cover printed by Livesey Limited, Shrewsbury, UK
Printed and bound by Smithers Rapra Technology Limited

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Preface

Because of their unique and highly desirable properties, polyimides are used for many applications ranging from aerospace to microelectronics, to optics, to membranes, to composites. Currently there is tremendous activity in the realm of polyimides, and all signals indicate that this high tempo will continue unabated for some time to come. Moreover, as new and improved variants of these materials become available, new applications will emerge.

Of especially great interest are processable polyimides e.g., polymers soluble in organic solvents or demonstrating large ‘windows’ between their softening and degradation temperatures. Usually such polyimides are based on expensive and not easily available monomers such as systems containing 1,1,1,3,3,3-hexafluoroisopropylidene groups.

Recently a large variety of inexpensive and available monomers were developed based on chloral, 1,1,1-trichloro-2,2-di-(*p*-chlorophenyl)ethane (DDT) and 2,4,6-trinitrotoluene (TNT); all of these monomers have been used for the preparation of processable polyimides.

It is interesting to note that utilisation of DDT and TNT – toxic and explosive materials – seems to be very important for environment. Part of this work was done in the frames of NATO ‘Science for Peace’ Program.

We sincerely and fervently hope this publication will be useful to anyone interested or involved in this fascinating and technologically important class of materials.

This book is the result of a strong, effective and efficient scientific collaboration developed for more than twenty years between France and Russia.

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1

Introduction

Access to raw materials for monomers and polymers is clearly important for the rapid and successful development of high molecular weight compounds. This is particularly true of speciality polymers including heat- and fire-resistant polymers, mainly polyimides, whose production has been actively pursued during the last four decades [1–10].

One raw material potentially useful for the synthesis of monomers is chloral, whose annual output in the USA in 1971 amounted to 50,000 tonnes [11-13]. Chloral is a starting material used for the manufacture of drugs, highly purified chloroform, herbicides (sodium trichloroacetate, dichloral urea) and pesticides (such as chlorophos) including dichlorodiphenyl-trichloroethane (DDT), a widely utilised insecticide [14], whose world output in 1956 amounted to 80,000 tonnes [15]. Some 4.5 million tonnes of DDT were consumed between 1942 and 1972 for pest control in agriculture [16]. The use of DDT during the long-term antimalaria campaign saved more than 1 billion people from malaria [17].

The human toxicity of DDT has been a subject of intense study during the last 20–25 years. This led the World Health Organisation to prohibit the use of DDT as an insecticide. The long-term use of DDT resulted in the development of resistance to the insecticide in many pests (over 200 species). As a result, most developed countries initiated programmes for the gradual replacement of DDT. The manufacture of DDT, and consequently that of chloral, has been in gradual decline since 1963 [12, 13, 17].

At present DDT finds limited use only in certain developing countries since other insecticides are considerably more expensive [18], although some industrial countries, too, reportedly use it for the control of synanthropous insects [18, 19]. The existing manufacturing capacity for DDT and chloral remains quite high and so a search for alternative uses of these chemicals is worthwhile. One approach is to use these substances as starting materials for the manufacture of polymers with desired properties.

Another raw material potentially useful for the synthesis of condensation monomers is 2,4,6-trinitrotoluene (TNT) a well-known military explosive [20, 21]. Presently in a number of countries a large amount of ammunition liable to liquidation has been accumulated. Its major explosive component is TNT, and thus its utilisation has become a basic challenge [20, 21].

This book reviews some of the results of investigations of chemical conversions of chloral and TNT to new aromatic di(poly)amines and aromatic tetracarboxylic acid dianhydrides useful for the preparation of new polyimides combining good thermal, mechanical and electrical properties with improved processability.

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2

Chloral-Derived Monomers

Most of the syntheses for condensation monomers using chloral employ well-known reactions between chloral and aromatic hydrocarbons, alkylaromatic hydrocarbons or substituted aromatic hydrocarbons [1, 2]. These are then followed by subsequent transformations of the diaryltrichloroethanes thus obtained.

Chloral condensations with aromatic hydrocarbons (and related derivatives) give rise to diaryltrichloroethane compounds, and are brought about in the presence of acid catalysts, proceeding with the formation of carbinol intermediates (**Scheme 2.1**). Commonly used catalysts include concentrated H_2SO_4 and its monohydrate, HCl, HF, P_2O_5, Lewis acids and a series of other acid agents [1, 2].

Of numerous chloral condensations with aromatic hydrocarbons the most interesting for the synthesis of condensation monomers are the reactions with benzene [3], toluene [4], acenaphthene [5], phenol [6], anisol [7], acetanilide [8] and halobenzenes like chlorobenzene [9] and fluorobenzene [10]. In general terms, these reactions proceed according to **Scheme 2.2** and give the desired 1,1,1-trichloro-2,2-diarylethanes in high yields. Substituted benzenes show different reactivities which are primarily determined by orientation effects of the substituents [11].

Subsequent transformations of the 1,1,1-trichlorodiarylethanes into desired systems include:

(1) transformation of the central 1,1,1-trichloroethane group,

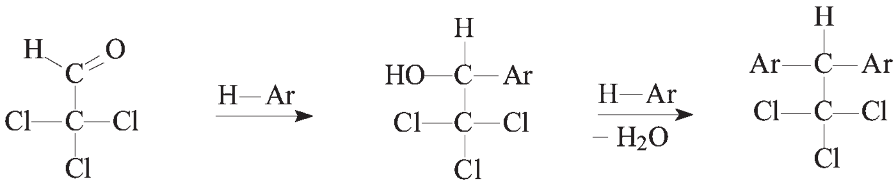
(2) hydrogen substitution in the aromatic nuclei of the diaryltrichloroethane moiety, and

(3) transformation of functional groups introduced into the aromatic nuclei of the diaryltrichloroethane portion of the molecule.

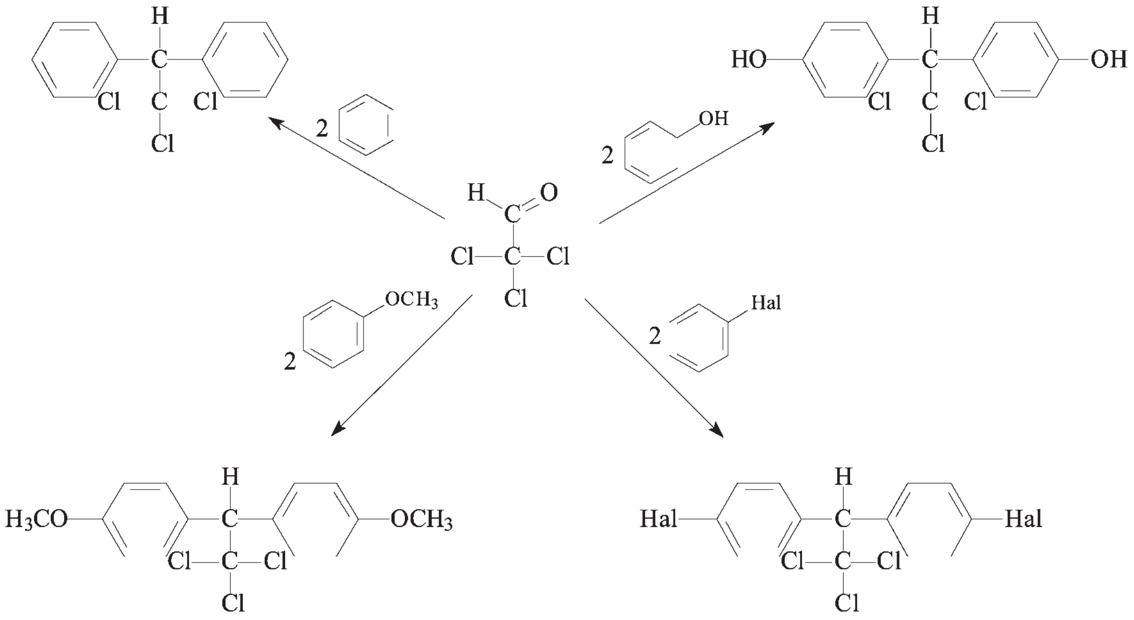
The central trichloroethane group may be transformed into 1,1-dichloroethylene and carbonyl groups:

Of the numerous reactions the most thoroughly studied is dehydrochlorination [12] (**Scheme 2.3**). Common dehydrochlorinating agents include alcoholic alkali [4], liquid ammonia [13], methylamine [13], LiCl in dimethylformamide (DMF) [14], MOH or M_2CO_3 (M = K or Na) in DMF [15] and tertiary and heterocyclic amines [16]. Moreover, some diaryltrichloroethanes, such as dichlordiphenyltrichloroethane (DDT), may undergo thermal dehydrochlorination near 170–200 °C.

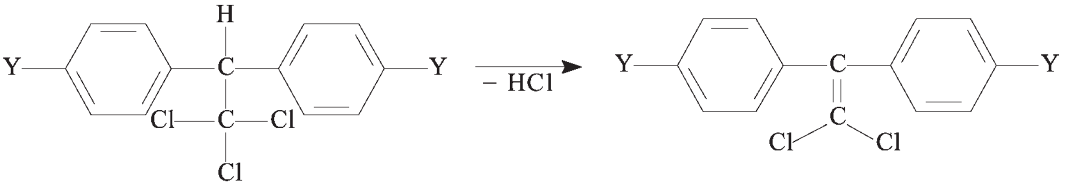
A widely known reaction involving 1,1-dichloroethylene groups is their oxidation into carbonyls [17, 18] (**Scheme 2.4**). The most common oxidants are CrO_3, AcOH, HNO_3, AcOH and $K_2Cr_2O_7$/AcOH.



Scheme 2.1

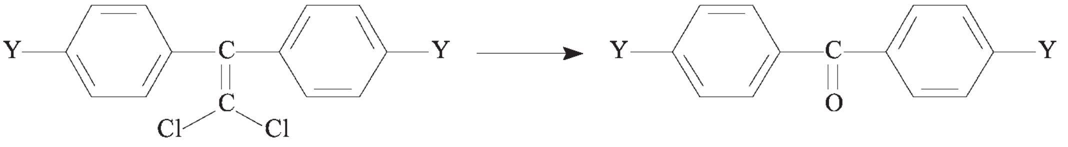


Scheme 2.2



Y = —H , —Cl , —OCH$_3$, —CH$_3$, —OH , —NH$_2$

Scheme 2.3



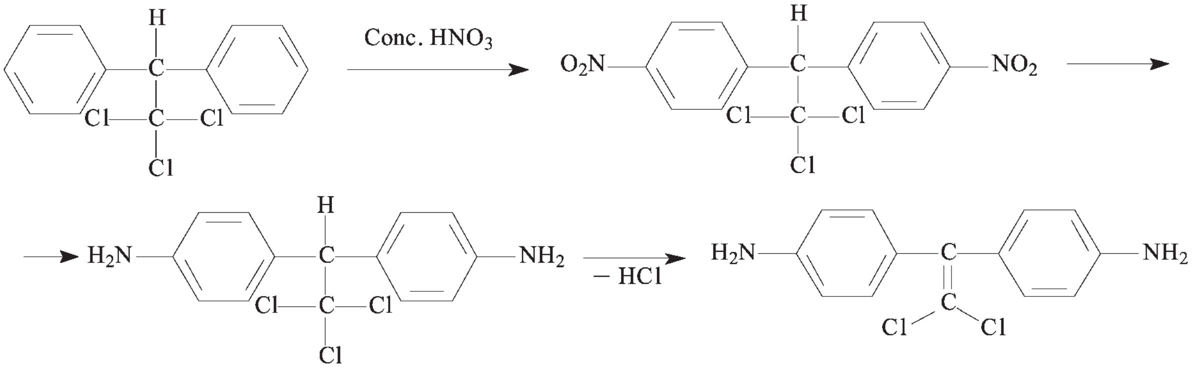
Y = —H , —Cl

Scheme 2.4

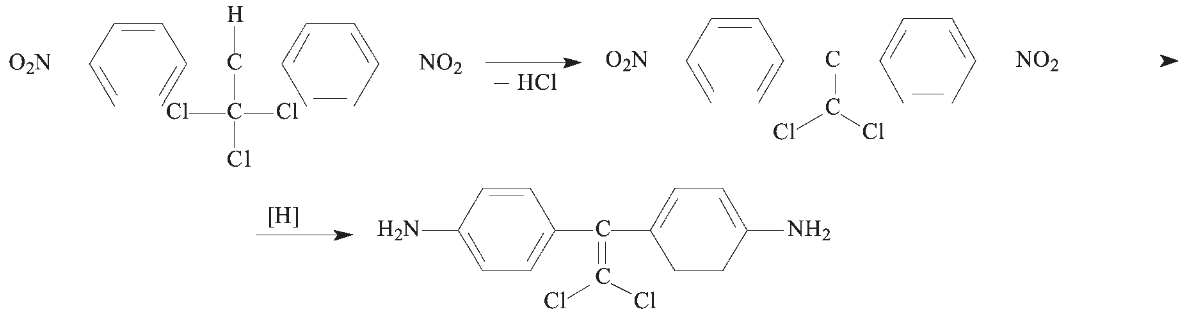
Of the aromatic substitution reactions, the most widely employed is nitration [19–22].

The reactions mentioned previously have been used for the preparation of different diamines and tetramines useful for polyimide synthesis.

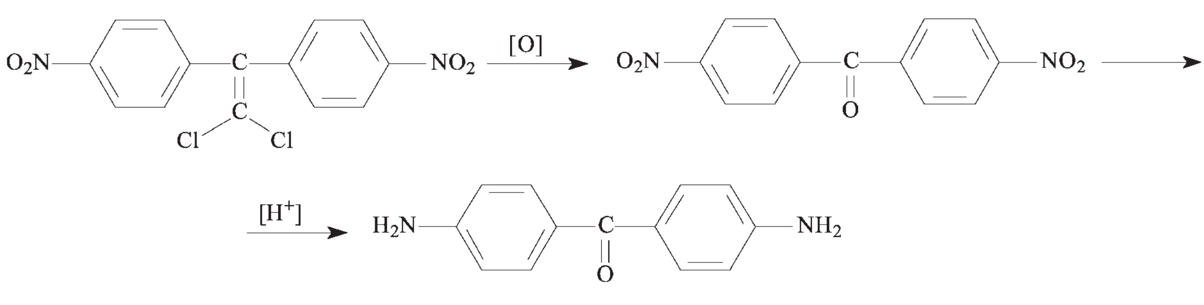
Nitration of 1,1,1-trichloro-2,2-diphenylethane [19] followed by reduction of the 1,1,1-trichloro-2,2-di-(*p*-nitrophenyl)-ethane thus formed [19] leads to the formation of 1,1,1-trichloro-2,2-di-(*p*-aminophenyl)-ethane, which can be dehydrochlorinated with the formation of 1,1,1-trichloro-2,2-di-(*p*-nitrophenyl)-ethylene [20] (**Scheme 2.5**). The same diamine can be prepared using dehydrohalogenation of 1,1,1-trichloro-2,2-di-(*p*-nitrophenyl)-ethane followed by hydrogenation of the 1,1,1-trichloro-2,2-di-(*p*-nitrophenyl)-ethylene thus formed [19] (**Scheme 2.6**). Oxidation of 1,1,1-trichloro-2,2-di-(*p*-nitrophenyl)-ethylene leads to the formation of 4,4′-dinitrobenzophenone [19], which can be reduced to 4,4′-diaminobenzophenone [19] (**Scheme 2.7**).



Scheme 2.5



Scheme 2.6



Scheme 2.7

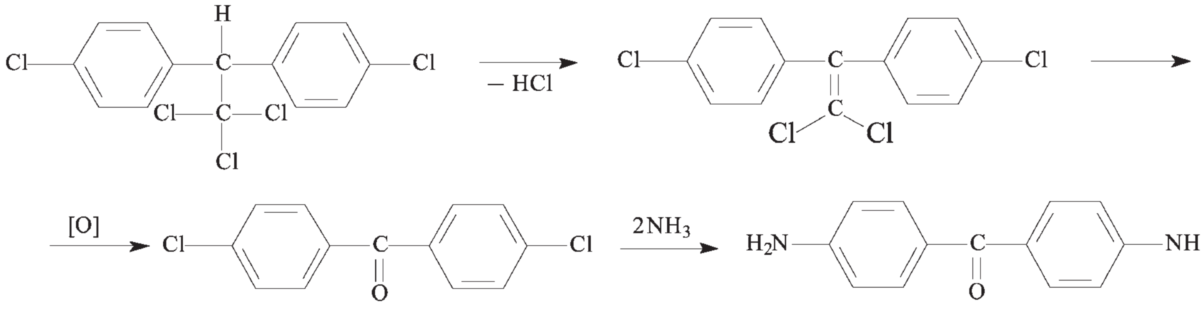
Several aromatic diamines were prepared using DDT as starting compound. 4,4′-Diaminobenzophenone was prepared using a three-stage process, including dehydrochlorination of DDT, oxidation of the 1,1-dichloro-2,2-di-(4-chlorophenyl)-ethylene thus formed and amination of 4,4′-dichlorobenzophenone [20, 23] (**Scheme 2.8**).

Nitration of DDT and its dehydrochlorination product 1,1-dichloro-2,2-di-(4-chlorophenyl)-ethylene led to the formation of bis(3-nitro-4-chlorophenylene) compounds containing 1,1,1-trichloroethane and carbonyl bridging groups [19, 20]. These compounds were converted to the corresponding bis(3-amino-4-chlorophenylenes) 1,1-dichloro-bis-(3-amino-4-chlorophenyl)-ethylene and 3,3′-diamino-4,4′-dichlorobenzophenone in accordance with **Scheme 2.9** [5, 22, 24].

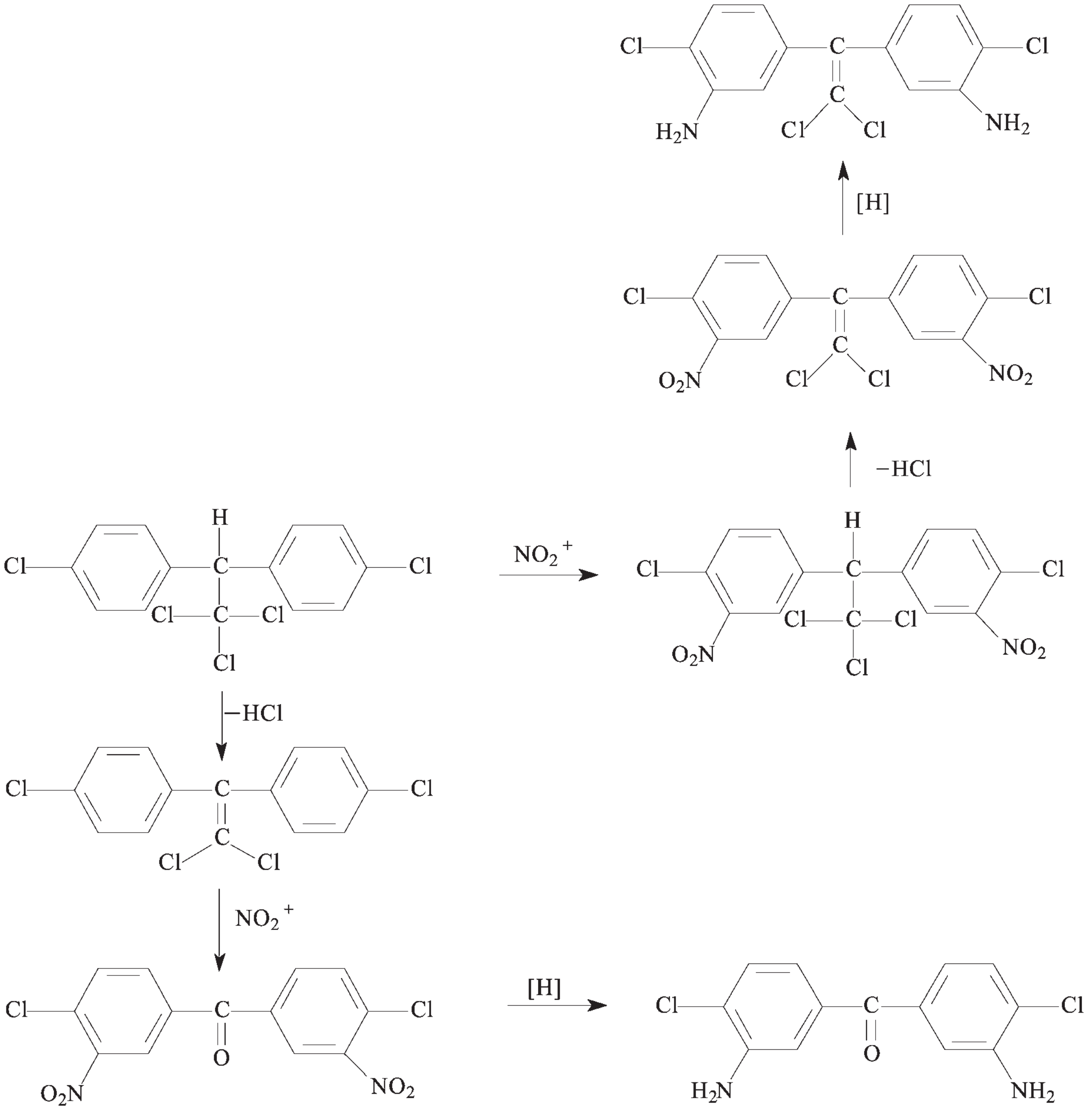
3,3′-Dinitro-4,4′-dichlorobenzophenone was used for the preparation of 3,3′-dinitro-4,4′-bis(dime thylamino)benzophenone. The latter was reduced using catalytic Pd/C and Pd/Al_2O_3 to give 3,3′-diamino-4,4′-dimethylaminobenzophenone [25] (**Scheme 2.10**).

Tetranuclear aromatic diamines were prepared on the basis of bis-phenols derived from 1,1,1-trichloro-2,2-di-(*p*-methoxyphenyl)-ethane under the action of pyridine hydrochloride [26, 27]. Interaction of the bis-phenols with two-fold molar amounts of *p*-nitrochlorobenzene led to the formation of 4,4′-bis(*p*-nitrophenoxy)-arylenes, which were reduced to the corresponding 4,4′-bis(*p*-aminophenoxy)-arylenes [28] (**Scheme 2.11**). Similar compounds containing two additional amino groups were prepared by the interaction of 3,3′-dinitro-4,4′-dichlorobenzophenone with two-fold molar amounts of potassium *p*-nitrophenolate [29] followed by reduction of the tetranitro compounds thus formed [29] (**Scheme 2.12**).

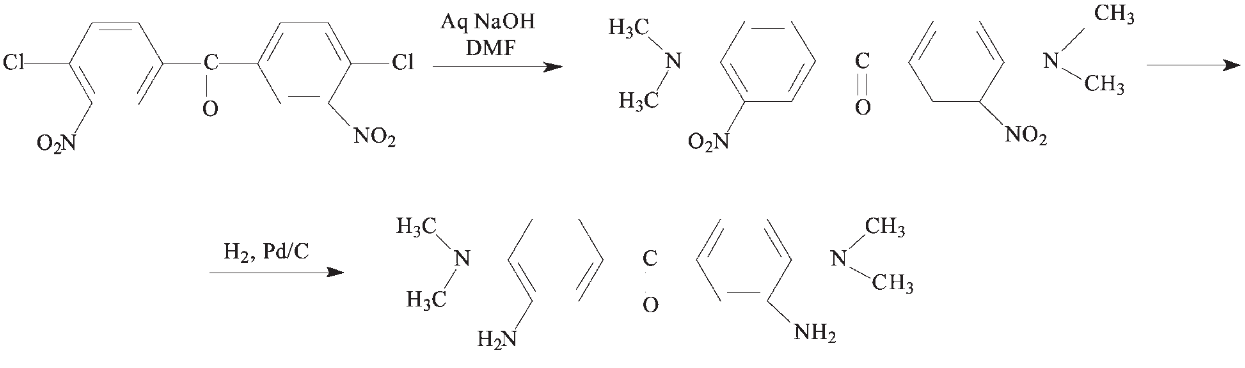
Along with new aromatic diamines and tetramines based on chloral and its derivatives, new aromatic tetracarboxylic acid dianhydrides were developed. These products were prepared by the interaction of bis-phenols – chloral derivatives – with two-fold molar amounts of nitrophthalimides followed by transformation of bis-phthalimides, containing two ether bonds, into the corresponding aromatic tetracarboxylic acid dianhydrides [30] (**Scheme 2.13**).



