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Polymer 41 (2000) 5021–5037

polymer

New condensation aromatic polymers containing phenoxy, thiophenoxy, and phenylsulphone side groups

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Received 27 September 1998; received in revised form 7 April 1999; accepted 12 April 1999

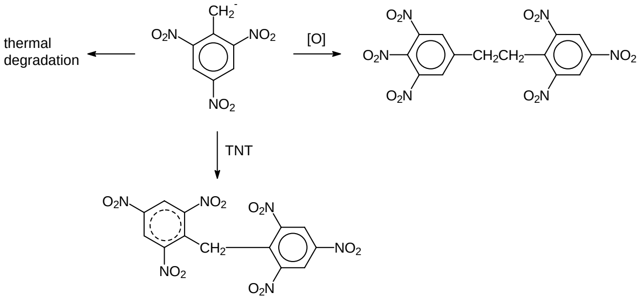
Abstract

New condensation monomers—primarily diamines containing phenoxy, thiophenoxy and phenylsulphone substituents were obtained from 2,4,6-trinitrotoluene (TNT). Interaction of some dinitro compounds containing strong electron-withdrawing groups in *meta*-positions with bis-phenols under conditions of aromatic nucleophilic polynitro substitution reactions led to the formation of aromatic oligoethers. Based on aromatic diamines containing phenoxy and thiophenoxy substituents under conditions of traditional polycondensation and polycyclo condensation reactions, aromatic polyamides and polyimides demonstrating improved processability combined with high thermal stability were obtained. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: 2,4,6-trinitrotoluene; Polyimides; Oligoethers

1. Introduction

Aromatic condensation polymers containing bulky aromatic side groups are of great interest because of their improved solubility in organic solvents and, as a result, improved processability [1–7]. Usually for the preparation of substituted polyamides [1,2,7] and polybenzobisazoles [4,5] substituted dicarboxylic acids or their derivatives are used. Very few works were done on the preparation of the substituted condensation polymers from substituted diamines [3,6]. Some of these diamines [6] are rather unavailable and based on expensive starting materials. On the contrary, a large variety of substituted diamines may be obtained starting with TNT—a major explosive component of ammunition liable to liquidation [8]. 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 [9,10] 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 takes place:



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 turned from TNT to the product of its demethylation—1,3,5-trinitrobenzene (TNB).

TNT demethylation has been described previously [11,12] and different demethylation variants are technologically acceptable; the most important is a process including oxidation of the methyl group and subsequent decarboxylation

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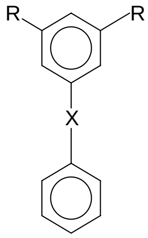
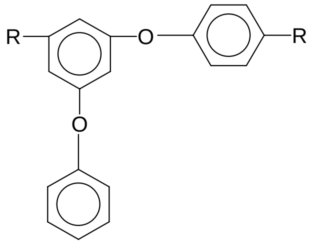
PII: S0032-3861(99)00564-9

Table 1
Yields and some properties of the dinitro compounds and diamines of general formula