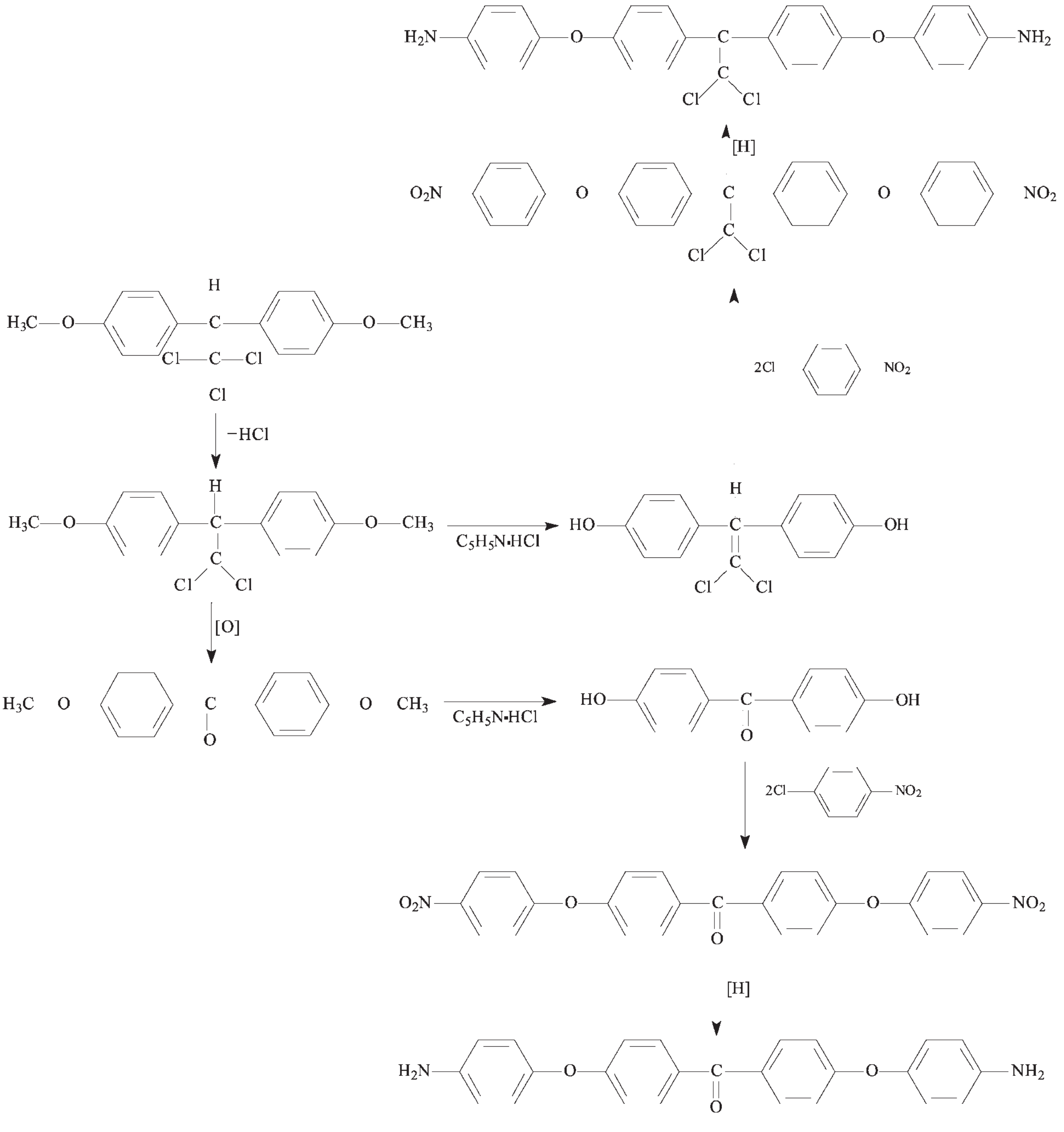
Scheme 2.8



Scheme 2.9

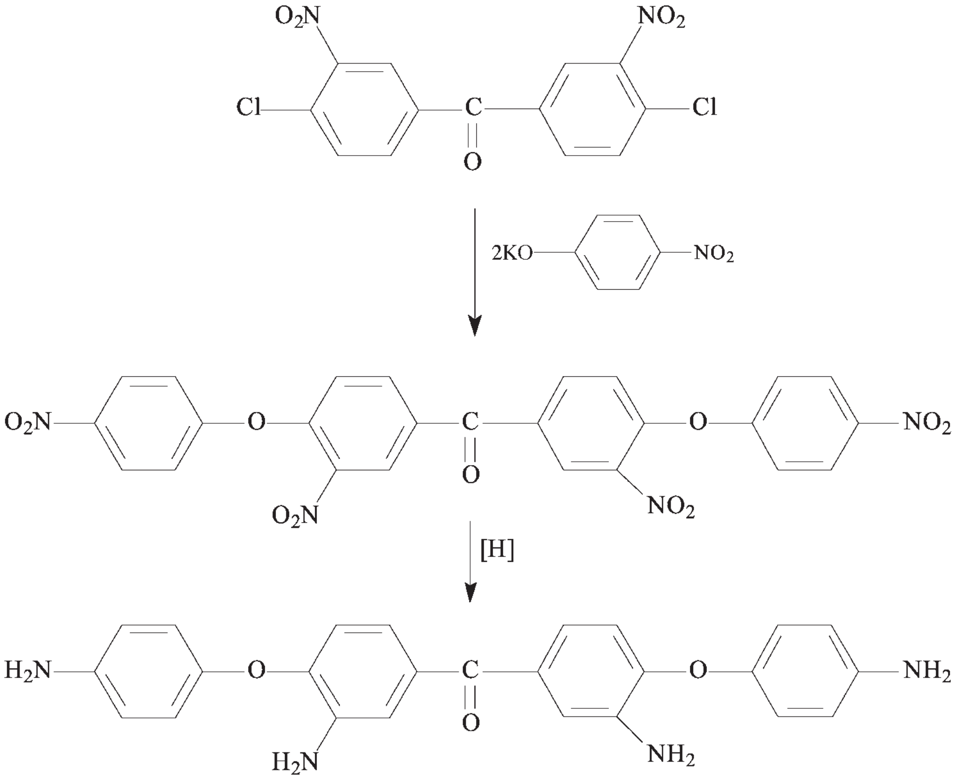


Scheme 2.10

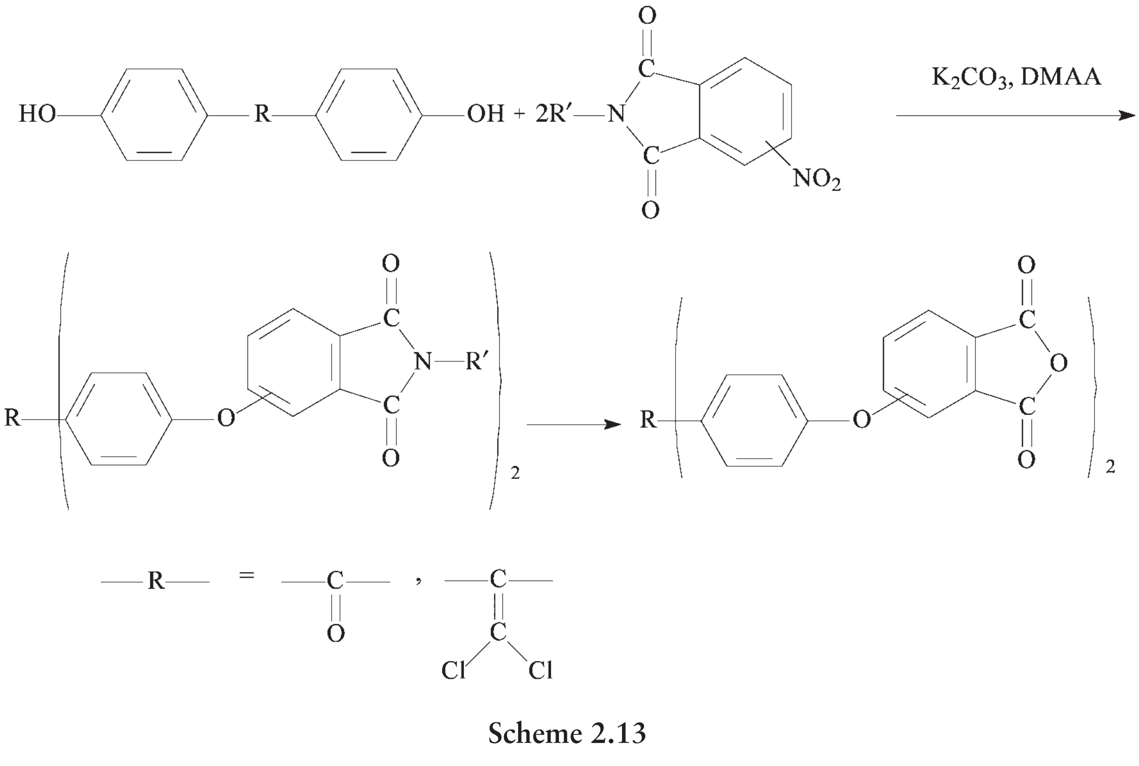


H$_2$N
O
C
C
Cl
Cl
O
NH$_2$
[H]
O$_2$N
NO$_2$
2Cl
H
H$_3$C—O
O—CH$_3$
Cl—C—Cl
−HCl
C$_5$H$_5$N•HCl
HO
OH
[O]
H$_3$C O
O CH$_3$

Scheme 2.11



Scheme 2.12



Scheme 2.13

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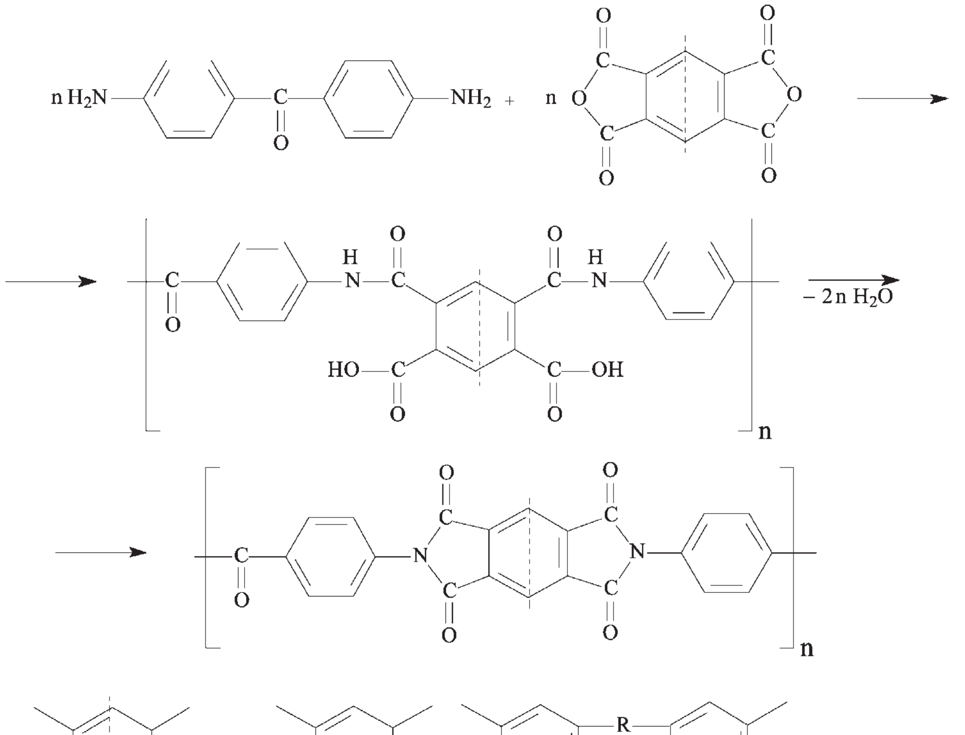
3 Polyimides Based on Chloral Derivatives

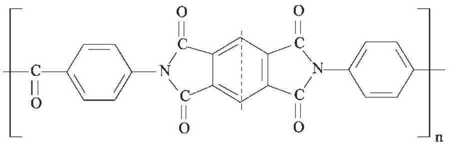
Considerable research effort has been devoted in recent years to the use of chloral derivatives for the synthesis of linear heterocyclic polymers. Of these, the most common are aromatic polyimides [1–12]. Many of these polymers have been synthesised from compounds like 4,4′-diaminobenzophenone, and other diamines, which, as demonstrated in the previous chapter, can be obtained from chloral. Polyimides prepared from these diamines were largely synthesised by the conventional two-step procedure [11, 12] involving mild reaction of the diamines with the bis(phthalic)anhydrides, isolation of poly(*o*-carboxy)amide (PCA) prepolymers, and then processing into products followed by thermal or chemical imidisation [13–16] (**Scheme 3.1**). Some properties of polyimides prepared from 4,4′-diaminobenzophenone are provided in **Table 3.1**.

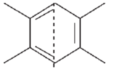
As can be seen from **Table 3.1**, polyimides based on 4,4′-diaminobenzophenone and common dianhydrides of tetracarboxylic acids (those of pyromellitic, diphenyloxide-3,3′,4,4′-tetracarboxylic and benzophenone-3,3′,4,4′-tetracarboxylic acids) possess good thermal properties. However, when in their cyclised forms they are practically insoluble in organic solvents, which restricts the possibility of their investigation, processing and use.



Scheme 3.1

Table 3.1. Some properties of polyimides of the general formula:



	T_{soft}, °C	$T_{10\%}$, °C	Film properties at 25 °C	
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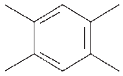
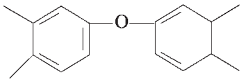
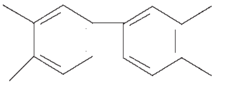
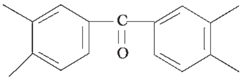
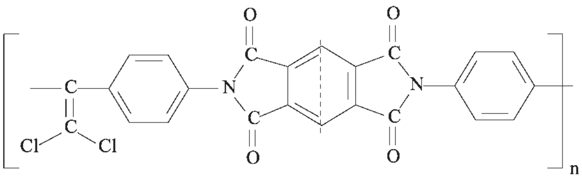
	—	520	1250	20
	290	480	1410	16
	307	490	1240	6
	290	460	1500	14

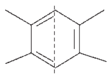
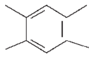
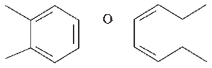
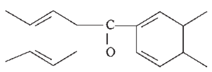
To improve the solubility of polyimides, Korshak and co-workers used 1,1-dichloro-2,2-bis(4-aminophenyl)-ethylene as the starting nucleophile [17] (**Scheme 3.2**). The resulting polymers turned out to be of relatively high molecular weight (η_{red} = 1.2–1.4 dl/g), heat resistant (T_{soft} > 270 °C) and fire resistant (oxygen index (OI) = 36–39) (**Table 3.2**). Polypyromellitimide was soluble in H_2SO_4 only, but polyimides based on the dianhydrides of benzophenone-3,3′,4,4′-tetracarboxylic acid and diphenyloxide-3,3′,4,4′-tetracarboxylic acid were also soluble in *m*-cresol and a trichloroethane (TCE)/phenol (3:1) mixture. Diphenyloxide-3,3′,4,4′-tetracarboxylic acid was soluble even in *N*-methyl-2-pyrrolidone (NMP) (**Scheme 3.2**).

A significant gain in polymer solubility was attained by employing diamines containing chlorine atoms in the *o*-positions with respect to the amino groups. These were 3,3′-diamino-4,4′-dichlorobenzophenone and 1,1-dichloro-2,2-di(3-amino-4-aminophenyl)-ethylene [18–20] (**Scheme 3.3**).

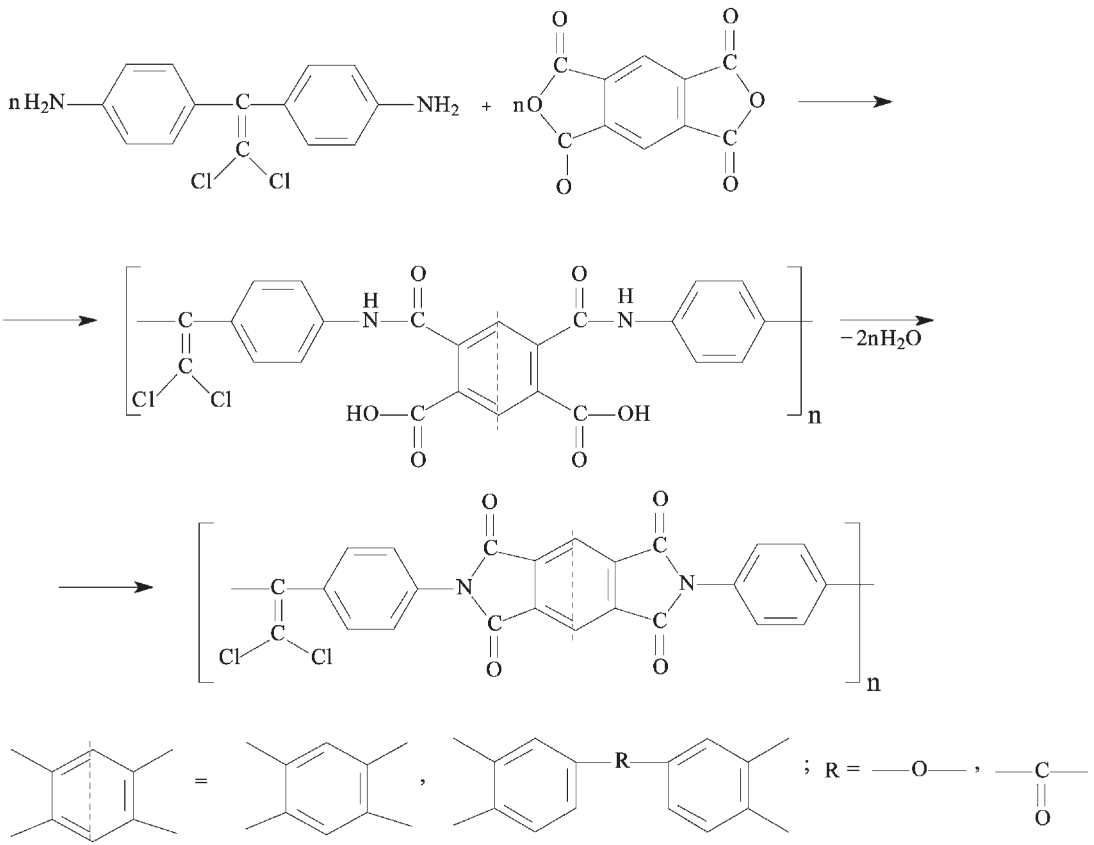
The synthesis of the poly-(*o*-chlorophenyl)-imides was accomplished in two steps involving low-temperature reaction between the diamines and bis(phthalic anhydrides) in NMP followed by catalytic imidisation of the PCA directly in the reaction solutions using the catalytic complex pyridine:acetic anhydride. The synthesis of polyimides from 1,1-dichloro-2,2-di-(3-amino-4-aminophenyl)-ethylene proceeded homogeneously throughout the course of the reaction, as did reactions of 3,3′-diamino-4,4′-dichlorobenzophenone with the dianhydride of diphenyloxide-3,3′,4,4′-tetracarboxylic acid. As to reactions of 3,3′-diamino-4,4′-dichlorobenzophenone with the dianhydrides of pyromellitic and diphenylsulfone-3,3′,4,4′-tetracarboxylic acids, these were homogeneous at the PCA formation step but heterogeneous at the polyimide formation step. Some properties of these polyimides are given in **Tables 3.3 and 3.4.**

Table 3.2. Properties of polyimides of the general formula

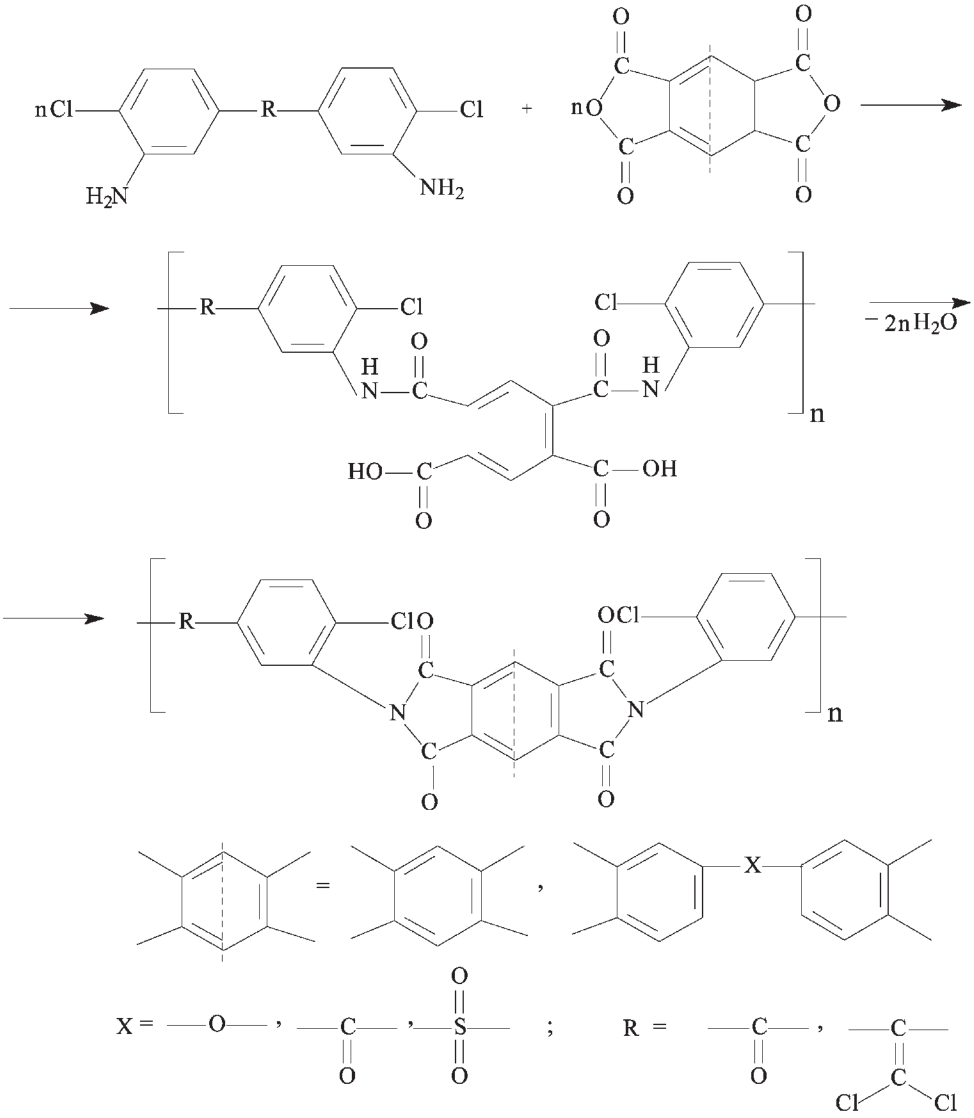


	η_{red} (H_2SO_4, 25 °C), cm^3/g	T_g, °C	$T_{10\%}$, °C	Solubility			LOI
				NMP	MC	TCE/ phenol (3:1)	
	130	—	360	–	–	–	39
	120	280	400	+	+	+	36
	140	270	390	–	+	+	38

NMP: N-methyl-2-pyrrolidone; MC: m-cresol; TCE: trichloroethane; LOI: Limiting oxygen index.

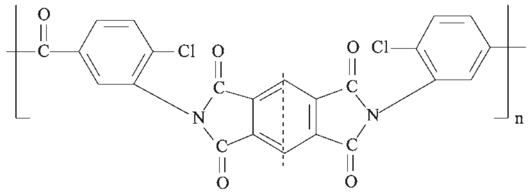


Scheme 3.2



Scheme 3.3

Table 3.3. Some properties of polyimides of the general formula:



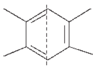
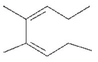
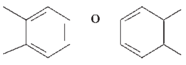
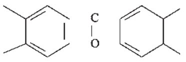
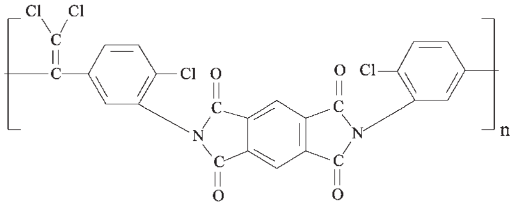
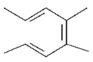
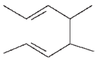
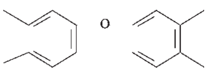
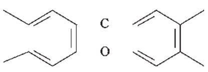
	η_{red} (NMP, 25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	Solubility			LOI
				NMP	MC	$CHCl_3$	
	0.25	—	450	+	–	–	512
	0.19	240	520	+	+	+	465
	0.28	245	520	+	+	–	47.4

Table 3.4. Some properties of polyimides of the general formula:

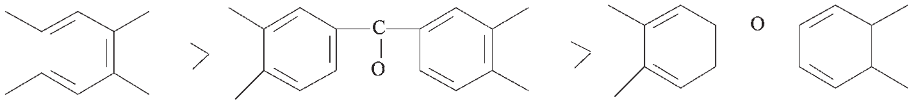


	η_{red} (NMP, 25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	Solubility			LOI
				NMP	MC	$CHCl_3$	
	0.28	310	400	+	+	+	62.5
	0.20	225	450	+	+	+	55.4
	0.31	232	440	+	+	+	53.2

The primary thermal characteristics of the polyimides were determined by dynamic thermogravimetric analysis (TGA) as well as thermomechanically. Although the data for dynamic TGA should be treated with some reservation, one can conclude the following:

- For thermal stability polypyromellitimides are somewhat inferior to polyimides based on the anhydrides of other aromatic tetracarboxylic acids. This is apparently due to the higher chlorine content per unit polymer weight in the former.

- The thermal stability of polyimides prepared from 1,1-dichloro-bis(3-amino-4-chlorophenyl)-ethylene is lower than that of polyimides prepared with other 3,3′-diamino-4,4′-dichloroarylenes, in particular 3,3′-diamino-4,4′-dichlorobenzophenone. This suggests a negative effect of 1,1-dichloroethylene groups on thermal stability in these polymers. Based on softening temperatures, the heat resistance of polyimides with different dianhydride residues decreases in the series:



The effect of aromatic diamine residues on the heat resistance of polyimides is less clear cut. It was only by comparing thermomechanical curves of polypyromellitimides obtained from 3,3-diamino-4,4′-dichlorodiphenylmethane, and 1,1-dichloro-2,2-di(3-amino-4-chlorophenyl)-ethylene that the system containing the 1,1-dichloroethylene group was found to be less heat resistant. With polyimides prepared from other dianhydrides this rule holds true as well but is less distinct.

The investigation of the fire resistance of these polyimides demonstrated that the introduction of chlorine into the aromatic nuclei produces a much greater increase in the OI than does the use of systems containing 1,1-dichloroethylene bridging groups. Although the highest fire resistance was observed for polyimides prepared from 1,1-dichloro-2,2-di(3-amino-4-chlorophenyl)-ethylene, those constructed from 3,3′-diamino-4,4′-dichlorobenzophenone and 3,3′-diamino-4,4′-dichlorodiphenylmethane possessed rather high oxygen indices as well.

Polyimides prepared from 3,3′-diamino-4,4′-dichloroarylenes, particularly those containing 1,1-dichloroethylene groups, are peculiar in that they are soluble in organic solvents. Polymers formed from 1,1-dichloro-2,2-di(3-amino-4-chlorophenyl)-ethylene are soluble in amide and phenolic solvents. They are even soluble in chloroform regardless of the dianhydride structure. The high solubility of these systems may be due to a combination of such factors as:

(1) asymmetrical structure of macromolecular chains containing *m*-phenylene fragments,

(2) the presence of bulky substituents like chlorine,

(3) the presence of groups like 1,1-dichloroethylene fragments, and

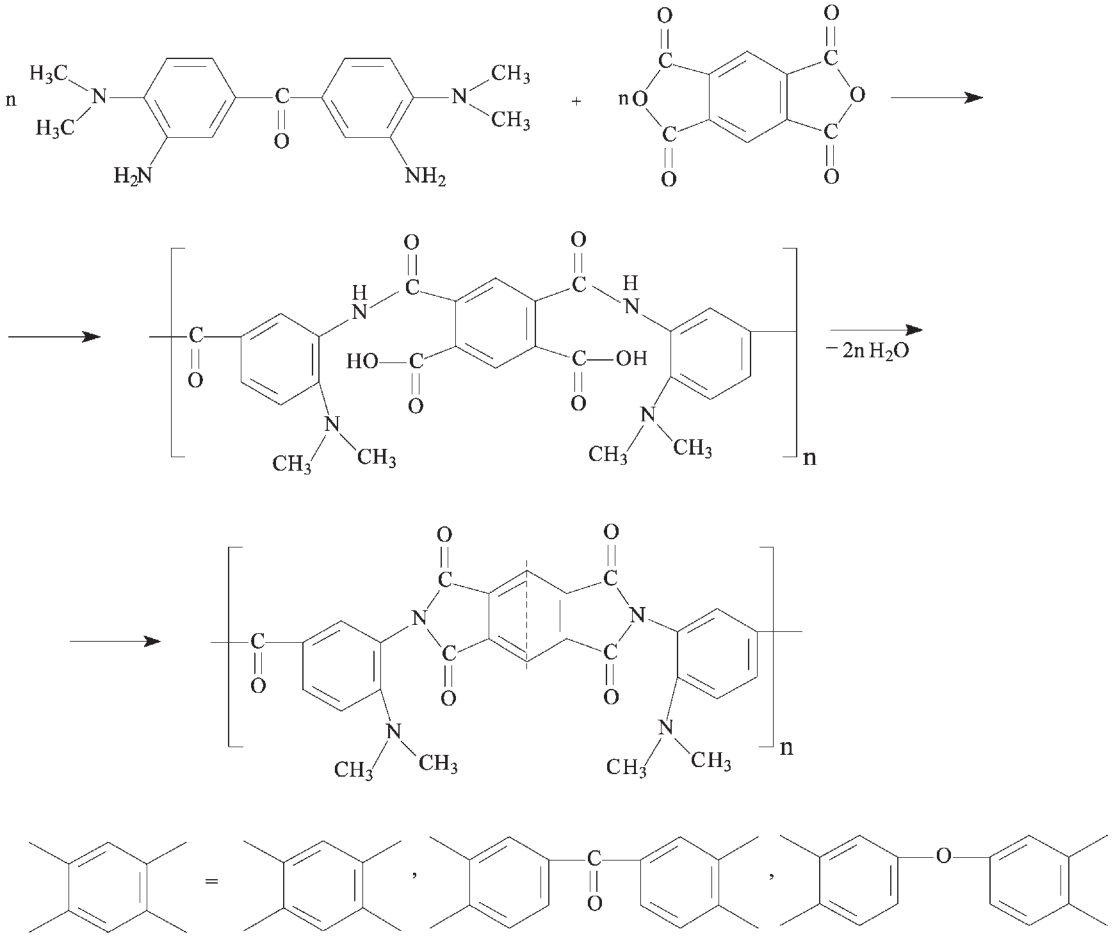
(4) mild conditions for synthesis (catalytic polycyclodehydration) in which case side reactions, e.g., crosslinking, are essentially avoided.

On passing from polyimides constructed from 1,1-dichloro-2,2-di(*p*-aminophenyl)-ethylene to systems prepared from 3,3′-diamino-4,4′-dichlorobenzophenone and 3,3′-diamino-4,4′-dichlorodiphenylmethane, solubility somewhat decreases. The resulting polypyromellitimides are insoluble in phenolic solvents and chloroform, while they remain soluble in NMP.

Poly(*o*-chlorophenyl)imides described previously have a series of valuable properties. However, they possess rather poor low viscosities: η_{red} of their solutions amount to 0.2–0.3 dl/g. This appears to result from the poor nucleophilicity of the starting diamines which is due to: (1) the electron-withdrawing character of chlorine *ortho* to the amino groups; (2) electron-withdrawing character of the bridging carbonyl and dichloroethylene groups; and (3) shielding of the amino groups by the bulky chlorine in the *ortho* position.

Their poor viscosities and, consequently, low molecular weight characteristics make the synthesis of products with favourable strength and deformation properties problematic.

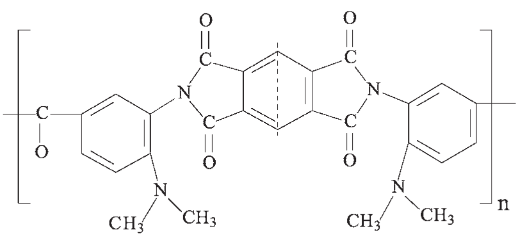
Polyimides with better viscosity characteristics have been obtained from 3,3′-diamino-4,4′-bis(dimethylamino)-benzophenone and different aromatic tetracarboxylic acid dianhydrides [21] (**Scheme 3.4**).

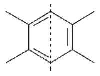
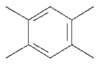
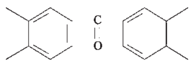
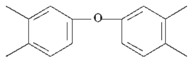


Scheme 3.4

Reactions of 3,3′-diamino-4,4′-bis(dimethylamino)-benzophenone with the dianhydrides of aromatic tetracarboxylic acids (pyromellitic, benzophenone-3,3′,4,4′-tetracarboxylic and diphenyloxide-3,3′,4,4′-tetracarboxylic acids) were carried out using a two-stage process including room temperature reaction of starting monomers in NMP, formation of PCA and subsequent cyclodehydration of the

Table 3.5. Some properties of polyimides of the general formula:



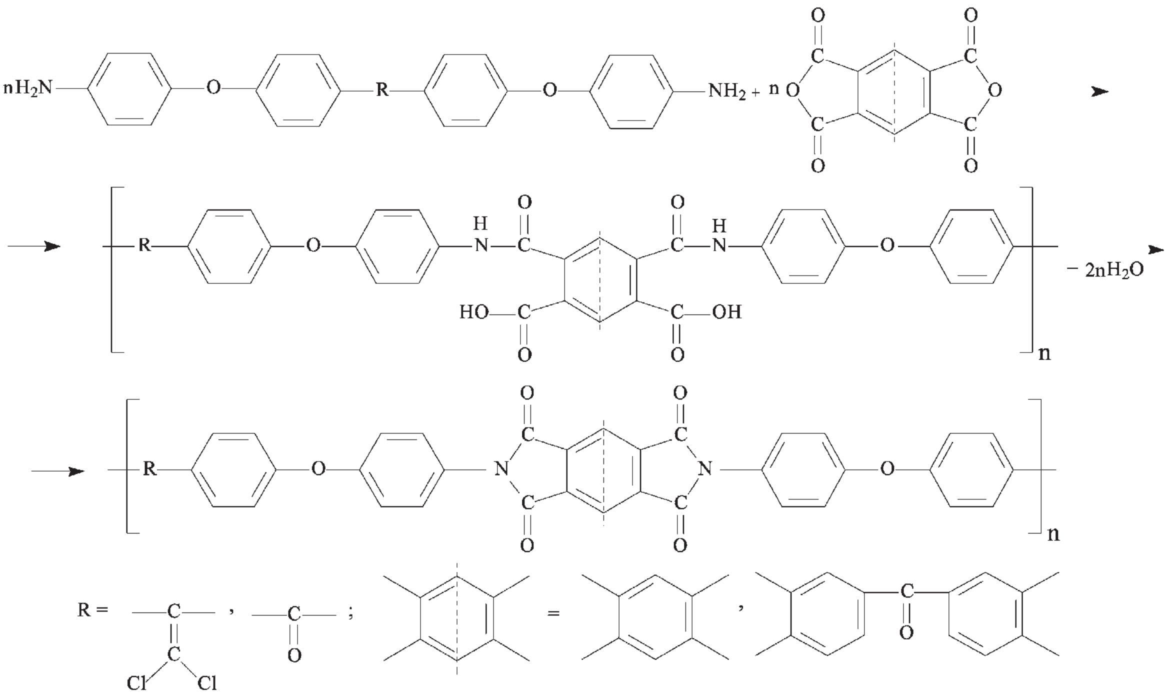
	η_{red} (NMP, 25 °C), dl/g	T_g, °C	Weight loss temperature (TGA, air), °C			
			5%	10%	20%	50%
	0.56	—	288	324	390	492
	0.52	280	298	341	428	512
	0.48	270	279	331	419	521

latter in refluxing solutions using different catalysts, e.g., complex acetic acid anhydride–pyridine, acetic acid anhydride without pyridine and H_3PO_4. In all cases, polyimide formation proceeded homogeneously and led to polymers having comparable viscosities. The acetic acid anhydride–pyridine complex is a well-known imidisation catalyst; successful imidisation catalysis using acetic anhydride without pyridine may be attributed to the autocatalytic action of dimethylamine side groups. All polyimides are soluble in aprotic dipolar solvents (NMP, DMA, dimethylformamide (DMF), dimethylsulfoxide (DMSO)) The good solubility of the polyimides is due to the presence of *m*-phenylene units and dimethylamine bulky polar substituents along the polymer chains. General properties of dimethylamine-substituted polyimides are given in **Table 3.5**.

Even higher viscosities are typical for polyimides based on tetranuclear diamines, e.g., 4,4′-di-(*p*-aminophenoxy)-benzophenone and 1,1-dichloro-2,2 di(*p*-aminophenoxy)-ethylene. Polyimides were prepared according to the method for the synthesis of PCA by low-temperature polycondensation in NMP. Polyimides were prepared by catalytic cyclodehydration of PCA directly in the reaction solutions using the catalytic system pyridine–acetic acid anhydride (1:1) [22] (**Scheme 3.5**).

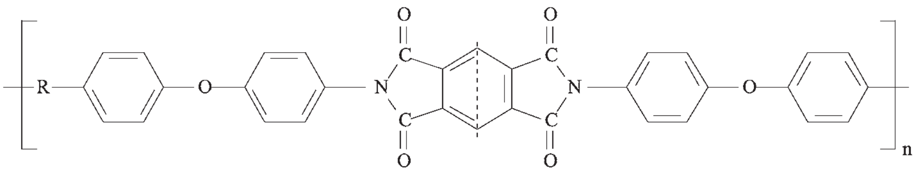
Imidisation of PCA based on 4,4′-di-(*p*-aminophenoxy)-benzophenone was accompanied by the precipitation of the polymers from the reaction solutions, which is partially due to crystallinity in the polyimides formed. This appears to hinder the solubility of the polymers in amide and phenolic solvents. Polyimides based on 1,1-dichloro-2,2-di-(*p*-aminophenoxyphenyl)-ethylene are more soluble. The polymer formed from this diamine and the dianhydride of benzophenone-3,3′-4,4′-tetracarboxylic acid is soluble in a TCE/phenol (3:1) mixture.

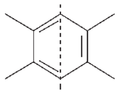
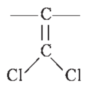
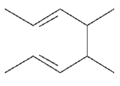
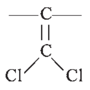
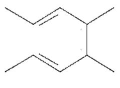
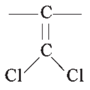
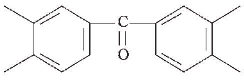
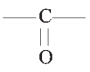
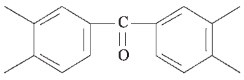
Some properties of these polyimides are presented in **Table 3.6**. These polymers are promising as film-forming materials and as construction materials [23–25] for various applications.



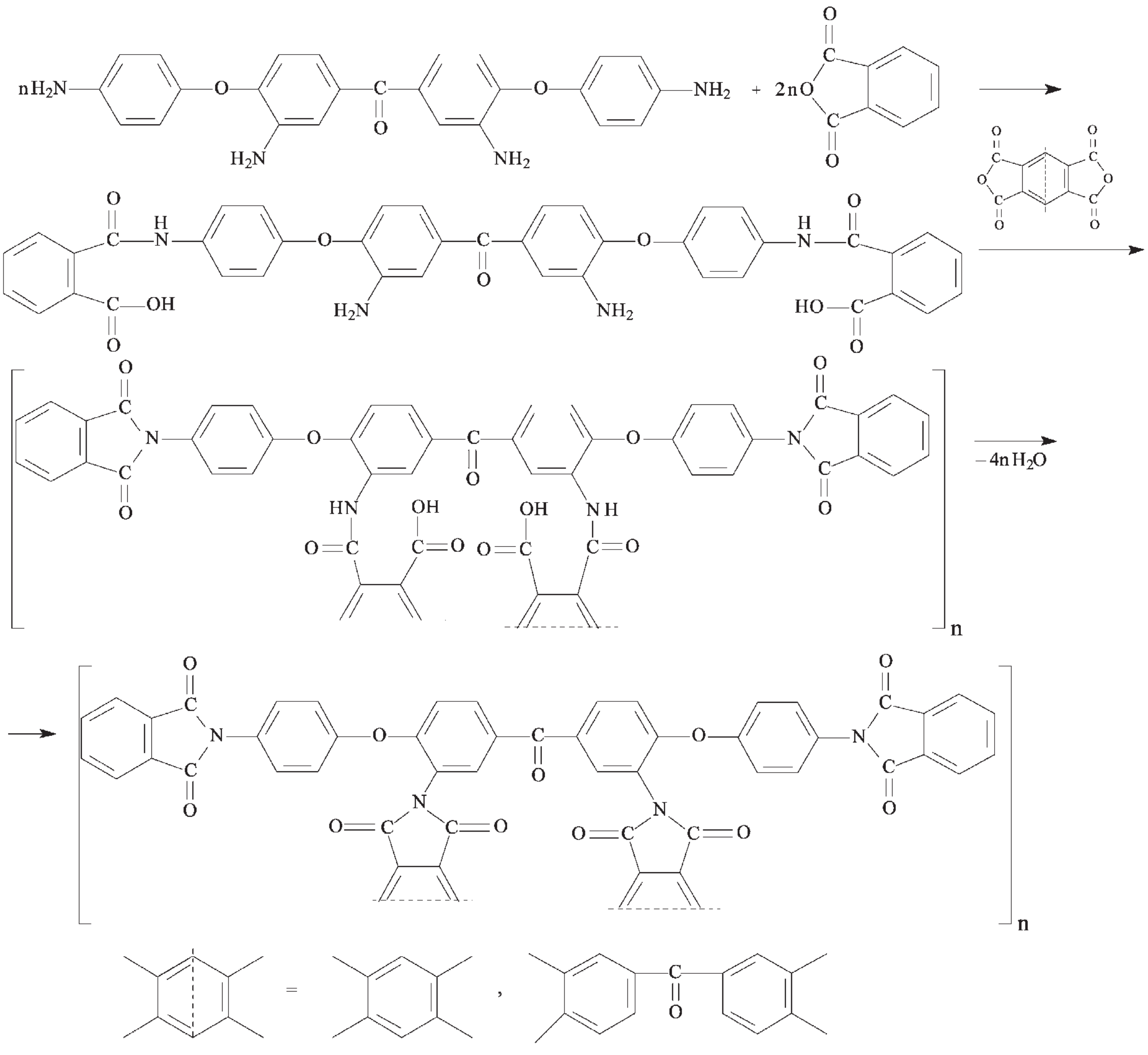
Scheme 3.5

Table 3.6. Properties of polyimides of the general formula:



–R–		η_{red}, dl/g	$T_{10\%}$, °C	LOI
		0.45 (H_2SO_4)	480	37
		0.42 (H_2SO_4)	490	33
		1.40 (TCE/phenol)	500	35
		0.40 (H_2SO_4)	485	32

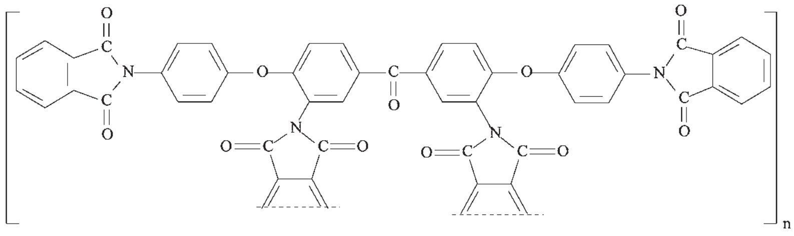
To further increase the solubility of the polyimides, an attempt was made to introduce bulky substituents, such as *N*-phthalimide and *N*-(*p*-phenoxy)-phthalimide groups, into the macromolecules. This was accomplished by using aromatic tetramines for the synthesis of the polyimides, two of the tetramine groups being used for chain propagation and the other two for the introduction of phthalimide-containing *o*-substituents. The use of bis[3-amino-4(*p*-aminophenoxy)]-benzophenone as the tetramine [14, 26] allowed for the introduction of *N*-(*p*-aminophenoxy)-phthalimide groups into the polymers. Polyimides formed from bis[3-amino-4-(4-aminophenoxy)]-benzophenone were synthesised according to **Scheme 3.6** [26, 27].

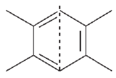
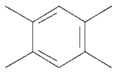
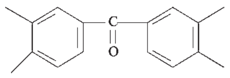
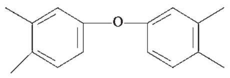


Scheme 3.6

The structures of the polymers obtained according to **Scheme 3.6** are shown in an idealised form since reactions can actually take place at a variety of positions on the starting tetramine monomer [28]. The polymers are characterised by a high solubility in organic solvents (NMP, DMF, DMAC, DMSO, *m*-cresol, TCE, chloroform and cyclohexanone) resulting from an asymmetric polymer

Table 3.7. Some properties of polyimides of the general formula:



	η_{red}, dl/g	T_g, °C	$T_{10\%}$ (TGA), °C	LOI[a]	Solubility[b]		
					DMF	MC	$CHCl_3$
	0.60	295	440	31.8	s	s	s
	0.50	265	452	31.4	s	s	s
	0.36	245	490	30.7	s	s	s

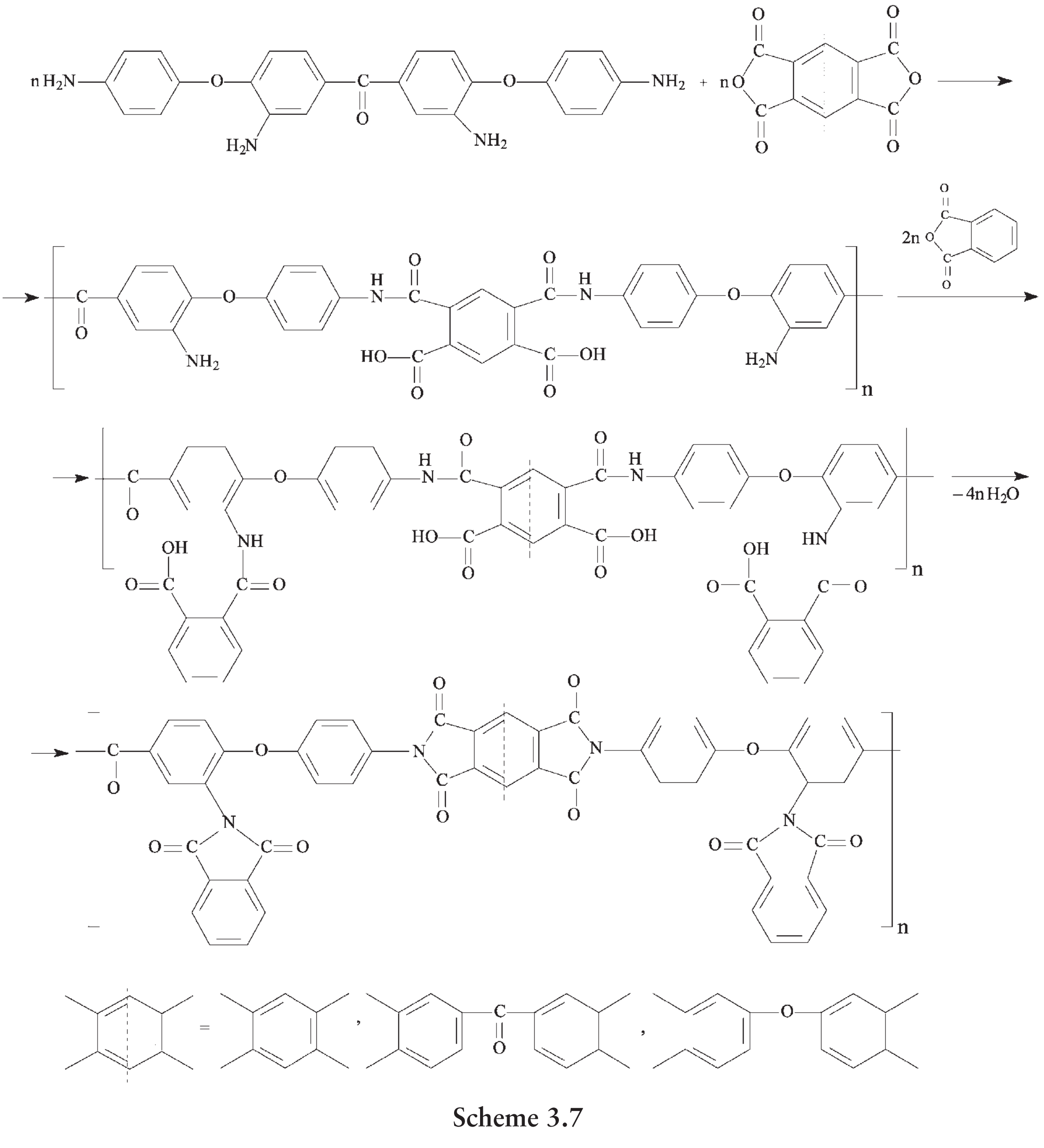
structure, the presence of flexible ether groups and bulky pendant substituents. These polymers have relatively low softening temperatures of 245–295 °C (**Table 3.7**), which facilitates their processing into finished articles [26, 27].

An alternative order of introducing acylating reagents onto the bis[3-amino-4-(*p*-aminophenoxy)]-benzophenone, that is, the addition of first bis(phthalic anhydride) and then phthalic anhydride to the tetramine, yields polyimides containing predominantly *N*-phthalimide *o*-substituents (**Scheme 3.7**). These polyimides are characterised by higher viscosities and softening temperatures (**Table 3.8**) but poorer solubilities as compared to those polymerised according to **Scheme 3.6**.

Aromatic bis(*o*-phenylendiamines) prepared from chloral derivatives, in particular 3,3′,4,4′-tetraminobenzophenone, were also used for the synthesis of polyimides possessing good solubilities in amide and phenolic solvents in combination with high thermal and heat resistance. In these respects, they were little different from polyimides formed from other bis(*o*-phenylendiamines) [29, 30].

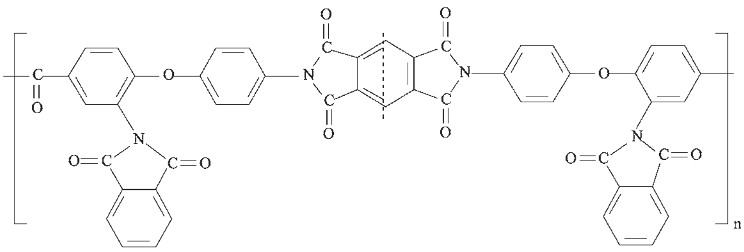
Another approach to the synthesis of polyimides from chloral derivatives involves the use of dianhydrides of isomeric tetracarboxylic acids containing central carbonyl or 1,1-dichloroethylene groups and two ether bonds as the starting electrophilic compounds [31–33] (**Scheme 3.8**).

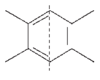
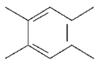
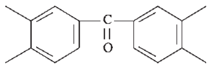
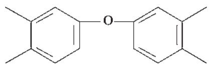
The synthesis of these polyimides has been carried out in phenolic solvents and yielded high-molecular-weight amorphous polymers readily soluble in chlorinated hydrocarbons and dipolar aprotic solvents. Among the polyimides obtained are systems based on the dianhydride containing a carbonyl central group. **Table 3.9** presents some of their properties. The polyimides listed in **Table 3.9** are characterised by high oxygen indices and coke numbers, but their main advantage is a large temperature window between softening and thermal degradation, which allows for their processing by injection and extrusion moulding.

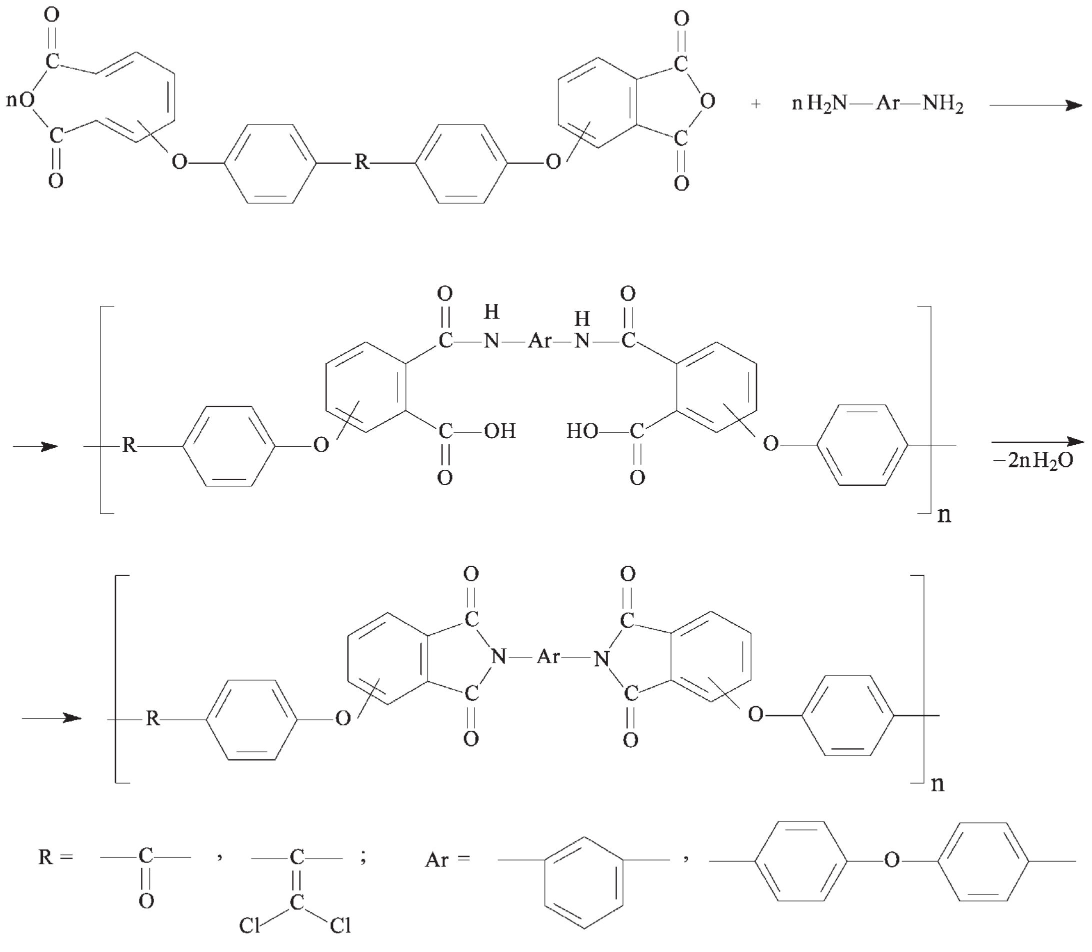


Scheme 3.7

Table 3.8. Some properties of polyimides of the general formula:

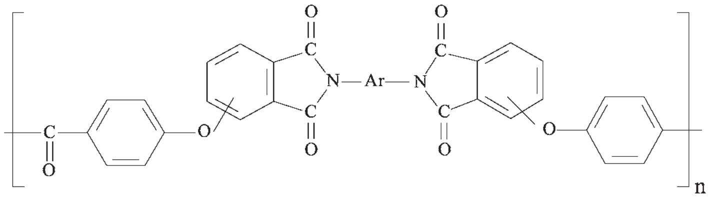


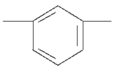
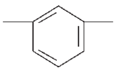
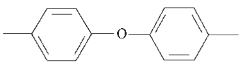
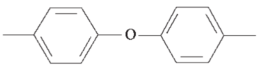
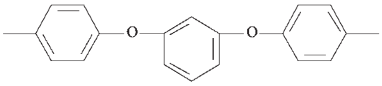
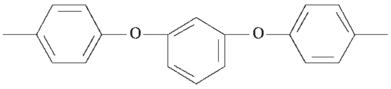
	η_{red}, dl/g	T_{soft}, °C	$T_{10\%}$ (TGA), °C	LOI	Film properties	
					σ, MPa	ε, %
	1.24	325	470	32.1	120	35
	1.12	295	455	33.4	100	42
	0.87	285	450	31.0	90	50



Scheme 3.8

Table 3.9. Some properties of polyetherimides of the general formula:



–Ar–	Isomer	[η] (*m*-cresol), dl/g	T_g, °C	Temperature weight loss (TGA), °C	
				Air	N_2
	3,3′	0.27	248	530	523
	4,4′	1.35	239	523	538
	3,3′	2.00	252	522	529
	4,4′	0.33	210	510	546
	3,3′	1	216	513	525
	4,4′	0.93	194	470	525

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4

TNT-Based Aromatic Diamines

A large variety of aromatic diamines can be obtained starting with trinitrotoluene (TNT) – a major explosive component of ammunition liable to liquidation [1, 2]. A general scheme for the transformation of TNT into different aromatic amines is shown in **Scheme 4.1**.