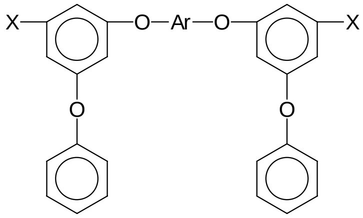
–X–	–R	M.p. (°C)	Yield (%)	^{1}H NMR (ppm) (DMSO-d_6)	Elementary analysis	
					Calculated (%)	Found (%)
–O–	–NO_2	119.5–120.5	75	8.71(t,1H), 8.09 (d,2H) 7.49(tm,2H), 7.33(tm,1H) 7.13 (dm,2H)	C 55.39 H 3.10 N 10.77	C 55.80 H 3.20 N 10.90
–O–	–NH_2	92–93.5	63	7.33(t,2H), 7.04(t,1H), 6.93(d,2H), 5.60(t,H), 5.44(d,2H), 4.85(br s, 4H).	C 71.98 H 6.04 N 13.99	C 71.90 H 6.14 N 14.13
–S–	–NO_2	97–98	89	8.58(t,1H),.23(d,2H), 7.63(m,2H), 7.57(m,3H).	C 52.17 H 2.92 N 10.14 S 11.60	C 52.28 H 3.02 N 10.35 S 11.47
–S–	–NH_2	59.5–60.5	68	7.26(m,5H), 5.83(d,2H), 5.76(t,1H), 4.91(br.m.,4H)	C 6.64 H 5.59 N 12.95 S 14.82	C 6.95 H 5.83 N 13.18 S 14.66
–SO_2–	–NO_2	167.5	93	9.07(t,1H),.96(d,2H), 8.17(m 2H),7.76(m,3H)	C.46.76 H 2.62 N 19.09 S 10.40	C 47.16 H 2.95 N 9.35 S 10.08
–SO_2–	–NH2	209–210	80	7.84(m,4H), 7.62(m,3H), 6.33(d,2H), 5.99(T,1H), 5.20(yIII.c.4H).	C 58.05 H 4.87 N 11.28 S 12.91	C 58.52 H 5.08 N 11.57 S 12.67

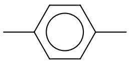
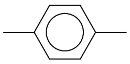
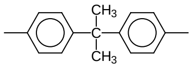
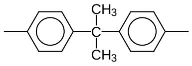
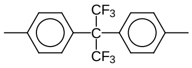
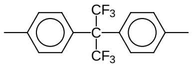
Table 2
Yields and some properties of the compounds of general formula



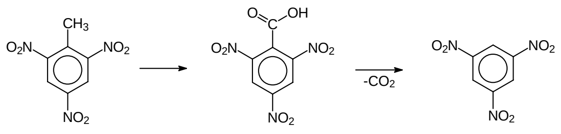
–R	–R′	M.p. (°C)	Yield (%)	^{1}H NMR (ppm) (DMSO-d_6)	Elementary analysis	
					Calculated (%)	Found (%)
–NO_2	–NH–C(O) CH_3	146–147	71	10.06(br s, 1H), 7.66 (d, 2H), 7.47 (t, 2H), 7.33 (t, 2H), 7.26 (t, 1H), 7.16 (d, 2H), 7.02 (t, 1H), 2.05 (s, 3H)	C 66.99 H 4.43 N 7.70	C 65.71 H 4.40 N 7.54
–NO_2	–NH_2	114–115	89	7.44 (t, 2H), 7.30–7.19 (m, 3H), 7.13 (d, 2H), 6.91 (t, 1H), 6.85 (d, 2H), 5.11 (br s, 2H)	C 67.14 H 4.38 N 8.70	C 67.19 H 4.22 N 8.70
–NH_2	NH_2	79–80	69	7.36 (t, 2H), 7.09 (t, 1H), 6.99 (d, 2H), 6.74 (d, 2H), 6.56 (d, 2H), 5.81 (d, 2H) 5.66 (t, 1H), 5.24 (br s 2H), 4.90 (br s 2H)	C 74.04 H 5.52 N 9.59	C 73.81 H 5.41 N 9.39

Table 3
Yields and some properties of aromatic dinitrocompounds and diamines of general formula



–Ar–	–X	M.p. (°C)	Yield (%)	Elementary analysis	
				Calculated %	Found %
	$-NO_2$	149–150	62	C 67.24 H 3.76 N 5.23	C 67.00 H 3.76 N 5.00
	$-NH_2$	141–142	83	C 75.70 H 5.08 N 5.90	C 75.56 H 4.96 N 5.63
	$-NO_2$	110	54	C 71.55 H 4.62 N 4.28	C 70.96 H 4.37 N 4.12
	$-NH_2$	150	83	C 78.77 H 5.76 N 4.71	C 78.91 H 5.34 N 4.82
	$-NO_2$	58	60	C 61.42 H 3.17 N 3.99	C 61.23 H 3.19 N 3.69
	$-NH_2$	133	86	C 66.67 H 4.02 N 3.99	C 66.60 H 3.91 N 4.05

of the carboxyl group formed:



TNT

TNB

The present paper reviews some transformations of TNB into different substituted dinitrocompounds and diamines and preparation of the condensation polymers therefrom.