Reactions shown in **Scheme 4.1** include the following:

- Partial or complete reduction of the TNT nitro groups (Route A).
- Introduction of the substituents in the TNT aromatic nucleus and reduction of the substituted nitro compounds thus formed (Route B).
- Demethylation of the TNT leading to the formation of 1,3,5-trinitrobenzene (TNB) and following transformation (nitrodisplacement, reduction) leading to the target amines (Route C). Most attention has been paid to Route C as it is the most universal approach to the preparation of the substituted aromatic diamines.

The introduction of substituents can be achieved through nucleophilic substitution of nitro groups in TNT or its derivatives under the action of the corresponding nucleophiles. Yet, it is known [3, 4] that, in the interaction of TNT with bases, instead of substitution of nitro groups, the formation of stable anion σ-complexes is observed and a proton is eliminated from the methyl group yielding the 2,4,6-trinitrobenzyl anion with subsequent transformations of this anion taking place (**Scheme 4.2**).

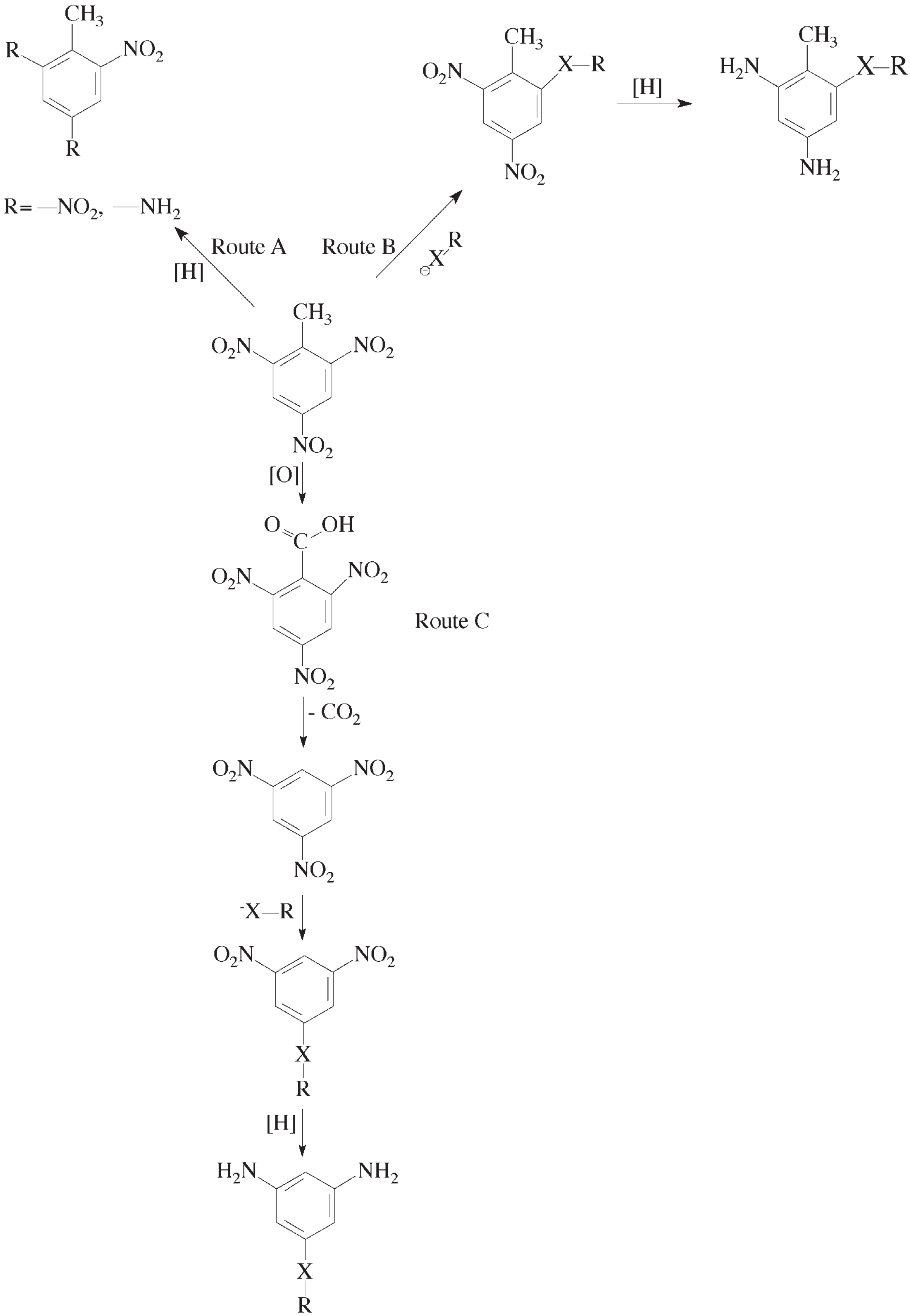
The main process that impedes substitution of the nitro group in TNT is deprotonation of the methyl group. In order to avoid such an undesirable reaction course we turn from TNT to the product of its demethylation – TNB.

TNT demethylation has been described previously [5, 6] and different demethylation variants are technologically acceptable; the most important is a process including oxidation of the methyl group and subsequent decarboxylation of the carboxyl group formed (**Scheme 4.3**).

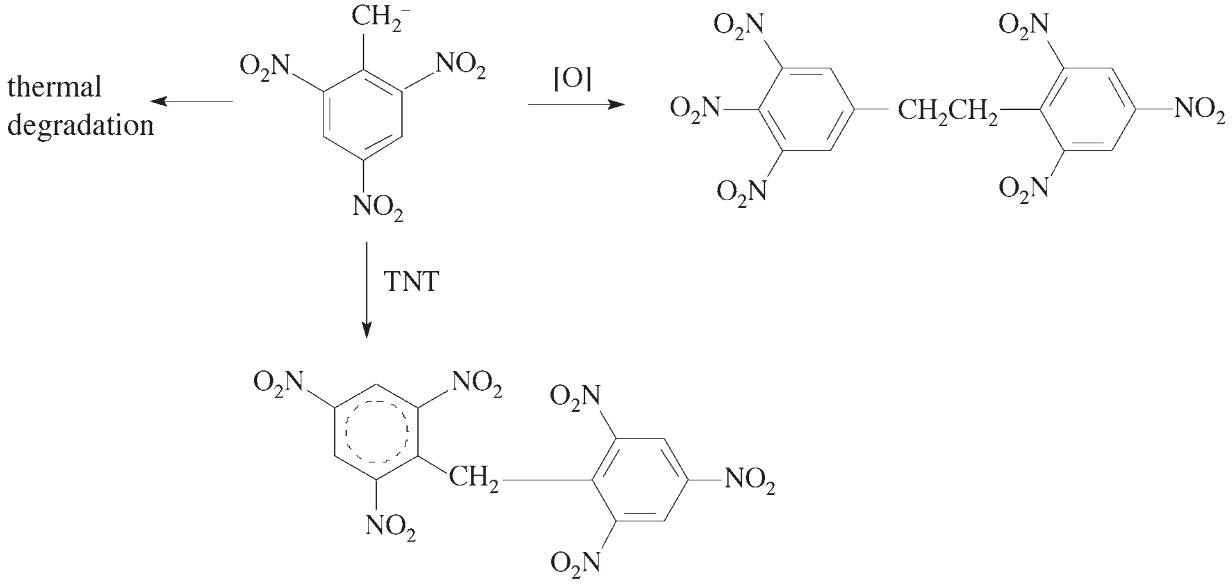
The nitro groups in TNB were replaced with alkoxy [7, 8] or perfluoroalkoxy [9–15] groupings using aromatic nucleophilic nitrodisplacement reaction [16–19] in accordance with **Scheme 4.4**. Monosubstituted dinitro compounds thus obtained were reduced to the corresponding diamines [7, 8, 11–15] in accordance with **Scheme 4.5**. The simplest of the target diamines, 3,5-diaminoanisole [7, 20, 21], was prepared in accordance with **Scheme 4.6**.

More attention has been paid to the replacement of the nitro groups in TNB [22, 23] for aryloxy groupings. In fact one, two or all nitro groups in TNB can be replaced with aromatic nucleophiles in accordance with **Scheme 4.7**.

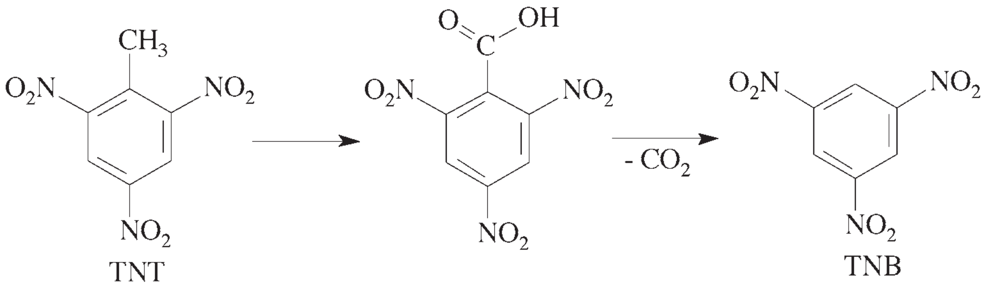
Displacement of the first nitro group in TNB proceeds smoothly under mild conditions (80 °C) and leads to the formation of 3,5-dinitrodiaryl ethers in high yields (60–95%) [22, 23]. Conditions for the


CH$_3$
R
NO$_2$
R
R= —NO$_2$, —NH$_2$
Route A
[H]
Route B
$^{\ominus}$X–R
O$_2$N
X–R
[H]
H$_2$N
NH$_2$
[O]
O
OH
Route C
- CO$_2$
$^{-}$X–R
X
R

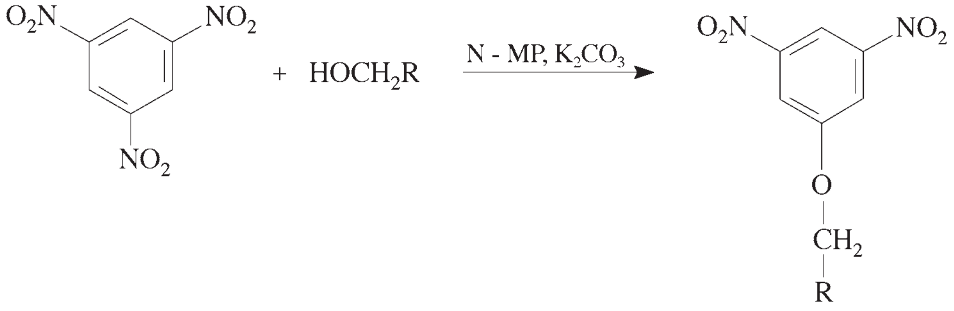
Scheme 4.1



Scheme 4.2



Scheme 4.3

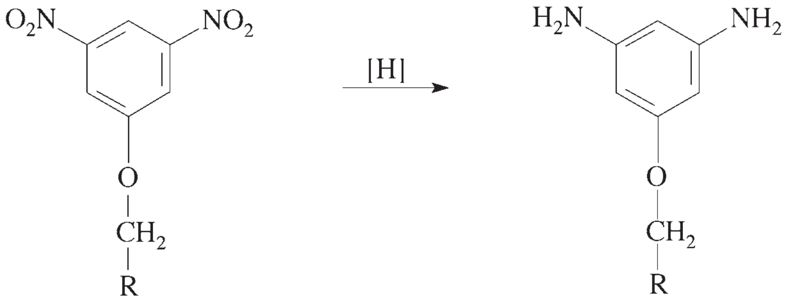


R = – H, $-(CH_2)_5CH_3$; $-(CF_2)_n-X$;

–X = –F, n = 1; –X = H, n = 2

–X = H, n = 4; –X = H, n = 6

Scheme 4.4

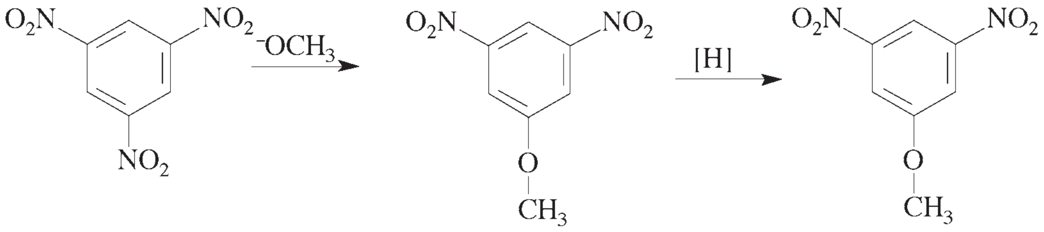


R = – H, $-(CH_2)_5CH_3$; $-(CF_2)_n-X$;

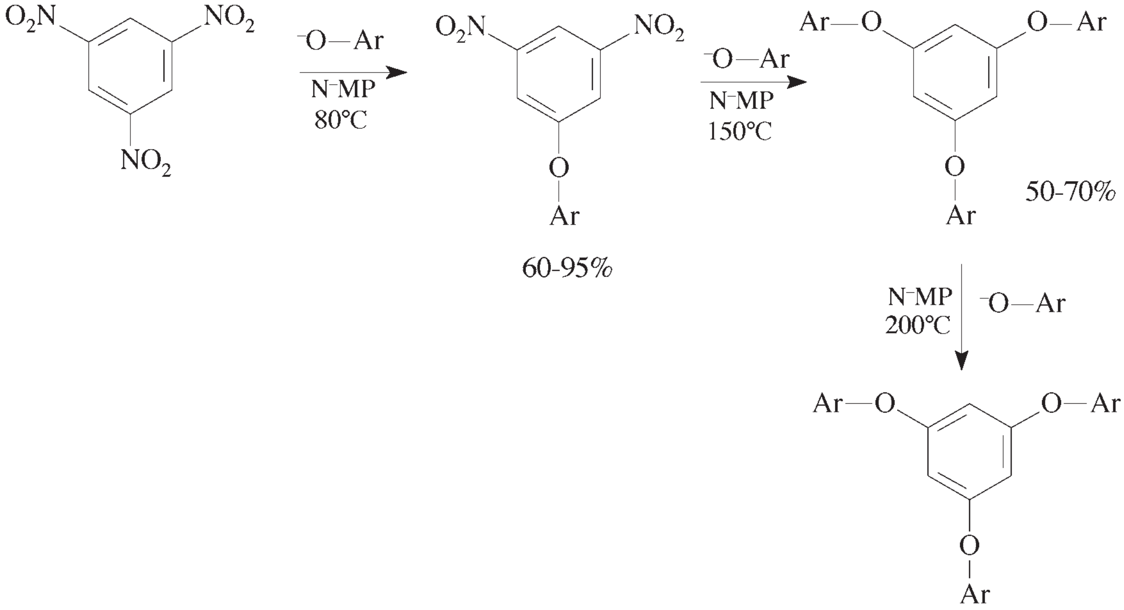
–X = –F, n = 1; –X = H, n = 2

–X = H, n = 4; –X = H, n = 6

Scheme 4.5



Scheme 4.6



Scheme 4.7

nitro group displacement in 3,5-dinitrodiaryl ethers are harsher; the reaction proceeds at 150 °C and leads to the formation of 3,5-diaryloxy-substituted nitrobenzenes in yields of 50–70%. Replacement of the nitro groups in 3,5-diaryloxy-substituted nitrobenzenes proceeds at 200 °C and leads to the formation of 1,3,5-triaryloxybenzenes in yields of 25–30%.

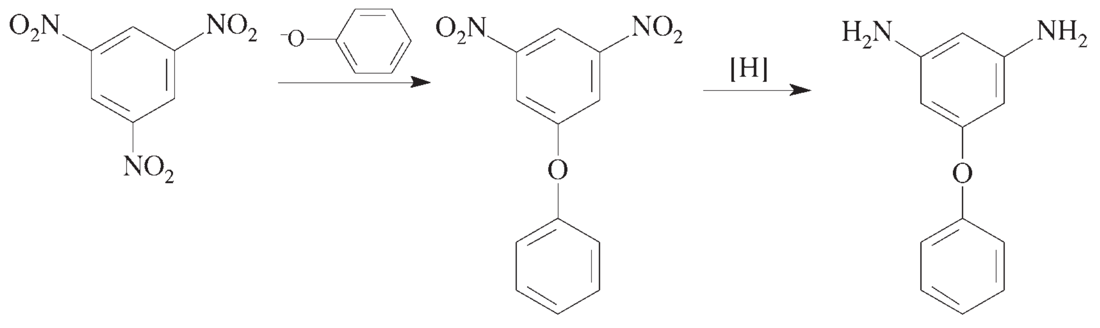
The mononitrosubstitution reaction of TNB was used to prepare new aryloxy-substituted dinitro compounds [22, 23], which were converted to the corresponding aryloxy-substituted diamines. The simplest dinitrocompound and diamine obtained are 3,5-dinitrodiphenyl ether and 3,5-diaminodiphenyl ether [21–23] (**Scheme 4.8**).

The nitro groups in 3,5-dinitrodiaryl ethers may be readily replaced with the residues of mono- and bis-phenols. The simplest 3,5-dinitrodiaryl ether – 3,5-dinitrodiphenyl ether – was reacted with 4-aminophenol or 4-acetamidophenol with the formation of 3-nitro-5-[4-amino(amido)]-phenoxydiphenyl ether; subsequent transformation of this product led to 3-amino-5-(4-aminophenoxy)-diphenyl ether [24] (**Scheme 4.9**).

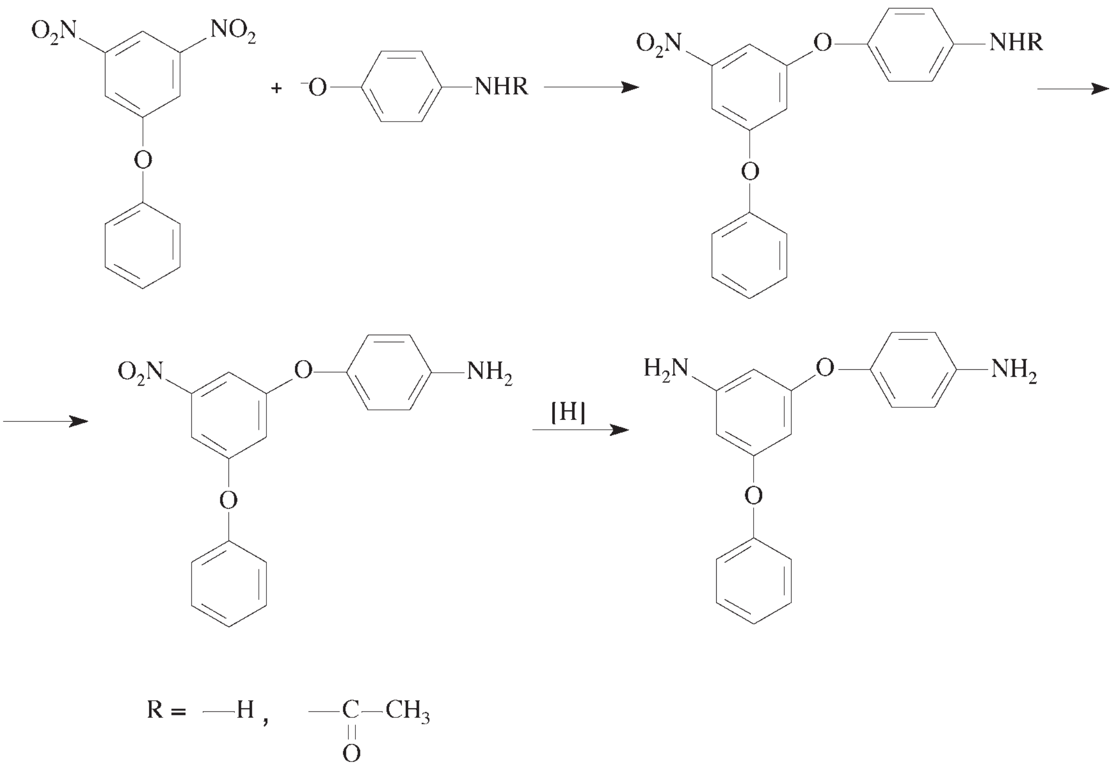
Replacement of the nitro groups in dinitrodiphenyl ethers with the residues of bis-phenols leads to the formation of dinitrocompounds and diamines containing no less than two ether bonds, potentially includable into the polymer main chains [25, 26]. Preparation of these compounds was carried out in accordance with **Scheme 4.10**.

An alternative approach to the same diamines includes interaction of bis-phenols with two-fold molar amounts of TNB [23] followed with the treatment of the tetranitrocompounds thus formed with phenol and reduction of the dinitrocompounds (**Scheme 4.11**).

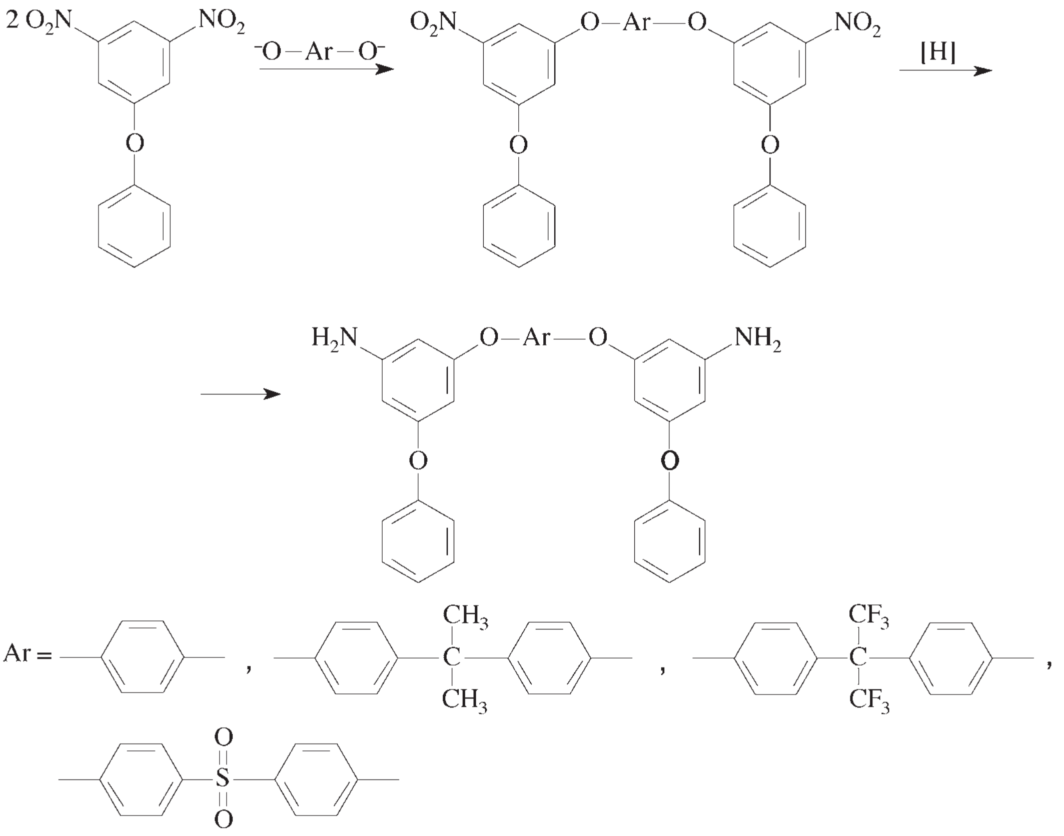
The mononitrosubstitution reaction of TNB was also used for the preparation of thiophenoxy-substituted dinitrocompounds [27, 28] and for the preparation of 3,5-dinitrodiphenylsulfide (**Scheme 4.12**). This compound was reduced with the formation of the corresponding diamine; alternatively the sulfide group of the compound was oxidised to the sulfone group [28] and then 3,5-dinitrodiphenylsulfone was reduced to the corresponding 3,5-diaminodiphenylsulfone [29] (**Scheme 4.13**). Along with the monomers containing the phenylsulfide group there was developed a new diamine containing benzothiazol-2-yl-sulfide substituent [30]. This compound – 3,5-diaminophenyl-benzothiazol-2-yl-sulfide – was obtained by the interaction of TNB with 2-mercaptobenzothiazole, which is less expensive than thiophenol (**Scheme 4.14**).



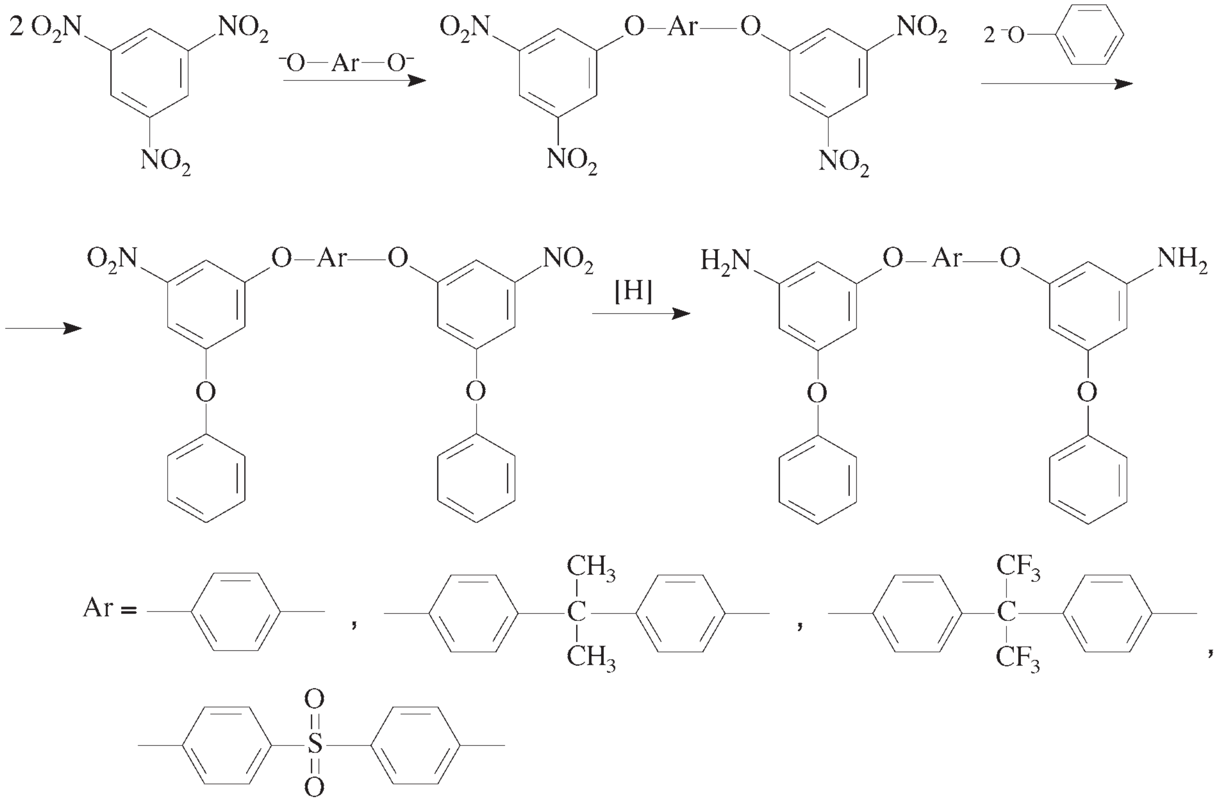
Scheme 4.8



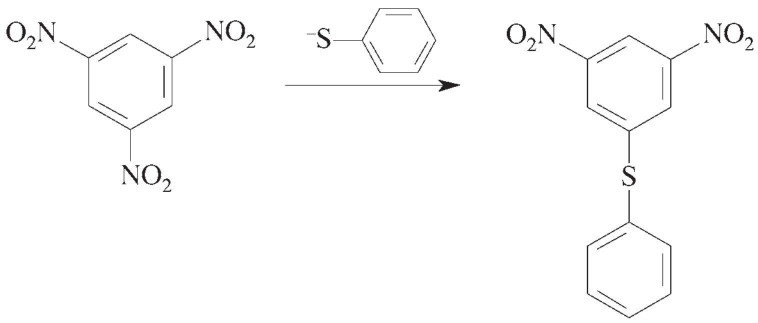
Scheme 4.9



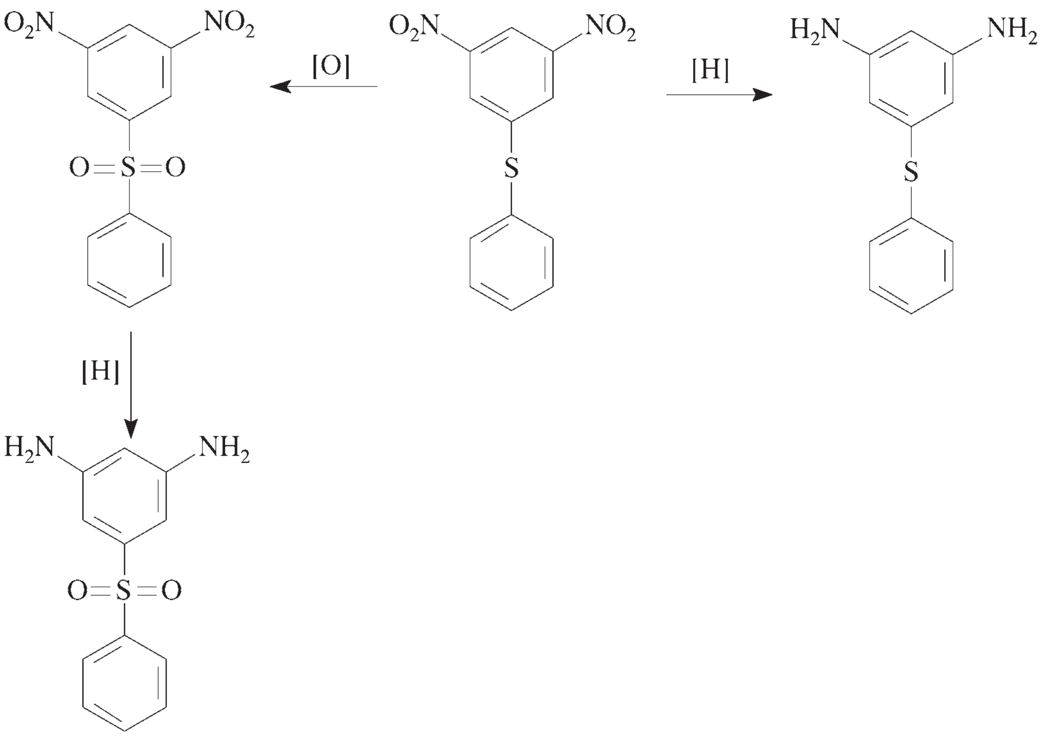
Scheme 4.10



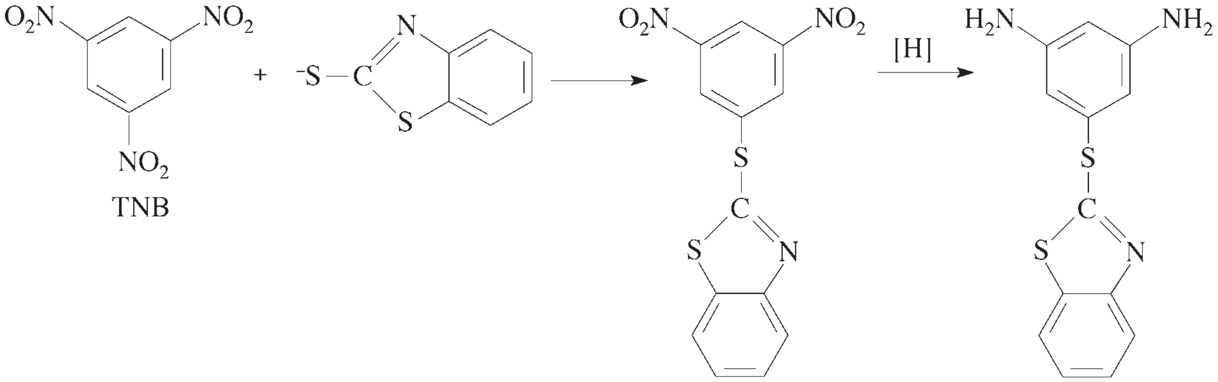
Scheme 4.11



Scheme 4.12



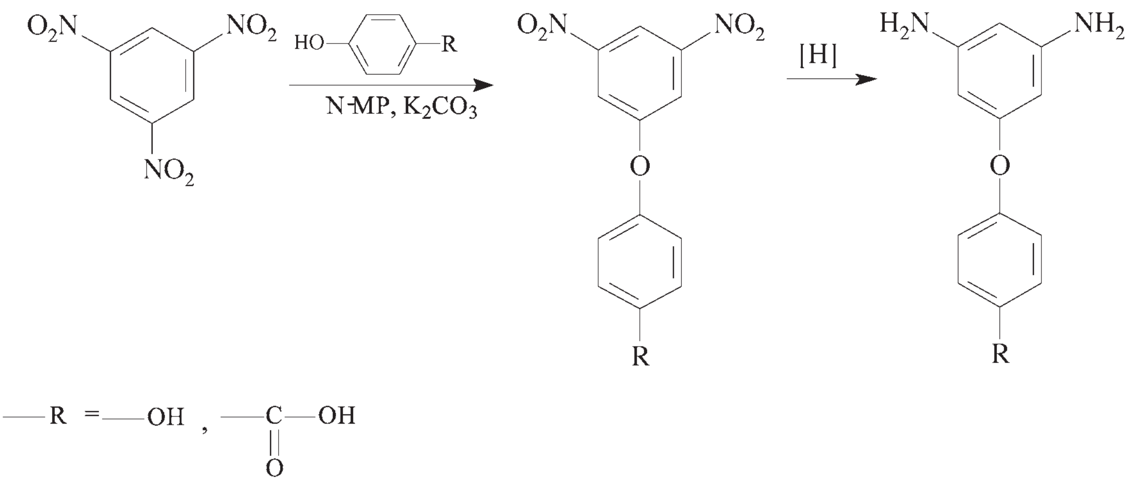
Scheme 4.13



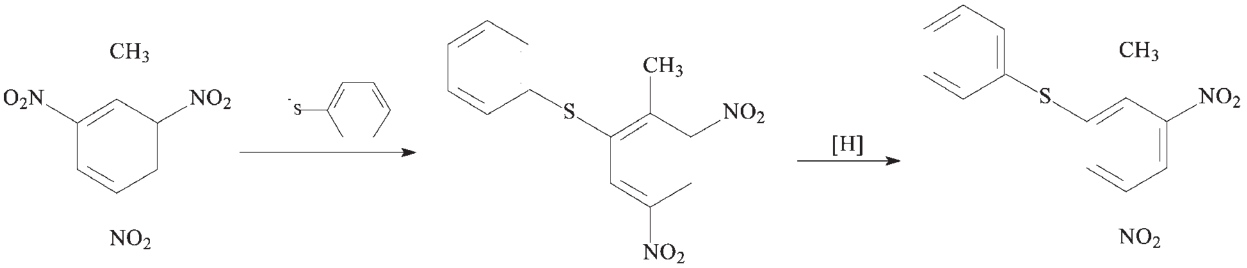
Scheme 4.14

Along with the dintrocompounds and diamines containing inert (non-reactive) bulky substituents, monomers were developed containing additional functional groups [31]. Among such groups the most interesting are hydroxylic groups [23, 31, 32] and carboxylic groups [33]. Diamines containing free hydroxylic and carboxylic groups – 3,5-diamino-4′-hydroxydiphenyl ether and 3,5-diamino-4′-carboxydiphenyl ether – were synthesised in accordance with **Scheme 4.15**.

Along with Route C for the preparation of substituted diamines, Route B was also used (**Scheme 4.1**). To avoid the side reactions (**Scheme 4.2**) TNB was interacted with a nucleophile combining low basicity with high nucleophilicity: thiophenol [34, 35]. Direct interaction of TNT with thiophenol



Scheme 4.15



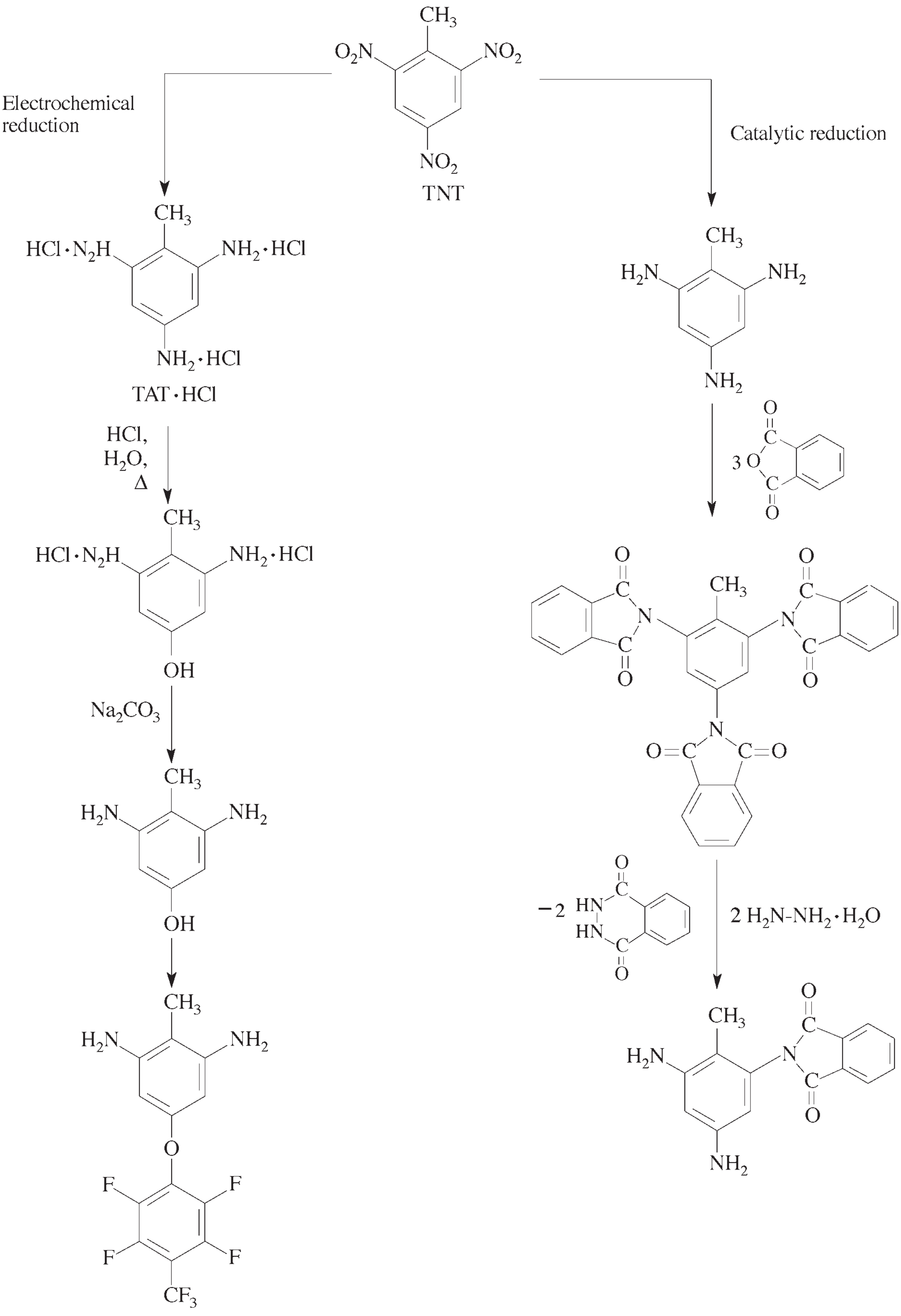
Scheme 4.16

and subsequent reduction of the dinitrocompound obtained were carried out [36–38] in accordance with **Scheme 4.16**.

An additional approach to new di- and triamines includes reduction of TNT [39] or reduction and subsequent transformations of 2,4,6-triaminotoluene (TAT) [37, 38, 40–42] thus obtained (Route A in **Scheme 4.1**). Preparation of TAT (free base or its salts) can be carried out in accordance with **Scheme 4.17**.

TAT and TAT·HCl are the most available and inexpensive TNT derivatives [39, 43, 44]. Catalytic hydrogenation of TNT led to the formation of free TAT [45]. Treatment of this compound with threefold molar amount of phthalic anhydride led to the formation of 2,4,6-tris(*N*-phthalimido)-toluene (**Scheme 4.17**), which under the action of hydrazine hydrate was transformed into 2,4-diamino-6-(*N*-phthalimido)-toluene (**Scheme 4.17**) [41].

Electrochemical reduction of TNT led to the formation of TAT·3HCl; selective acidic hydrolysis of this compound led to the formation of 2,6-diamino-4-hydroxytoluene dihydrochloride, which was neutralised to 2,6-diamino-4-hydroxytoluene [38, 40, 46]. The interaction of the last product with perfluorotoluene using aromatic nucleophilic substitution reactions led to the formation of 3,5-diamino-4-methyl-2′,3′,5′,6′-tetrafluoro-4-trifluoromethyldiphenyl ether [38, 47] (**Scheme 4.17**).


CH3
O2N
NO2
NO2
TNT
Electrochemical reduction
Catalytic reduction
HCl·N2H
NH2·HCl
NH2·HCl
TAT·HCl
HCl, H2O, Δ
OH
Na2CO3
H2N
NH2
F
CF3
3
2 H2N-NH2·H2O
−2

Scheme 4.17

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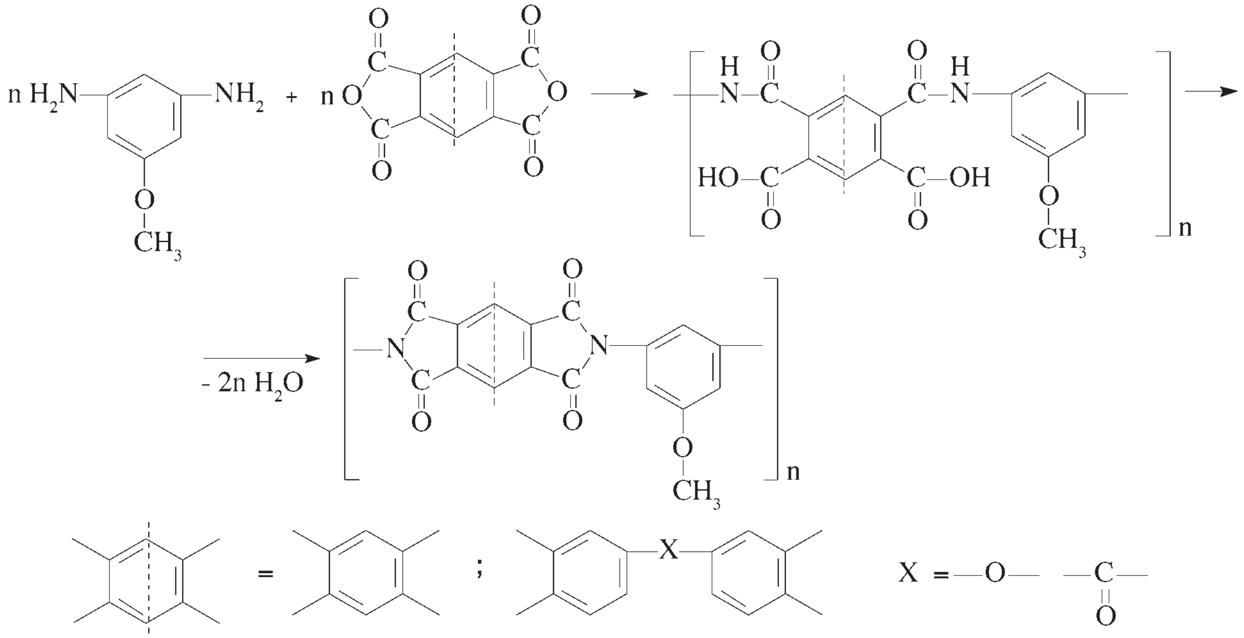
5

Polyimides Based on TNT-Derived Diamines

Trinitrotoluene (TNT)-based aromatic diamines are used for the preparation of substituted polyimides. Interest in substituted polyimides is very understandable due to the known poor tractability of unsubstituted aromatic polyimides [1–4]. As is known, the introduction of methoxy substituents to macromolecules of polyimides enhances their solubility in organic solvents [5]. One of the simplest TNT derivatives, 3,5-diaminoanisole, is used for the preparation of methoxy-substituted polyimides [6].

Polyimides can be synthesised by reacting 3,5-diaminoanisole with dianhydrides of pyromellitic, benzophenone-3,3′,4,4′-tetracarboxylic and diphenyloxide-3,3′,4,4′-tetracarboxylic acids in accordance with **Scheme 5.1**.

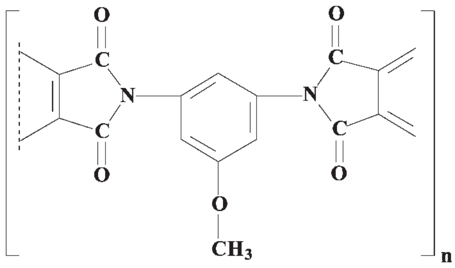


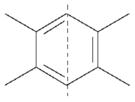
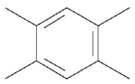
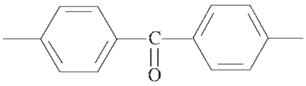
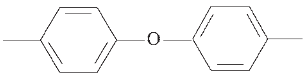
Scheme 5.1

A number of conventional synthetic procedures have been used to prepare polyimides [1–4]. These are the low-temperature condensation of 3,5-diaminoanisole with acid dianhydrides, conducted in amide solvents, followed by thermal imidisation of the poly(*o*-carboxy)-amides (PCA) formed; low temperature condensation of 3,5-diaminoanisole with acid dianhydrides, conducted in amide solvents, followed by catalytic imidisation of PCA using a 1:1 pyridine–acetic anhydride complex as a catalyst; and high temperature (160–180 °C) condensation of 3,5-diaminoanisole with acid dianhydrides, conducted in *m*-cresol, using quinoline, isoquinoline or benzoic acid as a catalyst.

The reaction between 3,5-diaminoanisole and acid dianhydrides in amide solvents (above all *N*-methyl-2-pyrrolidone, NMP) was conducted at room temperature. The process occurred in a homogeneous system and led to PCA with relatively high, reduced viscosities of solution (**Table 5.1**).

Table 5.1. Characterisation of polyimides of the general formula:



	η_{red} (0.5%, 25 °C), dl/g	T_g, °C	$T_{10\%}$ (TGA, air, ΔT = 4.5 °C/min), °C	Solubility		
				NMP	*m*-Cresol	TCE/ phenol
	1.12[a]	—	400	ins	ins	ins
	0.83[a]	310	400	ins	ins	ins
	0.89[a] 0.82[b] 0.47[c]	300	440	ins	s	s

[a] *Viscosity of PCA solution in NMP.*

[b] *Viscosity of polyimides prepared by catalytic imidisation of PCA using a pyridine–acetic anhydride complex; viscosity measured in trichloroethane (TCE)/phenol.*

[c] *Viscosity of polyimides solution (in TCE/phenol); polyimides synthesised by high-temperature condensation in m-cresol.*

ins: *insoluble*

s: *soluble*

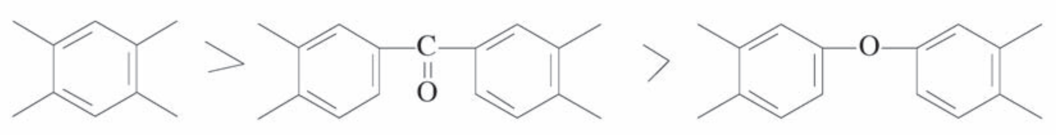
T_g: *Glass transition temperature*

TGA: *Thermogravimetric analysis*

Allowing for the fact that catalytic imidisation was reported [1, 2] to result in polyimides showing better solubility, catalytic imidisation of PCA was carried out by adding a catalytic complex to a solution of polymer and subsequently stirring the mixture at boiling point for several hours. In all the cases studied, imidisation led to precipitation of the polymer in the form of a swollen gel-like mass. Precipitation of the polymers from the reaction solutions did not preclude cyclisation at high conversions of *o*-carboxyamide fragments to imide ones.

Up to the decomposition temperature, polypyromelliteimide based on 3,5-diaminoanisole does not soften. The softening points of polyimides prepared from benzophenonetetracarboxylic and diphenyloxidetetracarboxylic acid dianhydrides are 300 and 310 °C, respectively, (**Table 5.1**).

Hence, heat resistance of the synthesised polyimides decreases with variation of the structure of the acid dianhydride fragment in the following order:



which agrees with conventional concepts concerning the relationship between polymer structure and heat resistance [7].

Examination of the thermal stability of the polyimides synthesised, carried out using differential thermogravimetric analysis (air, ΔT = 4.5 °C/min), revealed that, under the conditions specified, the 10% weight loss (used as a criterion of thermal stability) is almost independent of the structure of the polyimides (**Table 5.1**). For all polyimides examined, the 10% weight loss temperature was 400 °C. The relatively low thermal stability of these polyimides may be related to the presence of the methoxy groups.

None of the polyimides synthesised dissolve in amide solvents, including NMP. Moreover, the polyimide prepared from 3,5-diaminoanisole and diphenyloxidetetracarboxylic acid dianhydride is soluble in *m*-cresol and a mixed trichloroethane/phenol (3:1) solvent, whereas the polypyromelliteimide and polyimide based on benzophenonetetracarboxylic acid dianhydride do not dissolve in these phenolic solvents.