2. Experimental

2.1. Monomer syntheses

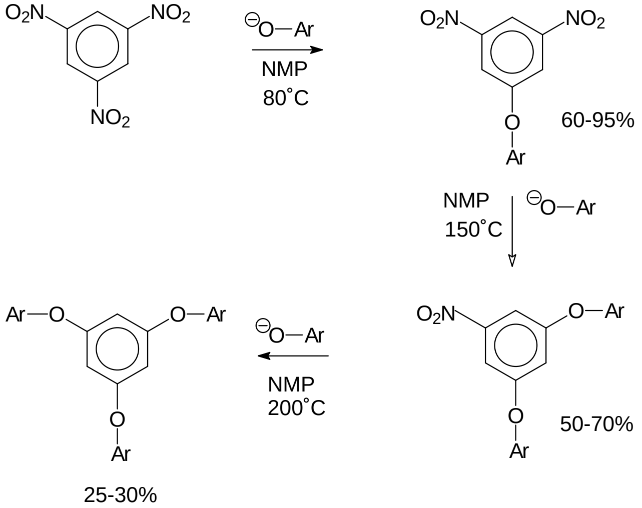
1-Substituted 3,5-dinitrobenzenes and amines were obtained in accordance with literature procedures [13–16]. Yields and properties of the dinitrocompounds and diamines are listed in Table 1.

1-Nitro-3-phenoxy-5-(4-acetamidophenoxy)benzene, 1-nitro-3-phenoxy-5-(4-aminophenoxy)benzene and 1-amino-3-phenoxy-5-(4-aminophenoxy)benzene were obtained in accordance with literature procedures [17,18]. Yields and properties of these compounds are given in Table 2.

Bis(3-nitro-5-phenoxy)diphenyl ethers of hydroquinone and bisphenols bis-(3-amino-5-phenoxy)diphenyl ethers of hydroquinone and bisphenols were obtained in accordance with literature procedures [18,19]. Yields and properties of these compounds are given in Table 3.

2.2. Aromatic dicarboxylic acid dichlorides

Terephthalic and isophthalic acid dichlorides (VNIPIM,



Scheme 1.

Tula) were distilled in vacuum. The m.p. of terephthaloyl chloride 84°C; lit. m.p. 83–84°C [20]. The m.p. of isophthaloyl chloride 43°C, lit. m.p. 42–43°C [20].

2.3. Aromatic tetracarboxylic acid dianhydrides

Pyromellitic acid dianhydride (VNIPIM, Tula) was sublimed at 220°C/4–5 × 10^{-2} Torr. The m.p. is 225,5°C; lit. m.p. 225–226°C [21].

Biphenyl-3,3′,4,4′- tetracarboxylic acid dianhydride (VNIPIM, Tula) was refluxed in acetic anhydride, washed with ether and dried. M.p. 285,5°C; lit. m.p. 286°C [22].

Benzophenone-3,3′,4,4′-tetracarboxylic acid dianhydride (VNIPIM, Tula) was sublimed at 220°C/4–5 × 10^{-2} Torr. M.p. 227°C, lit. m.p. 226–227°C [23].

Diphenyl ether-3,3′,4,4′-tetracarboxylic acid dianhydride (Oxy Chem) was sublimed at 220°C/4–5 × 10^{-2} Torr. M.p. 228,5°C; lit. m.p. 229°C [23].

1,1,1,3,3,3-Hexafluoro-2,2-bis(3,4-dicarboxyphenyl)propane dianhydride (dianhydride 6F) (Hoechst–Celanese) was used without additional purification. M.p. 246°C; lit. m.p. 246°C [24].