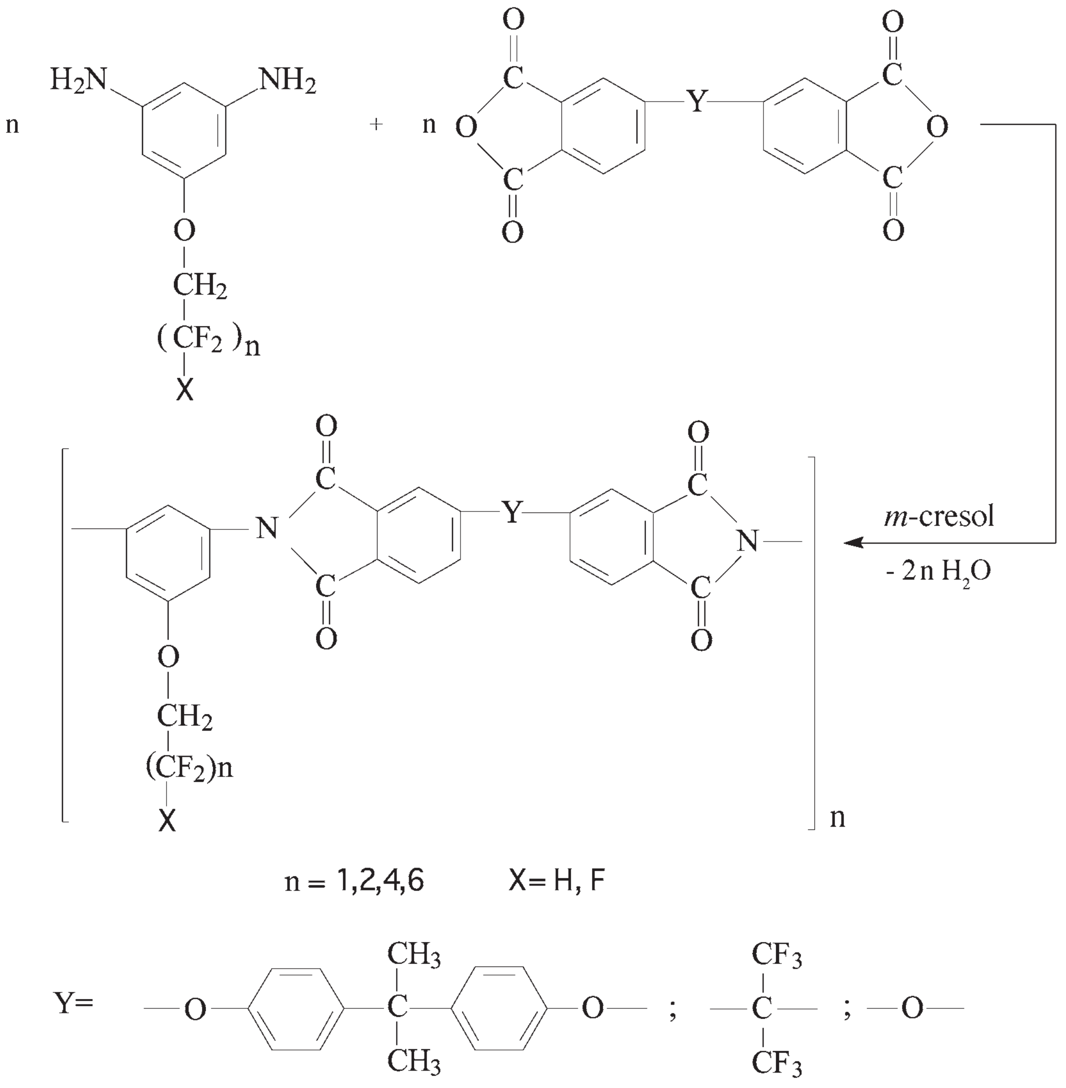
The fact that the polyimide based on diphenyloxidetetracarboxylic acid dianhydride is soluble in phenolic solvents enabled the authors to prepare (using solutions of this polymer in *m*-cresol and mixed trichloroethane/phenol solvent) almost colourless films showing (at 25 °C) a tensile strength of 114 MPa and a 9% elongation at break.

The attempt to synthesise this polyimide in *m*-cresol using high-temperature condensation was not very successful since, although the synthesis proceeded in a homogeneous system, the viscosity of the polymer solution in *m*-cresol was significantly lower than that of the corresponding polyimide prepared using the catalytic PCA-cyclisation process (**Table 5.1**).

Introduction of the hinge groups may cause a greater effect on polymer solubility; polyimides containing hexyloxy side groups demonstrate much better solubility than methoxy-substituted polyimides [8].

One additional class of polyimides containing aliphatic substituents includes polymers containing perfluoroalkoxy side groups [9–12]. Fluorinated polyimides have been used in the aerospace and electronic fields because they are thermally stable, mechanically strong and electrically insulating [13–17]. These technological areas also need transparent polyimides to cover solar cells and polyimides that have low permittivity to decrease the delay time of electrical circuits. The optoelectronics industry needs polyimides with transparency at wavelengths longer than those of visible light and a controllable refractive index. One of the most effective ways to satisfy these needs is to introduce fluorine into polyimide materials [18, 19]. Different approaches have been used for the introduction of fluorine into polyimides [19]. One widely used approach is the incorporation of fluorinated alkoxy side groups into starting products.

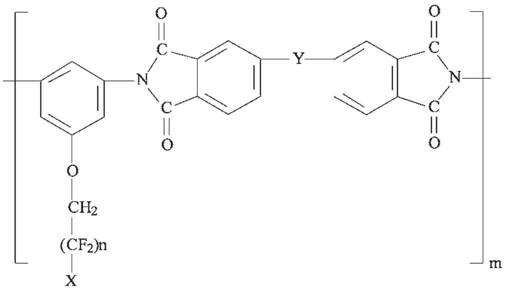
New representatives of such polyimides were prepared from TNT-based perfluoro-substituted *m*-phenylenediamines and different aromatic tetracarboxylic acid dianhydrides [9–12] in accordance with **Scheme 5.2**. Reactions were carried out in *m*-cresol using isoquinoline as catalyst. The reaction temperature was 160 °C and the reaction time 5 hours.

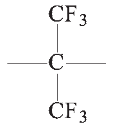
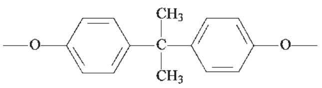
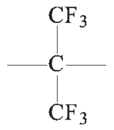
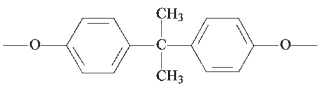
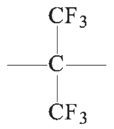
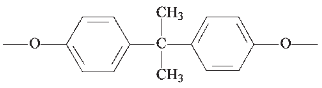
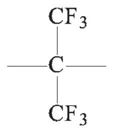
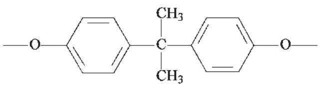


Scheme 5.2

All reactions proceeded homogeneously and led to the formation of polyimides completely soluble in NMP, and, depending on structure, in other organic solvents. All polyimides based on dianhydride A were soluble in chlorinated solvents, but did not dissolve in acetone; in contrast, all polyimides based on dianhydride 6F were soluble in acetone but insoluble in chlorinated hydrocarbons (**Table 5.2**). The good solubility of these polyimides is due to the presence of the fluorinated alkoxy side groups and flexibilising bridging groups [3, 20] and to their amorphous (X-ray analysis) structure.

Table 5.2. Solubility of polyimides of the general formula:



n	–X	–Y–	Solubility			
			NMP	THF	$CHCl_3$	Acetone
1	–F	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	s	s	ins	s
1	–F		s	s	s	ins
1	–F	—O—	s	s	ins	ins
2	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	s	s	ins	s
2	–H		s	s	s	ins
2	–H	—O—	s	ins	ins	ins
4	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	s	s	ins	s
4	–H		s	s	s	ins
4	–H	—O—	s	ins	ins	ins
6	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	s	s	ins	s
6	–H		s	s	s	ins
6	–H	—O—	s	ins	ins	ins

General properties of fluorinated polyimides are given in **Table 5.3**. As can be seen from the table, almost all the polyimides demonstrate high viscosities indicating rather high molecular weights (M_w) for these polymers. The polyimides obtained demonstrate T_g values (determined using a thermomechanical method) in the range 155–265 °C, decreasing (with some exceptions) with increasing length of the fluorinated alkoxy groups. The 10% weight loss temperatures for these polyimides (400–430 °C) are slightly higher than for methoxy-substituted polyimides.

From the solutions of polyimides in tetrahydrofuran (THF) strong, flexible and colourless films can be cast. Pressing of the polyimides carried out at temperatures 100 °C higher than T_g and 10 MPa leads to the formation of yellowish transparent moulded articles.

As can be seen from **Table 5.3**, the polyimides prepared demonstrate relatively low refractive indices (RI) and dielectric constants (ε). This observation is in a good agreement with known results [21].

Among the polyimides containing aromatic substituents, the most well-known systems are phenoxy-substituted polymers. Syntheses of phenoxy-substituted polyimides are carried out [22–27] in accordance with **Scheme 5.3**. Syntheses of the polyimides were carried out using three different methods [27]:

- Low-temperature solution polycondensation in NMP, followed by catalytic imidisation of the polyamic acids formed in reaction solutions using a pyridine–acetic anhydride (1:1) complex as catalyst (procedure 1);

- High-temperature solution polycondensation in NMP, using azeotrope-forming compounds (procedure 2); and

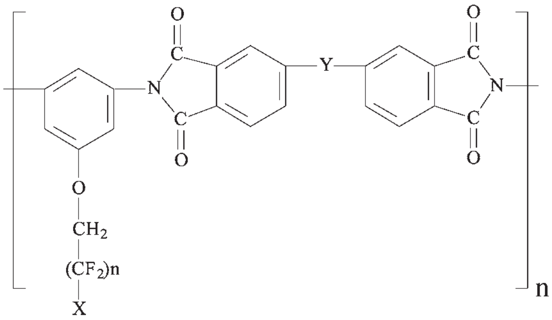
- High-temperature solution polycondensation in *m*-cresol using isoquinoline as catalyst (procedure 3).

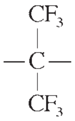
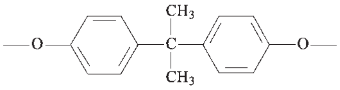
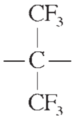
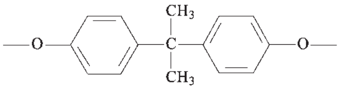
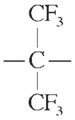
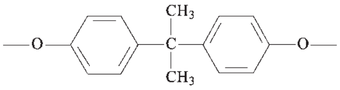
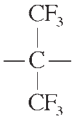
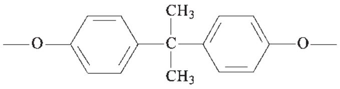
Properties of the polyimides based on 3,5-diaminodiphenyl ether and 1-amino-3-phenoxy-5-(4-aminophenoxy)-benzene are given in **Table 5.4**. Comparison of the polyimides obtained using different methods does not permit a conclusion to be reached as to which method is preferable – in almost all cases high molecular weight polyimides were obtained.

As can be seen from **Table 5.4**, all polyimides based on 3,5-diaminodiphenyl ether – with the exception of polypyromellitimides – are soluble in organic solvents [NMP, *m*-cresol and trichloroethane (TCE)/phenol mixture] indicating a positive influence of phenoxy substituents on the polymer solubility. The reduced viscosities of the polyimide solutions in NMP are 0.35–0.83 dl/g, the highest value corresponding to M_w = 48,000; some of the polyimides demonstrate good film-forming properties. Polyimides based on 3,5-diaminodiphenyl ether and such dianhydrides as dianhydride A and dianhydride 6F are soluble also in methylene chloride, carbon tetrachloride and THF. The T_g values of the polyimides are 180–380 °C and their 10% weight loss temperatures 500–550 °C, indicating large 'windows' between glass transition and degradation temperatures.

Polymers obtained using 3,5-diaminodiphenyl ether may be considered as *m*-phenylenediamine-based polyimides containing phenoxy side groups. A comparison of these two polymer group properties has demonstrated that introduction of phenoxy substituents leads to an increase of polymer solubility and decrease of T_g indicating that phenoxy side groups behave as chemical plasticisers; this conclusion is an agreement with the literature [5, 27–31].

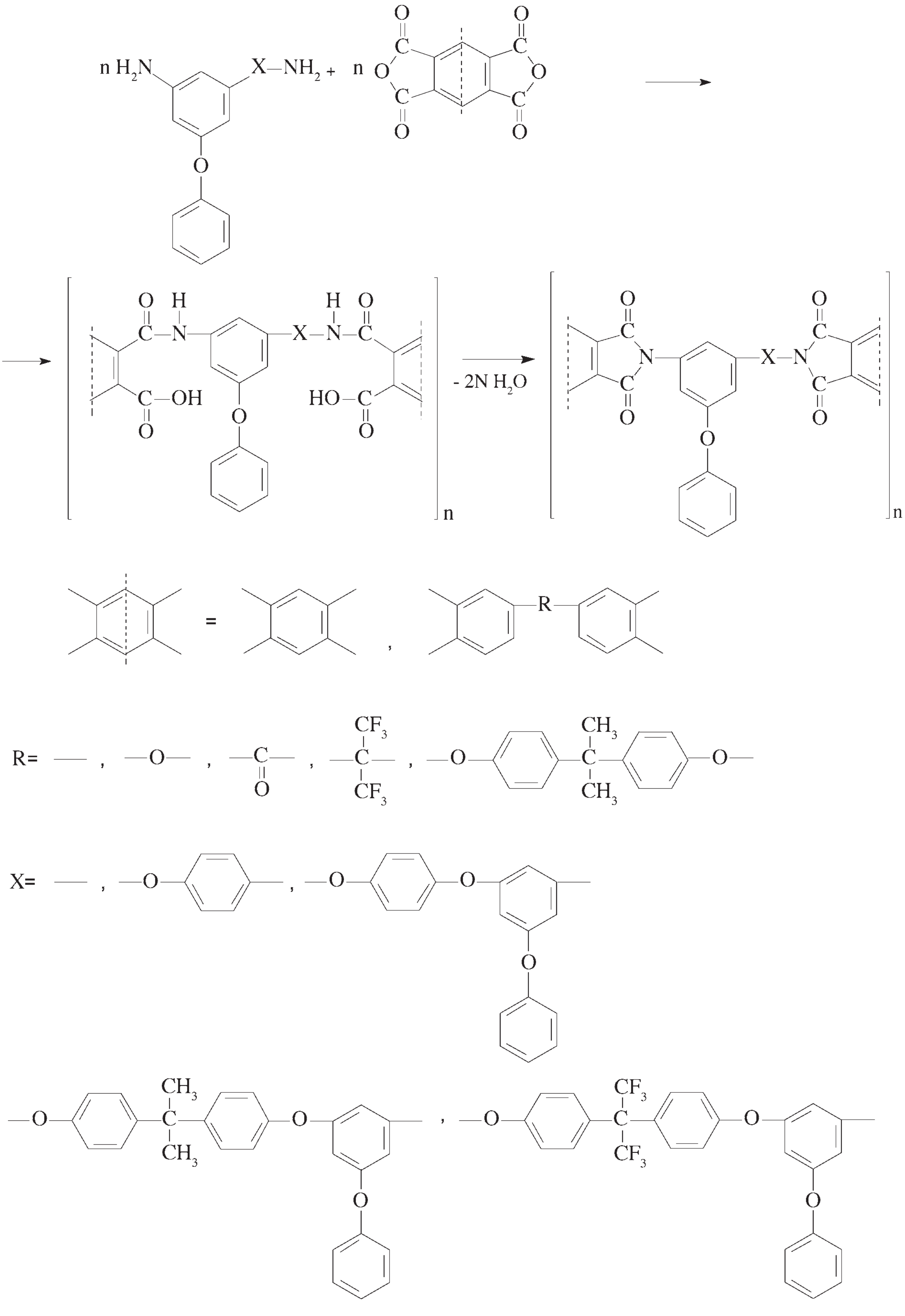
Table 5.3. Some properties of polyimides of the general formula:



n	–X	–Y–	η_{red} (NMP 0.5%, 25 °C), dl/g	ε	RI	T_g, °C	T_{degr}, °C
1	–F	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	0.84	2.94	1.53	265	420
1	–F		0.83	3.02	1.58	230	430
1	–F	—O—	0.37	3.23	1.57	260	425
2	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	0.58	2.89	1.52	215	410
2	–H		1.39	2.97	1.58	220	430
2	–H	—O—	1.55	3.14	1.56	220	410
4	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	1.13	2.78	1.50	184	400
4	–H		1.56	2.88	1.55	256	425
4	–H	—O—	0.57	2.97	1.53	255	405
6	–H	 $-\overset{CF_3}{\underset{CF_3}{C}}-$	0.86	2.70	1.48	180	400
6	–H		0.92	2.80	1.53	155	425
6	–H	—O—	0.45	2.85	1.51	165	405

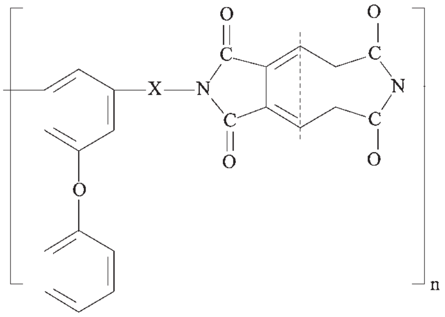
T_g: Glass transition temperatures determined using thermomechanical method.

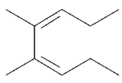
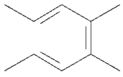
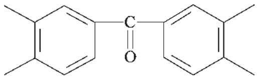
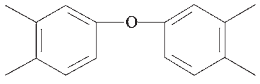
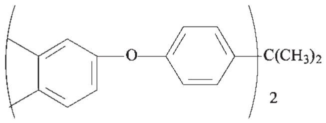
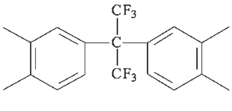
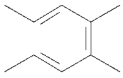
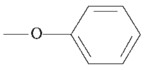
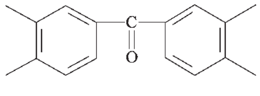
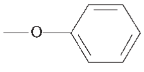
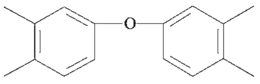
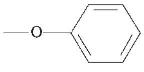
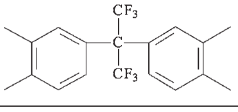
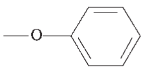
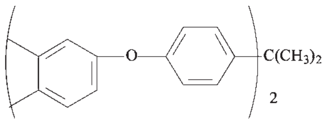
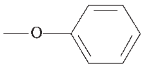
T_{degr}: 10% weight loss temperature determined using TGA method (air, ΔT = 4.5 °C/min).



Scheme 5.3

Table 5.4. Some properties of polyimides of the general formula:



	–X–	η_{red} (NMP, 0.5%, 25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	Solubility	
					NMP	*m*-Cresol
	—	0.66[a]	380	550	ins	ins
	—	0.35 15,000[b]	260	530	s	s
	—	0.83 48,000[b]	245	540	s	s
	—	0.30 44,000[b]	180	500	s	s
	—	0.70	260	530	s	s
		0.32[a]	278	550	ins	ins
		0.58[a]	230	510	s (150 °C)	ps
		0.47	220	520	s	s
		0.31	235	510	s	s
		0.60	215	525	s	s

[a] *Viscosity of polyamic acid.*

[b] *M_w, measured using sedimentation method in NMP.*

ins: insoluble; s: soluble; ps: partially soluble.

Polyimides based on 1-amino-3-phenoxy-5-(4-aminophenoxy)-benzene and such dianhydrides as dianhydride of diphenyloxide-3,3′,4,4′-tetracarboxylic acid, dianhydride A and dianhydride 6F are soluble in NMP, dimethylformamide (DMF), *m*-cresol, THF and chloroform. The polyimide based on benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride is partially soluble in *m*-cresol and NMP; it is insoluble in chloroform, THF and DMF. Polypyromellitimide is insoluble in all the solvents tested.

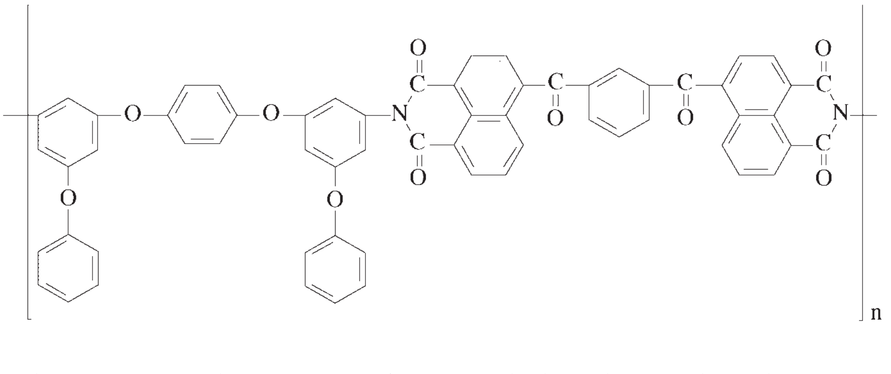
The properties of the polyimides based on bis(3-amino-5-phenoxy)-diphenyl ethers of hydroquinone and bis-phenols are listed in **Table 5.5**. As can be seen from the table, all polyimides – with the exception of polypyromellitimide based on bis(3-amino-5-phenoxy)-diphenyl ether of hydroquinone – are soluble in organic solvents (NMP, DMF, *m*-cresol, THF, chloroform and even butyrolactone (BL) and cycloxanone (CH)). The values of η_{red} of the polyimide solutions in NMP were between 0.22 and 10 dl/g, the highest value corresponding to M_w = 77,000 (measured using sedimentation method in NMP). Some of the polyimides demonstrate good film-forming properties. All polyimides listed in **Table 5.5** demonstrate low T_g (165–213 °C) and T_{degr} ($T_{10\%}$ = 470–550 °C), indicating their processability to form shaped articles.

Comparisons of polyimides based on different diamines obtained (**Tables 5.4 and 5.5**) indicate that the best solubility is typical for the polymers based on bis(3-amino-5-phenoxy)-diphenyl ethers of bis-phenols. For these polymers the lowest T_g values are also typical.

In addition to the polyimides containing five-membered imide rings (polyphthalimides), polyimides containing six-membered naphthylimide cycles (polynaphthylimides and polyperyleneimides) have been synthesised. These polymers are known to be more stable – hydrolytically and thermally – than polyphthalimides [32–36].

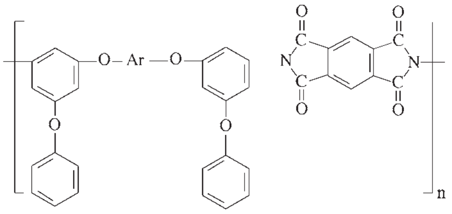
Syntheses of phenoxy-substituted polynaphthylimides and polyperyleneimides were carried out in accordance with **Scheme 5.4** [37, 38]. All polycondensation reactions were carried out under high-temperature solution polycondensation conditions in phenolic solvents (*m*-cresol, *m*- or *p*-chlorophenols) using benzimidazole and benzoic acid as catalysts. All the reactions proceeded homogeneously and led to the formation of deeply coloured polymers. General properties of the polymers are listed in **Table 5.6**.

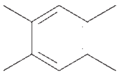
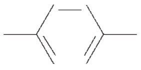
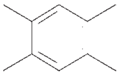
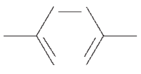
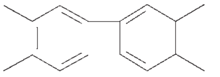
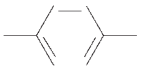
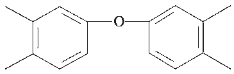
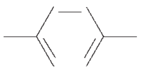
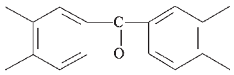
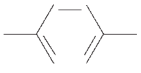
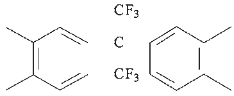
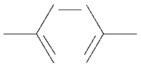
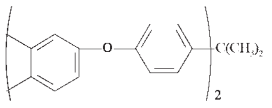
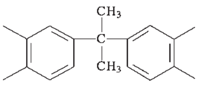
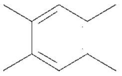
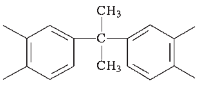
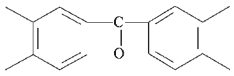
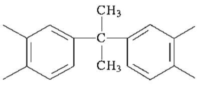
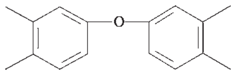
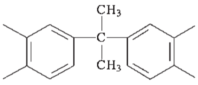
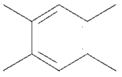
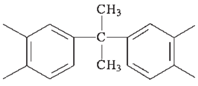
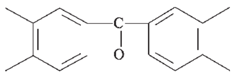
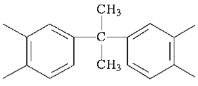
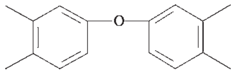
As can be seen from the data in **Table 5.6**, some of the polymers obtained combine solubility in organic solvents with excellent thermal properties. In some cases, the solubility of the polymers is very good. Thus, the polynaphthylimide of formula:



is soluble not only in NMP and a mixture of TCE and phenol (3:1), but also in DMF, $CHCl_3$ and *N*,*N*-dimethylacetamide (partially). Improved solubility of this polynaphthylimide when compared with polymers based on the same dianhydride and common aromatic diamines [35, 39] demonstrates the influence of the bis(3-amino-5-phenoxy)-diphenyl ether of hydroquinone structure on the solubility of the polymers.

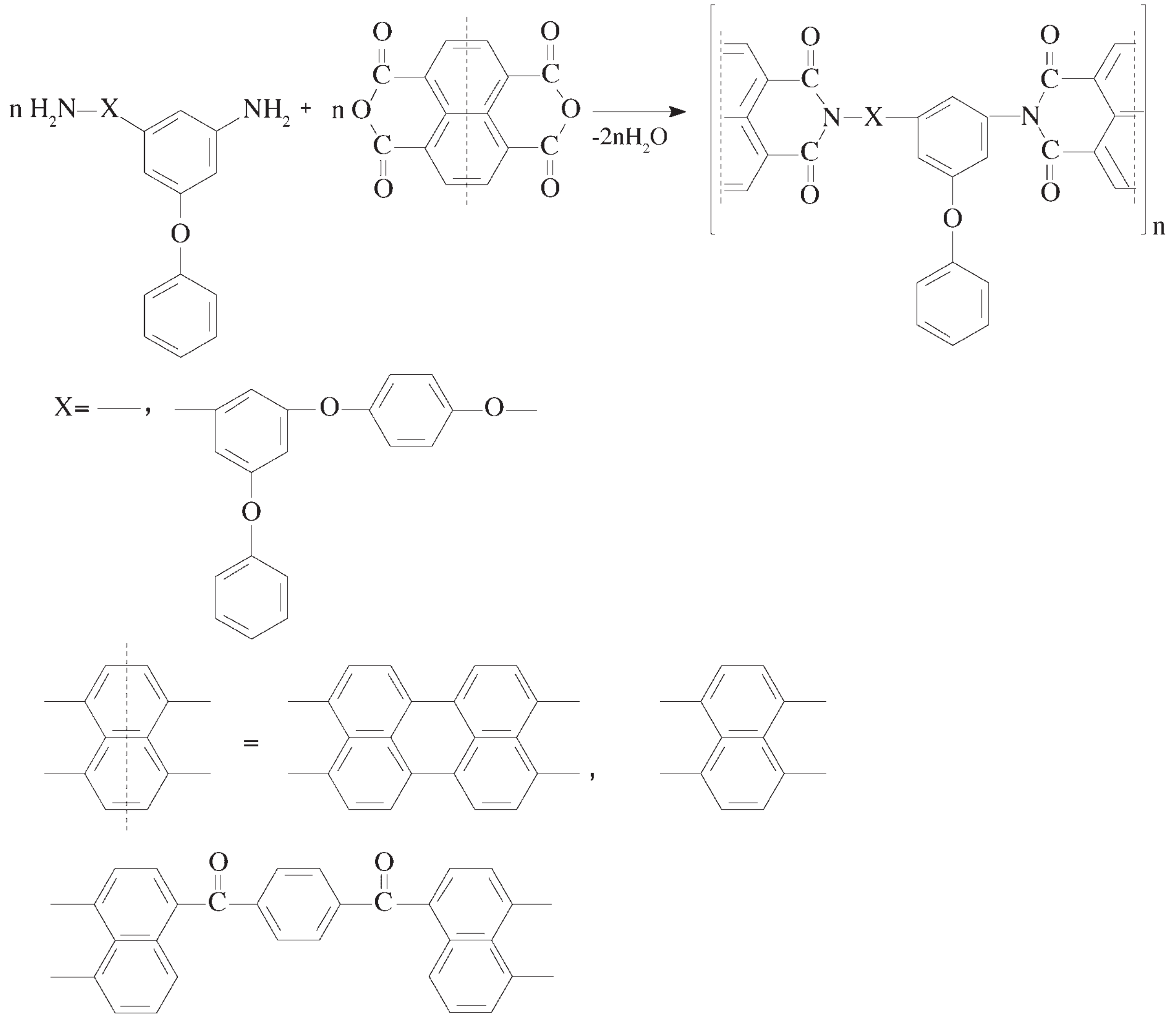
Table 5.5. Properties of polyimides of the general formula:



–Ar–		η_{red} (NMP, 0.5%, 25 °C), cm^3/g	T_g, °C	$T_{10\%}$, °C	Solubility	
					BL	CH
		—	210	520	ins	ins
		0.37	213	550	ins	ins
		0.67 M_w = 47,000[a]	170	520	ins	ins
		10 M_w = 77,000[a]	190	520	ins	ins
		0.65	188	500	s	s
		0.95	205	470	s	s
		0.42	195	470	ins	ins
		0.59	165	500	s	s
		0.50	165	490	s	s
		0.22	200	500	ins	ins
		0.34	197	480	s	s
		0.26	182	510	s	s

BL, butyrolactone; CH, cycloxanone.

[a] *Measured using sedimentation method in NMP.*



Scheme 5.4

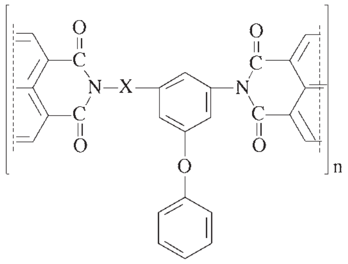
Polyimides containing phenylsulfide and phenylsulfone side groups [40, 41] were obtained in accordance with **Scheme 5.5**. General properties of the polyimides obtained are listed in **Table 5.7**.

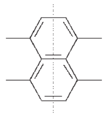
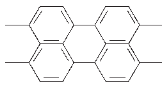
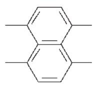
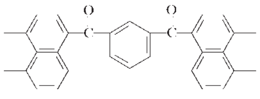
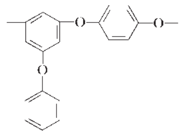
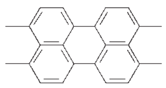
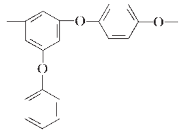
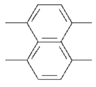
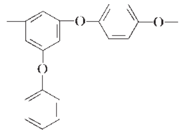
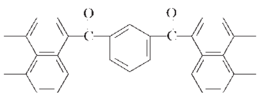
Comparison of the properties of the polyimides listed in **Table 5.7** demonstrates that polyimides based on 3,5-diaminodiphenylsulfone have much lower reduced viscosity when compared with the related polyimide based on 3,5-diaminodiphenylsulfide. This difference is probably due to the negative influence of the electron-withdrawing phenylsulfone group on the nucleophilic reactivity of the amino groups.

Polyimides based on 3,5-diaminodiphenylsulfide demonstrate that solubility in organic solvents strongly depends on the nature of the dianhydride used: polymers based on dianhydride 6F and dianhydride A are soluble in NMP, chloroform and acetone; polyimides based on diphenyloxide-3,3′,4,4′-tetracarboxylic and benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydrides are soluble in NMP only. Polyimides demonstrate high η_{red} in NMP (0.79–1.20 dl/g) and moderate (210–250 °C) T_g values combined with high (400–460 °C) T_{degr}.

Incorporation of additional methyl groups in such polyimides was realised using 2-methyl-3,5-diaminodiphenylsulfide as starting compound [42, 43].

Table 5.6. Properties of polynaphthylimides and polyperylenimides of the general formula:

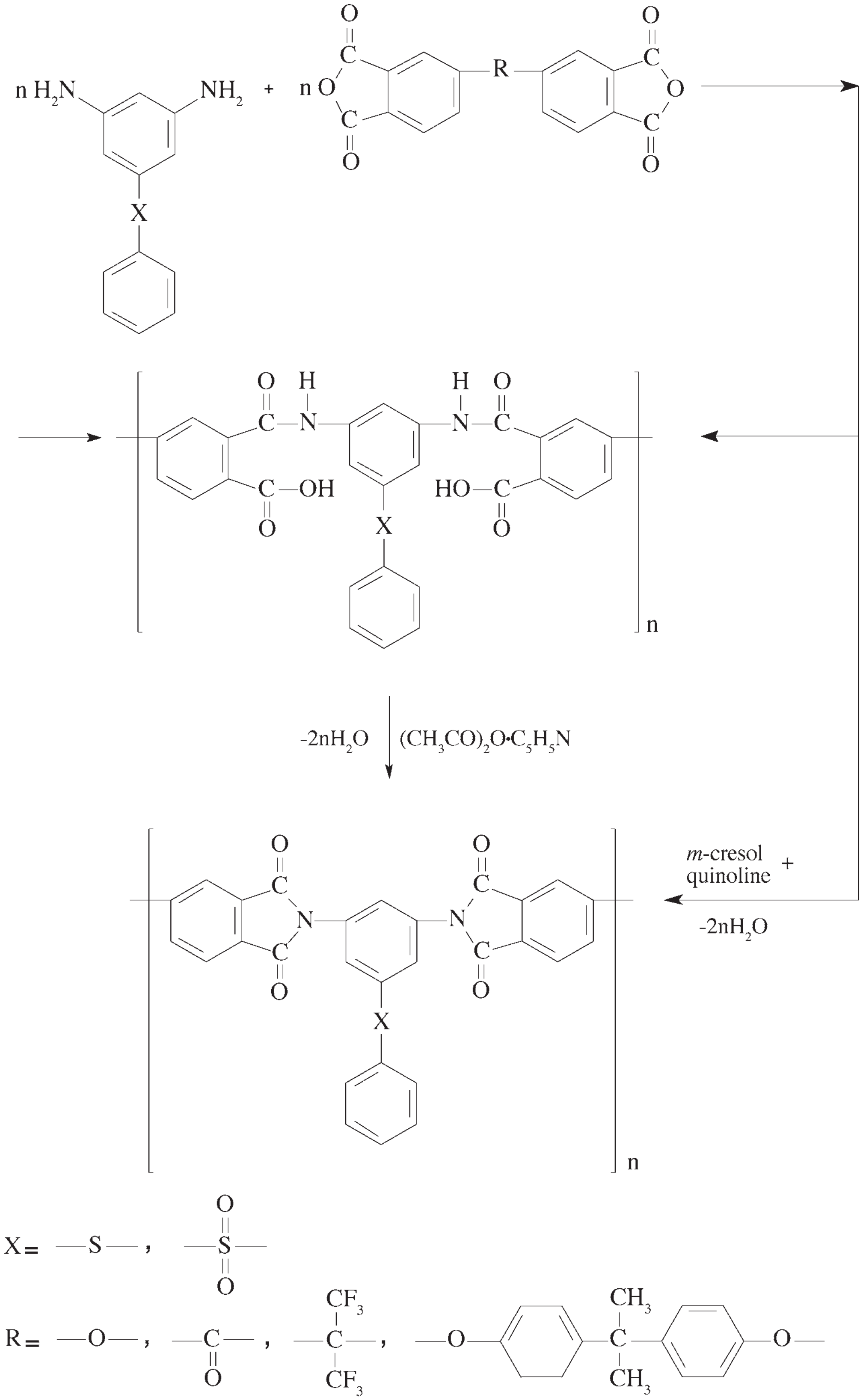


–X–		η_{red} (TCE/phenol), dl/g	T_g, C	T_{degr} (5%), °C	Solubility			
					NMP	TCE/phenol	DMF	$CHCl_3$
—		0.23	-	-	ins	s	ins	ins
—		0.20	—	500	s	s	ins	ins
—		0.89	315	470	ps	s	ins	ins
		0.23	—	475	ps	s	ins	ins
		0.37	260	480	s	s	s	ins
		0.45	250	480	s	s	s	s

s: soluble; ins: insoluble; ps: partially soluble.

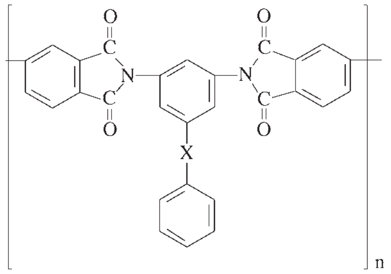
Interaction of 2-methyl-3,5-diaminodiphenylsulfide with aromatic tetracarboxylic acid dianhydrides was carried out in accordance with **Scheme 5.6**. Synthesis of the polyimides was carried out using two general procedures:

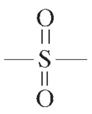
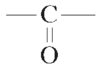
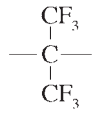
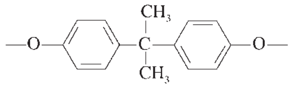
- Room temperature interaction of the diamines and tetracarboxylic acid dianhydrides, in NMP, leading to the formation of poly(*o*-carboxy)-amides followed by catalytic imidisation of these polymers with pyridine–acetic anhydride complex.
- High-temperature (160–180 °C) polycyclocondensation of the starting monomers in *m*-cresol, using quinoline as catalyst. In almost all cases polyimides obtained in *m*-cresol demonstrated higher solution viscosities than the same polymers synthesised in NMP.


n H₂N
NH₂
+
n O
R
X
H
OH
HO
n
-2nH₂O
(CH₃CO)₂O·C₅H₅N
m-cresol
quinoline
+
-2nH₂O
X =
S
R =
CF₃
CH₃

Scheme 5.5

Table 5.7. Some properties of polyimides of the general formula:

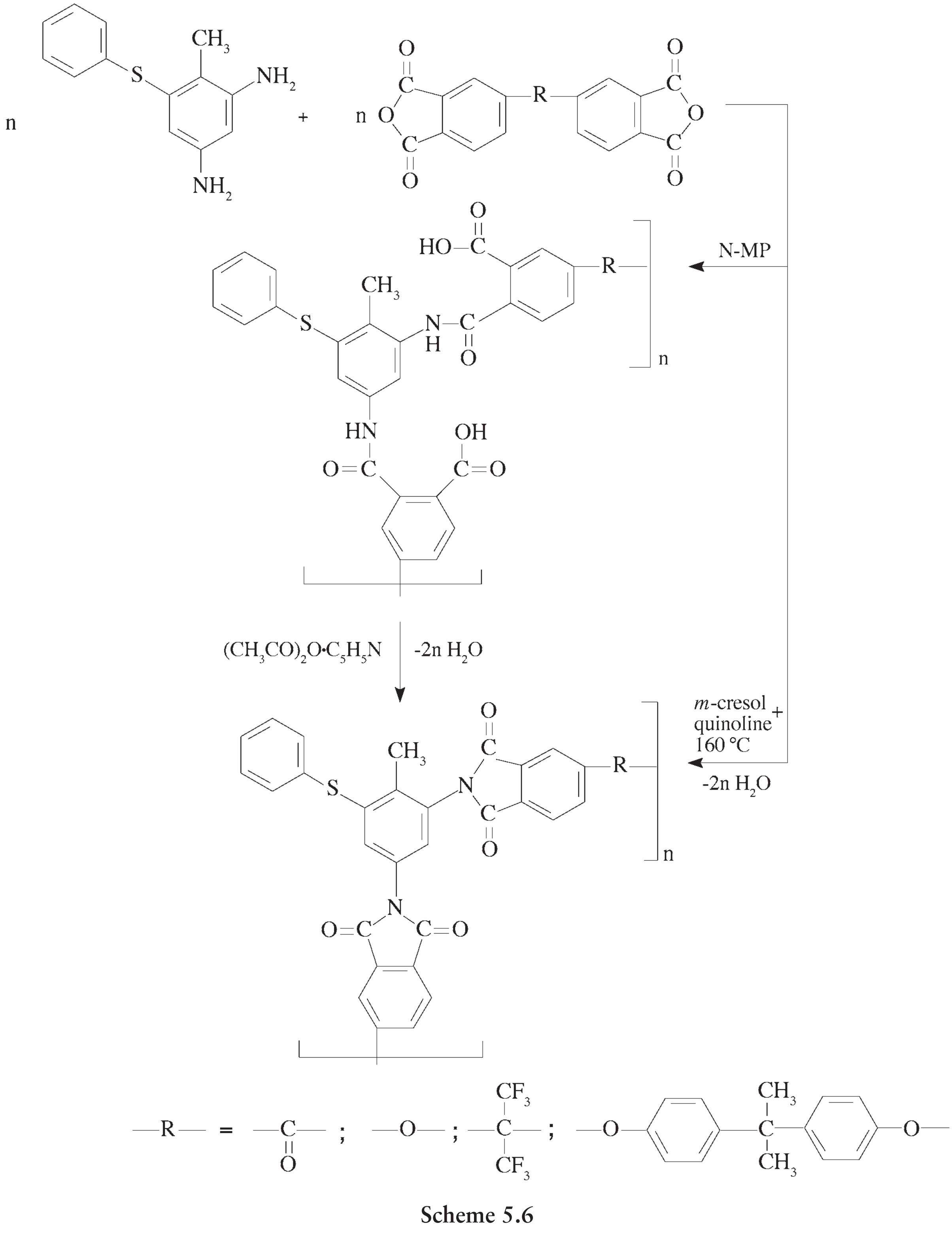


–X–	–R–	η_{red} (25 °C), dl/g	$T_{10\%}$, °C	T_g, °C	Solubility			
					NMP	THF	$CHCl_3$	Acetone
 $-SO_2-$	—O—	0.25	420	268	s	ins	ins	ins
—S—	—O—	1.20	400	240	s	ins	ins	ins
—S—	 $-C(=O)-$	0.90	460	250	s	ins	ins	ins
—S—	 $-C(CF_3)_2-$	0.79	415	220	s	s	ins	s
—S—		0.87	425	210	s	s	s	ins

The general properties of the polyimides obtained (calculated and experimentally determined) are given in **Table 5.8**.

Comparison of these properties with the properties of the polyimides prepared on the basis of 3,5-diaminodiphenyl sulfide [40, 39] indicates that polyimides containing additional methyl groups demonstrate better solubility. All polyimides tested show solubility in NMP, DMF and *m*-cresol. Moreover, the polyimide based on dianhydride 6F shows solubility in THF, cyclohexanone, methylene chloride, butyrolactone and even acetone. The polyimides based on dianhydride A exhibit almost the same solubility. These polymers form transparent films when cast from chloroform solutions. The T_g of the synthesised polyimides lie in the range 250–285 °C. These values are somewhat higher than those of polyimides lacking methyl groups. In contrast, the T_{degr} of polyimides based on 3,5-diaminodiphenyl sulfide are lower (310–370 °C) than those of polyimides lacking methyl groups [41, 42].

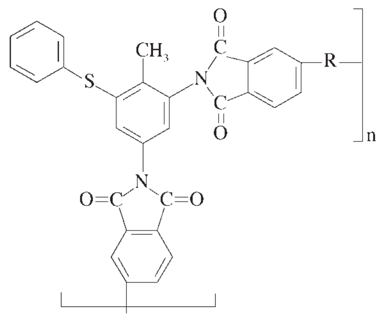
Synthesis of polyimides containing benzothiazole-2-sulfide groups was carried out using high-temperature polycyclocondensation in *m*-cresol in accordance with **Scheme 5.7** [41, 44]. All the polyimide synthesis reactions were homogeneous and yielded polymers having reduced viscosities η_{red} = 0.29–0.42 dl/g, T_g = 215–265 °C and 10% weight loss temperature = 325–400 °C (**Table 5.9**).

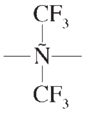
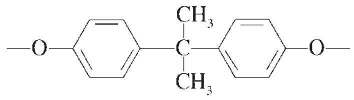


Scheme 5.6

All the resulting polyimides were soluble in NMP; polyimides based on dianhydride A were also soluble in THF, while polyimides derived from dianhydride 6F showed solubility in THF and chloroform. A positive influence of benzothiazole-2-yl side groups on polymer solubility was also reported in the literature [45, 46].

Table 5.8. Calculated and experimentally determined properties of polyimides of the general formula:



–R–	η_{red}, 25 °C, dl/g	T_g, °C/ T_g, °C^a	Solubility		CTE	ε	RI
			$CHCl_3$	NMP			
 $C=O$	1.10	285/288	ins	s	1.71	3.27	1.64
—O—	0.69	275/262	s	s	1.79	3.25	1.64
 $-N(CF_3)-$ with CF_3 above and below	0.65	250/268	s	s	1.77	2.98	1.59
	0.80	250/225	s	s	1.92	3.05	1.65

CTE: coefficient of thermal expansion

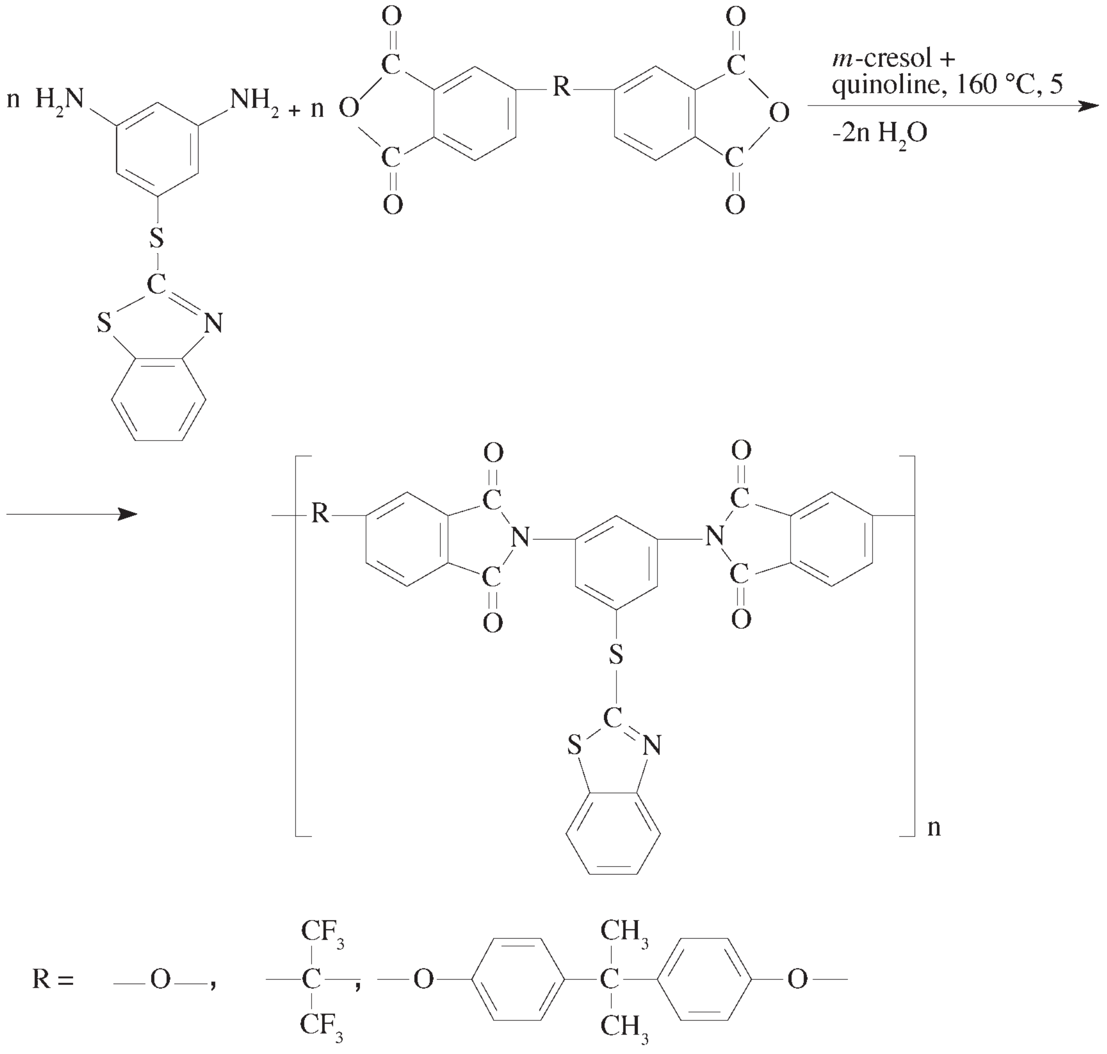
Polyimides containing *N*-phthalimido and methyl side groups were prepared by the interaction of 2,4-diamino-6-(*N*-phthalimido)-toluene with different aromatic tetracarboxylic acid dianhydrides [47] (**Scheme 5.8**).

2,4-Diamino-6-(*N*-phthalimido)-toluene was reacted with aromatic tetracarboxylic acids, 3,3′,4,4′-tetracarboxydiphenyl ether, 3,3′,4,4′-tetracarboxybenzophenone and dianhydrides, dianhydride 6F and dianhydride A, using high-temperature polycondensation in *m*-cresol with quinoline as a catalyst (**Scheme 5.8**).

The synthesis of polyimides proceeded under homogeneous conditions and led to the formation of products free (according to infrared spectroscopy) of noncyclised fragments. Some characteristics of the synthesised polyimides are listed in **Table 5.10**.

All the polyimides show solubility in NMP, *m*-cresol and BL. Moreover, all polyimides, except for that based on 3,3′,4,4′-tetracarboxydiphenyl ether, are soluble in THF, chloroform and CH, while polyimides derived from dianhydride 6F also show solubility in acetone. This fact is explained by the presence of *N*-phthalimide and methyl substituents, *m*-phenylene fragments and hexafluoroisopropylidene groups, as well as by the mild conditions of the synthesis.

As demonstrated by differential scanning calorimetry (DSC) and thermomechanical measurements, the T_g of polyimides range from 275 to 360 °C; temperatures corresponding to a 10% weight loss



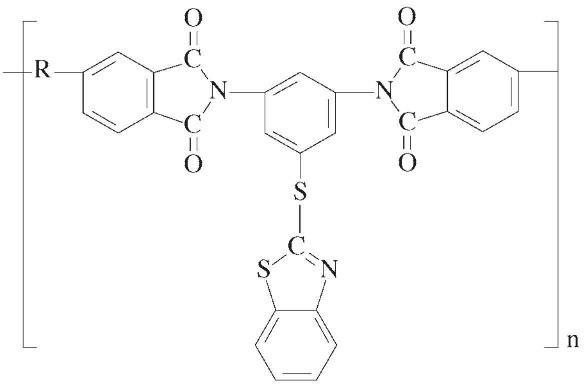
Scheme 5.7

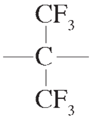
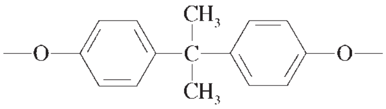
vary in the range 415–465 °C (according to the thermogravimetric analysis data in air; ΔT = 4.5 K/min). These results are summarised in **Table 5.10**.

Polymers of different isomeric structures were prepared on the basis of 2,4,6-triaminotoluene (TAT) – the simplest TNT derivative [48]. As this compound is trifunctional, at least one amino group must be blocked before the polycondensation reaction to avoid gelation. Preparation of the polyimides was carried out using the following approaches:

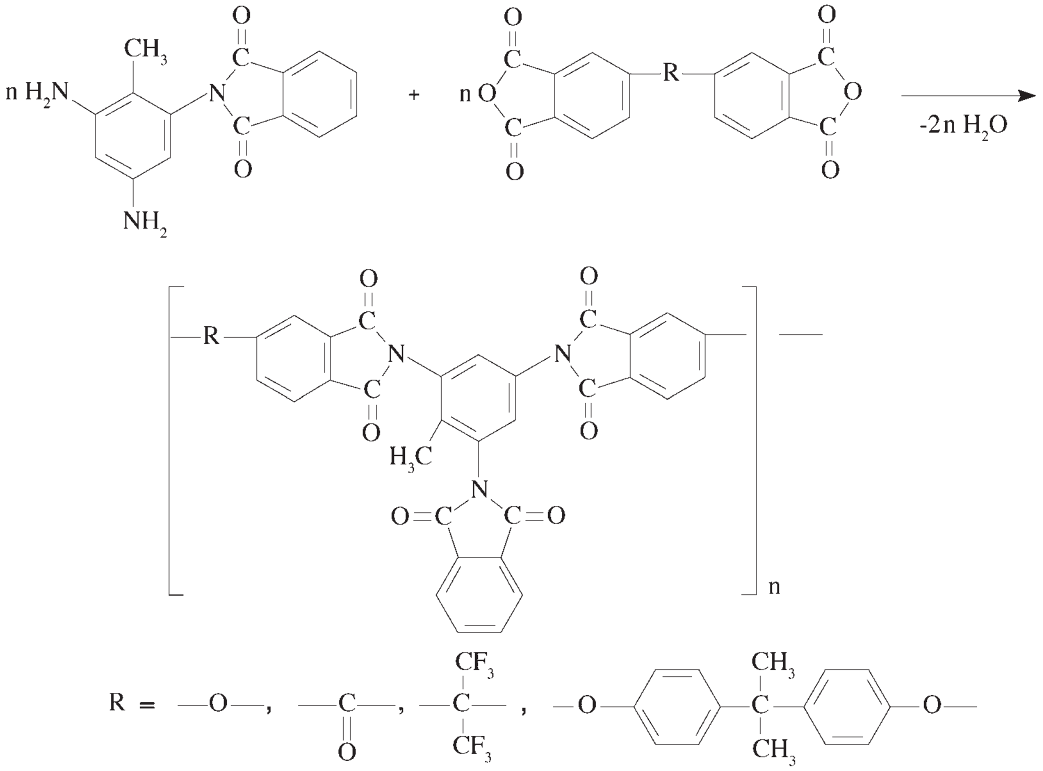
- low-temperature treatment of TAT with equimolar amount of phthalic anhydride leading to the formation of isomeric monobenzoyl-TAT (mainly),
- low-temperature treatment of the monobenzoyl-TAT thus formed with equimolar amounts of bis(phthalic anhydrides), and
- chemical imidisation of the polyamic acids containing amic acid side groups leading to the target polyimides containing *N*-phthalimide and methyl side groups (**Scheme 5.9**).