2,2-Bis-[4–(3,4–dicarboxyphenoxy)phenylpropane dianhydride (dianhydride A) (NIOPIC, Moscow)was used without additional purification. M.p. 189°C; lit. m.p. 189–190°C [25].

Naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (VNIPIM, Tula) was used without additional purification. M.p. 440°C; lit. m.p. 440°C [20].

Isophthaloyl-bis(naphthalic acid)dianhydride was obtained in accordance with a literature procedure [26]. M.p. 434°C; lit. m.p. 434°C [26].

2.4. Polymers synthesis

Synthesis of the oligoether was carried out in accordance with literature procedures [27,28] using NMP and Sulpholane (Aldrich) as solvents.

The polyamides were prepared using two methods:

- low-temperature solution polycondensation in NMP (method A) [29];
- low-temperature solution polycondensation in chloroform using triethylamine as HCl acceptor (method B) [29].

Method A: In a three-necked flask equipped with a mechanical stirrer, argon inlet and charging funnel was placed 1-phenoxy-3,5-diaminobenzene (2,5 mmol) and 1 ml of NMP. To the obtained solution of the dichloride (2,5 mmol) was added when cooling. After 10 min the solution became viscous; it was stirred at room temperature for 2 h and precipitated in methanol. Polymers were washed with methanol in a Soxhlet apparatus for 5 h and dried at 70°C/20 Torr.

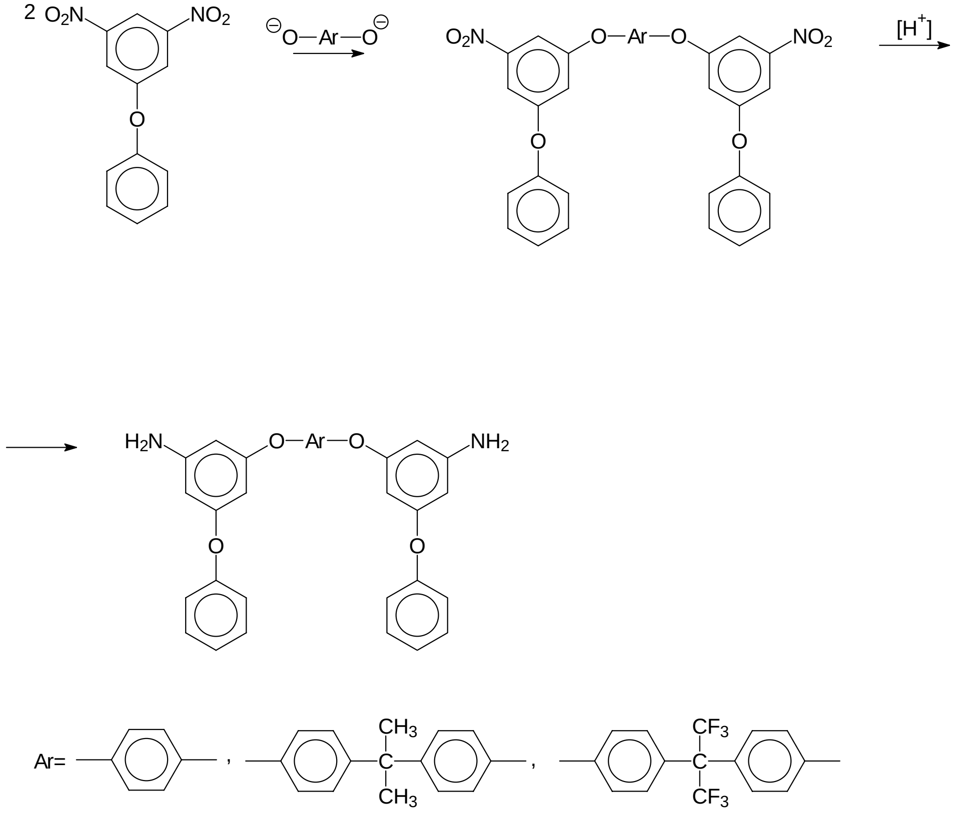
Method B: In a three-necked flask equipped with a mechanical stirrer, argon inlet and dropping funnel was placed 1-phenoxy-3,5-diaminobenzene (2,5 mmol) and 1 ml of chloroform. To the slurry formed was added, dropwise, 0.69 ml of triethylamine and a solution of the dichloride (2.5 mmol) in 1 ml of chloroform. The reaction mixture was stirred at room temperature for 2 h and poured into methanol. Polymers were washed with methanol in a Soxhlet apparatus for 5 h and dried at 70°C/20 Torr.