Table 5.9. Some characteristics of polyimides of the general formula:



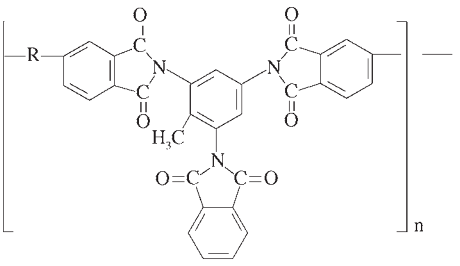
–R–	η_{red} (25 °C), dl/g	T_g, °C	$T_{10\%}$[a], °C
—O—	0.29	240	400
 $-\overset{CF_3}{\underset{CF_3}{C}}-$	0.34	265	400
	0.42	215	320

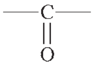
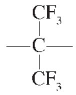
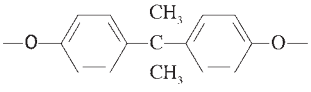
[a] *Dynamic TGA, in air; the rate of heating was 4.5 K/min.*



Scheme 5.8

Table 5.10. Some characteristics of polyimides of the general formula:



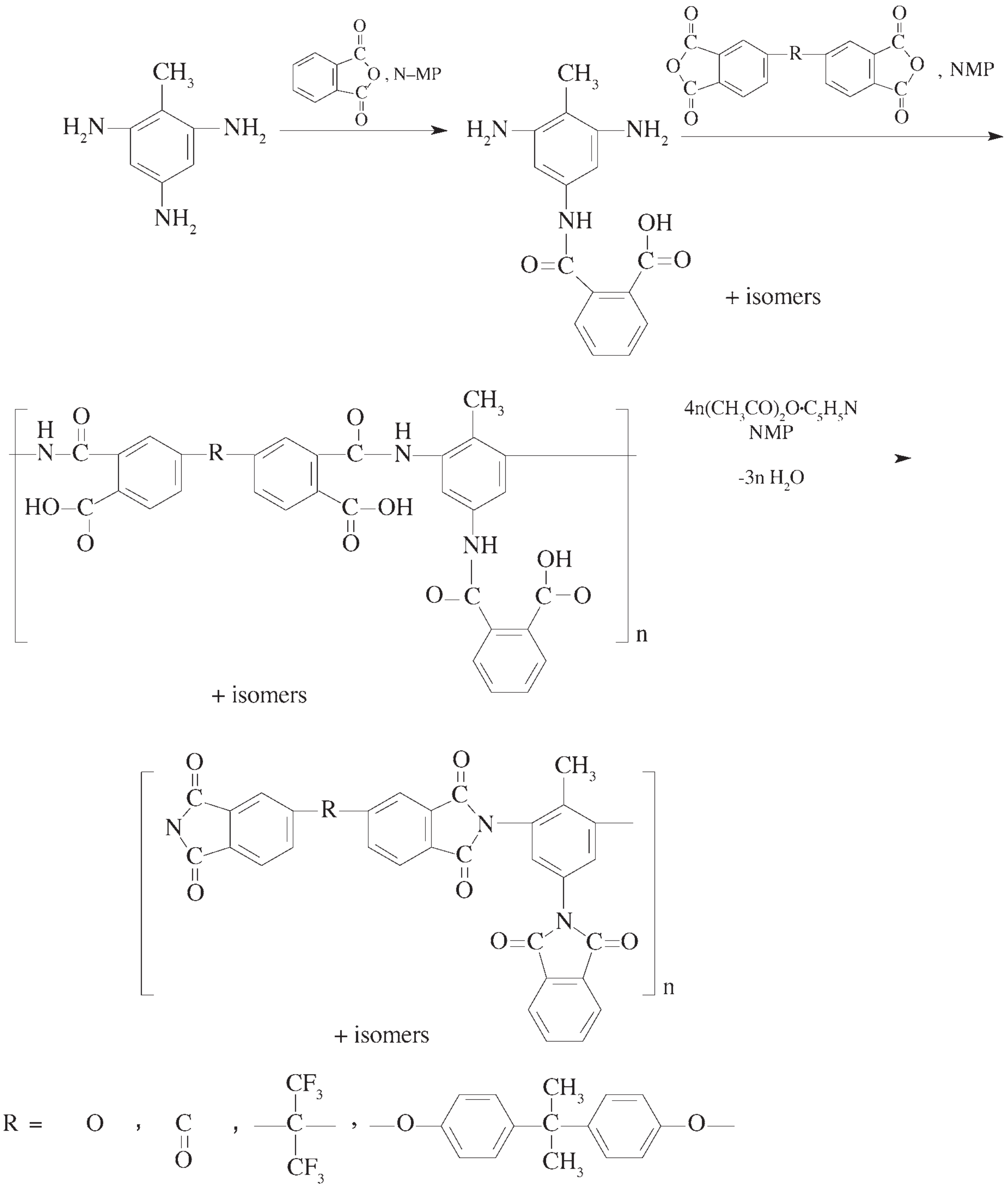
–R–	η_{red} (25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	Solubility		
				Acetone	$CHCl_3$	THF
—O—	0.18	330	430	ins	ins	ins
 $-\underset{\displaystyle O}{\underset{\|}{C}}-$	0.32	360	450	ins	ins	ins
 $-\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}-$	0.25	350	415	s	–	s
	0.37	275	465	ins	s	s

All stages of these polyimide syntheses proceeded homogeneously and led to the formation of organo-soluble polyimides free (infrared spectroscopy) of noncyclised units. General properties of the organo-soluble methyl- and *N*-phthalimide-substituted polyimides are given in **Table 5.11**.

All polyimides obtained dissolved readily in NMP, DMF and TCE/phenol (3:1). The good solubility of these polyimides is due to the presence of methyl and *N*-phthalimide side groups in their macromolecules, the presence of different isomers and mild catalytic imidisation conditions.

Aromatic polyimides containing perfluorotolyloxy side groups were prepared by the interaction of 3,5-diamino-4-methyl-2′,3′,5′,6′-tetrafluoromethyldiphenyl ether with different aromatic tetracarboxylic acid dianhydrides [49] in accordance with **Scheme 5.10**. All polyimides shown in **Scheme 5.10** were prepared using high-temperature (160 °C, 4 hours) solution polycondensation in *m*-cresol using quinoline as catalyst. All reactions proceeded homogeneously leading to the formation of high molecular weight polyimides completely soluble in NMP, chloroform, acetone, etc. General properties of the polyimides obtained are listed in **Table 5.12**.

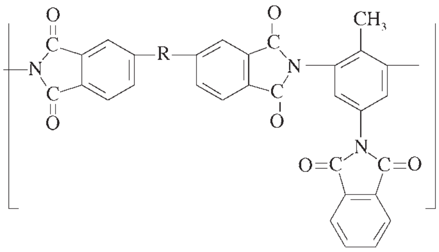
The glass transition temperatures of the polyimides are 195–250 °C; their 10% weight loss temperatures (dynamic thermogravimetric analysis, air, ΔT = 4.5 °C/min) are 390–422 °C. Of particular interest are the dielectric constants of these polyimides. At a relative humidity of 50% these constants are 2.70–2.90 and are comparable with constants of the best fluorinated polyimides [21, 50–55]. The lowest dielectric constant (2.70) was observed for polyimide based on 6F dianhydride, containing the highest amount of fluorine. Thermal treatment of this polymer film at 280–290 °C for 1 hour led to a decrease (2.45) of dielectric constant due to the possible formation of nanofoams [56].

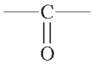
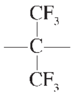
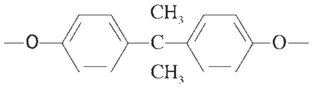


Scheme 5.9

Along with the synthesis of polyimides containing non-reactive substituents based on TNT derivatives, polyimides have been prepared containing functionalised side groups and, first of all, hydroxylic groups [57, 58]. In recent years, polyimides bearing free hydroxyl groups have attracted considerable attention [59–64]. Their ability to form hydrogen bonds leads to an increase in their glass transition temperatures, renders them soluble in amide solvents and enhances their moisture adsorption [61]. This latter factor opens the possibility of preparing membranes based on these polymers [61].

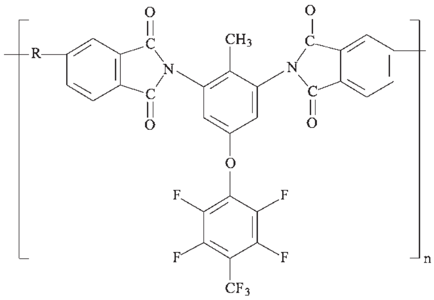
Table 5.11. General properties of aromatic polyimides of the general formula:

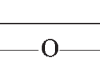
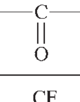
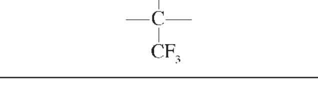


–R–	η_{red} (NMP, 25 °C), dl/g	M_w[a]	T_g, °C	$T_{10\%}$, °C
–O–	0.30	105,000	340	400
 $-\overset{\Large O}{\overset{\|\|}{C}}-$	0.30	105,000	340	420
 $-C(CF_3)_2-$	0.28	-	350	400
	0.17	-	270	410

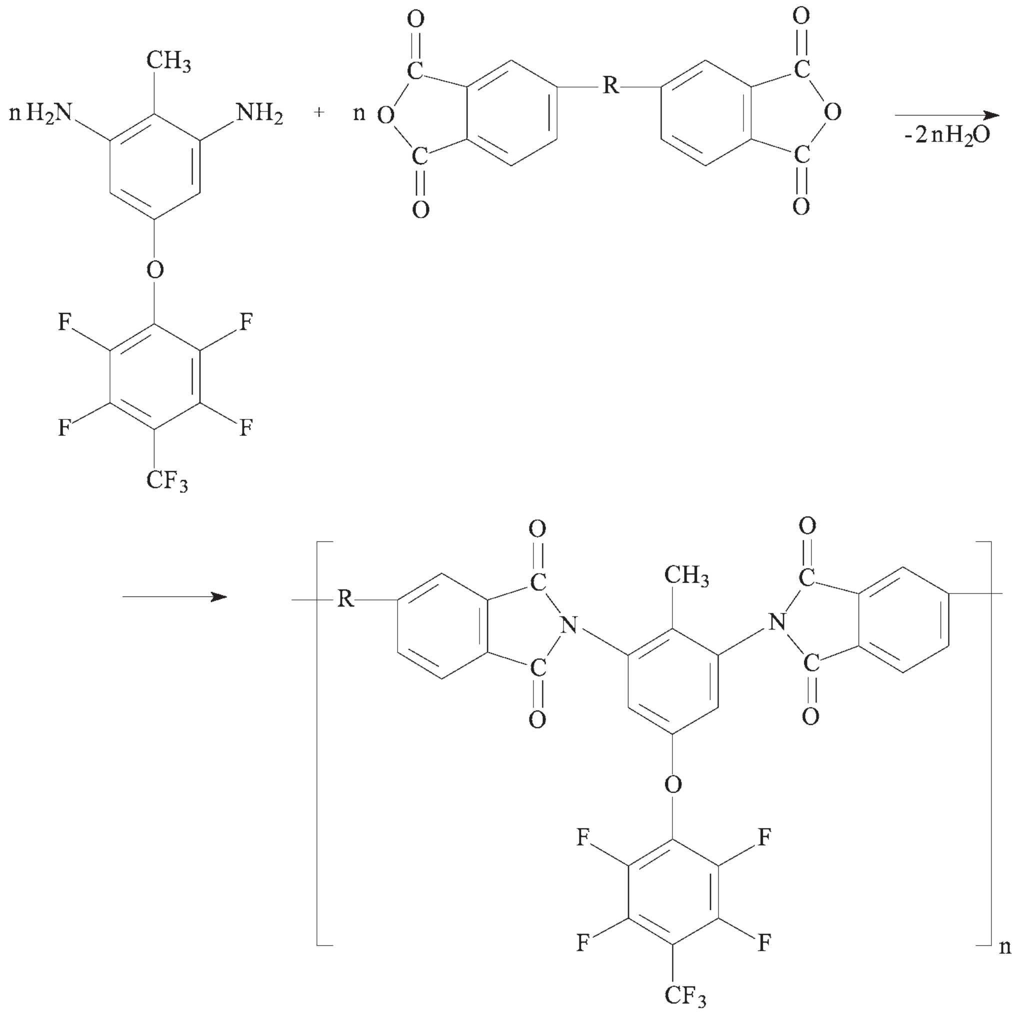
[a] *Molecular weights determined using sedimentation method in NMP.*

Table 5.12. Some characteristics of polyimides of the general formula:



–R–	η_{red} (NMP, 25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	ε (RH = 50%)
–O–	0.50	210	400	2.85
 $-\overset{\Large O}{\overset{\|\|}{C}}-$	0.40	230	390	2.90
 $-C(CF_3)_2-$	0.44	250	396	2.70
	0.63	195	422	2.80

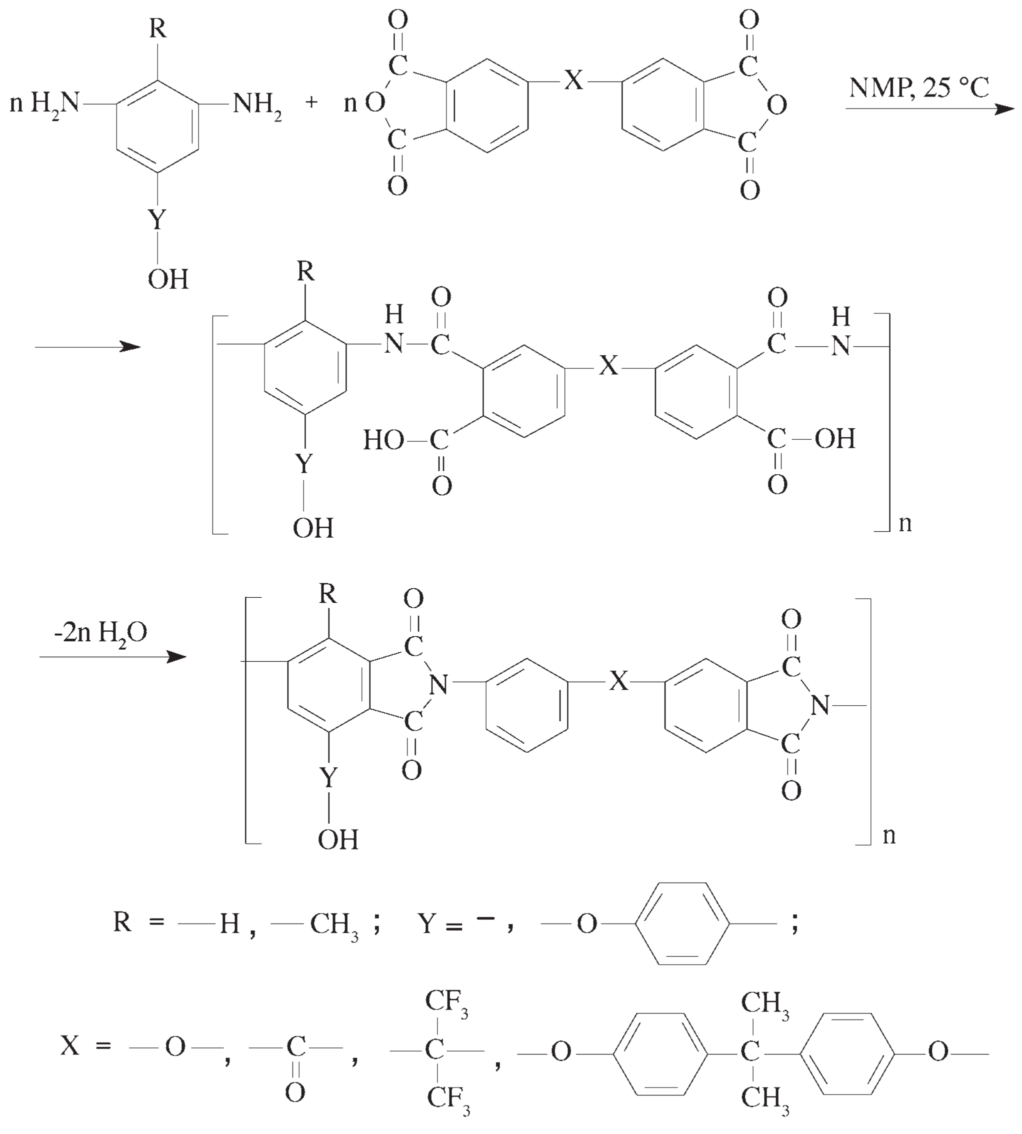
RH = Relative humidity.



Scheme 5.10

In addition, phenolic hydroxyl groups can be used as reactive sites to introduce other side groups: unsaturated substituents capable of forming 'crosslinked' structures [62], chromophores imparting nonlinear optical properties [65–67] and thermally unstable side groups, which can undergo thermal degradation to form 'nanofoams' exhibiting low dielectric permittivity [55–68].

Polyimides based on 3,5-diamino-4′-hydroxydiphenyl ether, 2,6-diamino-*p*-cresol and tetracarboxylic acid dianhydrides were prepared according to **Scheme 5.11**. Polyimides were synthesised via a two-stage route. In the first stage, PCA were prepared by the mild (25 °C) reaction in NMP. To prevent acylation of hydroxyl groups of polyimides, the second stage, polycyclisation of PCA, was carried out without imidisation catalysts, for example, a pyridine–acetic anhydride complex. After toluene was added to the reaction solutions of PCA (for azeotropic distillation of water), the temperature was raised to 180 ± 10 °C, and the solutions were allowed to stand for 6 ± 1 h. Note that, recently, this method for the synthesis of polyimides has received wide acceptance [27, 68, 69]. For all aromatic tetracarboxylic acid dianhydrides the reactions of PCA cyclisation were homogeneous and yielded polyimides with moderate viscosities (**Table 5.13**) and high cyclisation degrees.



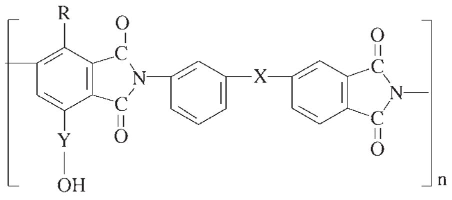
Scheme 5.11

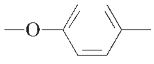
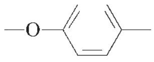
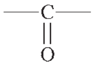
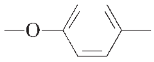
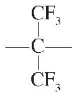
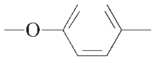
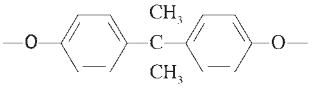
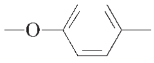
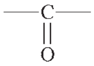
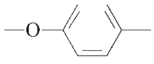
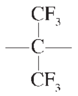
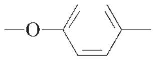
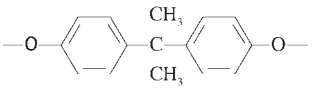
All the synthesised polyimides are amorphous polymers with T_g in the range 223–320 °C, which is typical for flexible-chain polyimides [70], and their T_{degr} lie in the range 350–439 °C (**Table 5.13**). The polyimides are soluble (**Table 5.13**), the polymers based on the dianhydride of 1,1,1,3,3,3-hexafluoro-2,2-bis(3,4-dicarboxyphenyl)-propane showing the highest solubility.

Polyimides based on 2,6-diamino-*p*-cresol were acylated with acryloylchloride [71, 72] to impart photosensitivity to these polymers. The acylation was carried out in accordance with **Scheme 5.12**. The extent of esterification of hydroxyl groups, as determined by ^{1}H-NMR spectroscopy, ranged from 60 to 40% for various polyimides (**Table 5.14**).

All the acylated polyimides retained solubility in organic solvents. This gave us reason to believe that photopolymerisation via the double bonds of polyimides could be conducted by the method of differential scanning photocalorimetry. This method, which is widely covered in the literature [73–76], is based on on the principle that heat released during any reaction can be measured.

Table 5.13. Some characteristics of polyimides of the general formula:

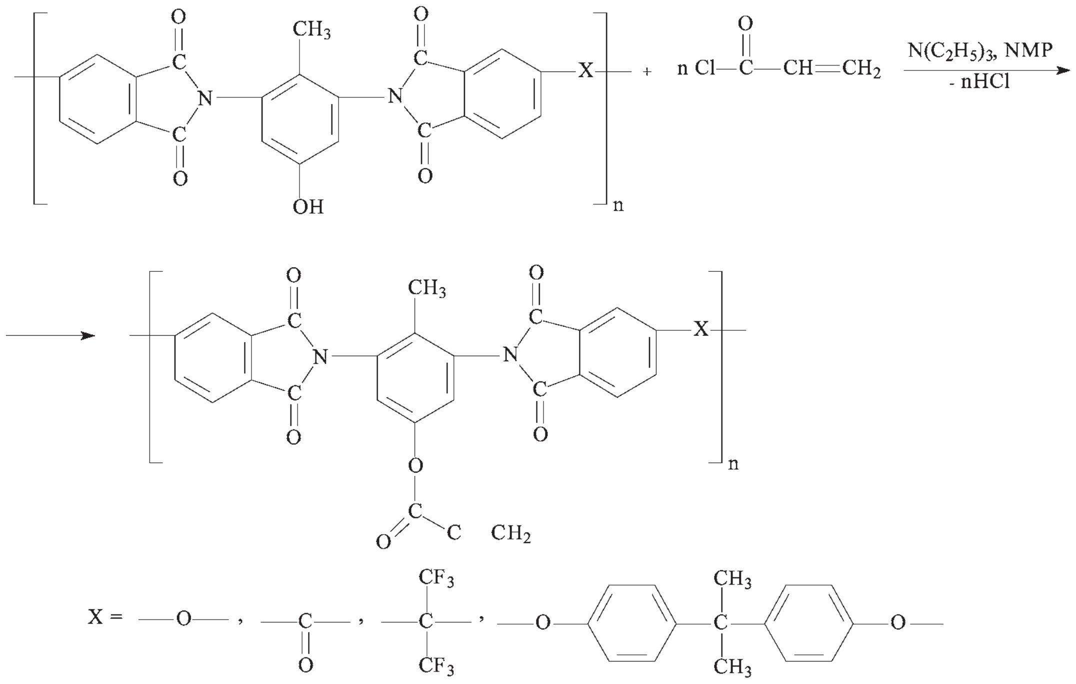


–R	–Y–	–X–	η_{red} (NMP, 25 °C), dl/g	T_g, °C	$T_{10\%}$, °C	Solubility		
						NMP	DMF	DMSO
–H		—O—	0.12	251	425	s	sw	s
–H		 $-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	0.58	277	439	s	sw	sw
–H		 $-C(CF_3)_2-$	0.28	282	427	s	s	s
–H			0.46	223	378	s	s	s
$-CH_3$	–	—O—	0.66	320	350	s	s	s
$-CH_3$		 $-\overset{\displaystyle O}{\overset{\Vert}{C}}-$	0.80	360	390	s	s	
$-CH_3$		 $-C(CF_3)_2-$	0.44	370	390	s	s	s
$-CH_3$			0.67	248	400	s	s	s

s: soluble; sw: swelling
DMSO: dimethylsulfoxide

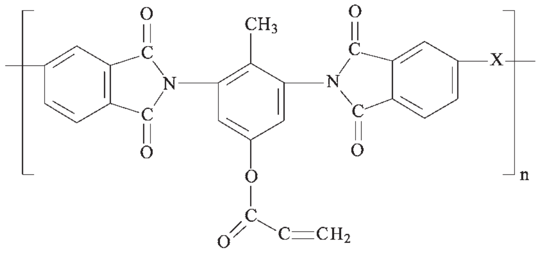
As a radical photoinitiator, we used 2-hydroxyisopropyl phenyl ketone (DAROCUR 1173; Ciba-Geigy), taken in an amount of 3 wt% based on polyimide (**Scheme 5.13**). The pattern of an exotherm obtained for the 1% solution of the polyimide (–X– = –O–), the high value of polymerisation enthalpy (352.4 J/g) and the short times of attaining the maximum peak (4.4 s) and the induction time (2.4 s) allow us to consider that this polyimide to be rather reactive from the point of view of polymerisation and formation of a crosslinked structure.

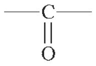
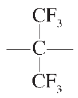
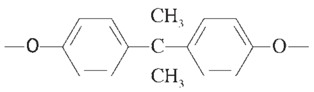
The increased activity of the polymer in photocrosslinking is apparently due to the maximum, in this row, extent of esterification of hydroxyl protons of the starting polyimide, as well as higher, compared to the other polyimides, chain flexibility due to the presence of an oxygen ‘bridge’.



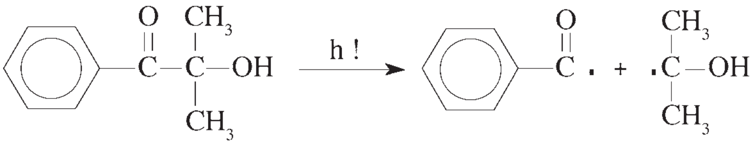
Scheme 5.12

Table 5.14. Extent of esterification and solubility of polyimides of the general formula:



–X–	Extent of esterification, %	Solubility		
		NMP	BL	CH
$-O-$	60	s	s	ins
 $-\underset{\underset{O}{\|}}{C}-$	50	s	s	ins
 $-\underset{CF_3}{\overset{CF_3}{C}}-$	45	s	s	s
 $-O-C_6H_4-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_4-O-$	40	s	s	s

s: soluble, ins: insoluble



Scheme 5.13

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6

Conclusion

The variety of ways in which chloral and trinitrotoluene (TNT) derivatives can be used to prepare novel polyimides and polymeric materials is very promising. The use of chloral and TNT derivatives allows for the synthesis of a large number of monomers which, in turn, can impart a variety of useful properties to their respective polymers. The possibility of preparing, from available raw materials, high-molecular-weight compounds with increased heat and thermal resistance in combination with improved solubility and, consequently, easiness of processing is especially attractive and may provide impetus for further work in this field.

Abbreviations

ε	Dielectric constant
^{1}H-NMR	Proton nuclear magnetic resonance
BL	Butyrolactone
CH	Cyclohexanone
CTE	Coefficient of thermal expansion
DDT	Dichlorodiphenyl-trichoroethane
DMA	*N*,*N*-dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
LOI	Limiting oxygen index
MC	*m*-Cresol
M_w	Molecular weight
NMP	N-methyl-pyrrolidone
OI	Oxygen index
PCA	Poly-(*o*-carboxy)-amide(s)
RH	Relative humidity
RI	Refractive Indices
TAT	Triaminotoluene(s)
TCE	Trichloroethane
T_{degr}	Degradation temperature
T_g	Glass transition temperature(s)
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TNB	Trintrobenzene
TNT	Trinitrotoluene

Subject Index

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ISBN: 978-1-84735-058-9

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