Synthesis of polyimide was carried out using three methods:

- low-temperature solution polycondensation in NMP, followed by catalytic imidisation of the polyamic acids formed, using pyridine: acetic anhydride (1:1) complex as catalyst (procedure A) [30];
- high-temperature solution polycondensation in NMP, using azeotrope-forming compounds (procedure B) [30];
- polycondensation in *m*-cresol using isoquinoline as catalyst (procedure C) [30].

Procedure A: In a four-necked flask equipped with a mechanical stirrer, argon inlet, charging funnel and condenser was placed the diamine (5 mmol) and NMP [(in quantity to prepare 20–25% solution of polyamic acid)]. To the solution formed was added an equimolar quantity of the aromatic tetracarboxylic acid dianhydride. The reaction mixture was stirred at room temperature for 4–5 h. To the solution obtained were added 20 mmol of acetic anhydride and pyridine. The reaction mixture was stirred at 100°C for 4 h and poured into water or methanol. The polymer was washed with methanol or acetone in a Soxhlet apparatus for 5 h and dried at 70°C/20 Torr.

Procedure B: In a four-necked flask equipped with a mechanical stirrer, thermometer, argon inlet and condenser were placed the diamine (0.01 mol) in 30 ml of NMP. To the solution obtained was added portionwise the aromatic tetracarboxylic acid dianhydride (0.01 mol). The reaction mixture was stirred at



Scheme 2.

room temperature for 24 h. After this time, 5 ml of toluene was added to the solution and heating started. At 155–160°C toluene–water azeotrope began to distill. The temperature of the reaction mixture rose to 190°C. The total reaction time was 4–5 h. The reaction mixture was cooled, diluted with NMP and poured into water. The polymers were filtered, washed with water, extracted with acetone in a Soxhlet apparatus for 5 h and dried at 70°C/20 Torr.

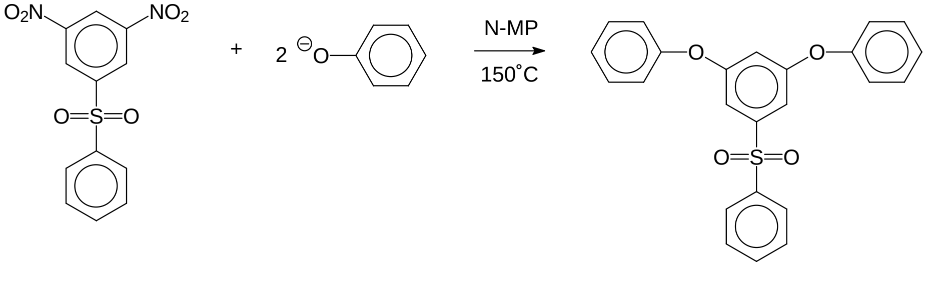
Procedure C: In a three-necked flask equipped with a mechanical stirrer, argon inlet and reflux condenser was placed the diamine (5 mmol) in 12 ml of *m*-cresol. To the solution formed were added 0.003 mmol of isoquinoline and 5 mmol of aromatic tetracarboxylic acid dianhydride. The reaction mixture was heated from 100 to 160°C over 4 h, cooled and precipitated in acetone. The polymer was filtered, washed with acetone in a Soxhlet apparatus for 5 h and dried at 70°C/20 Torr.

3. Results and discussion

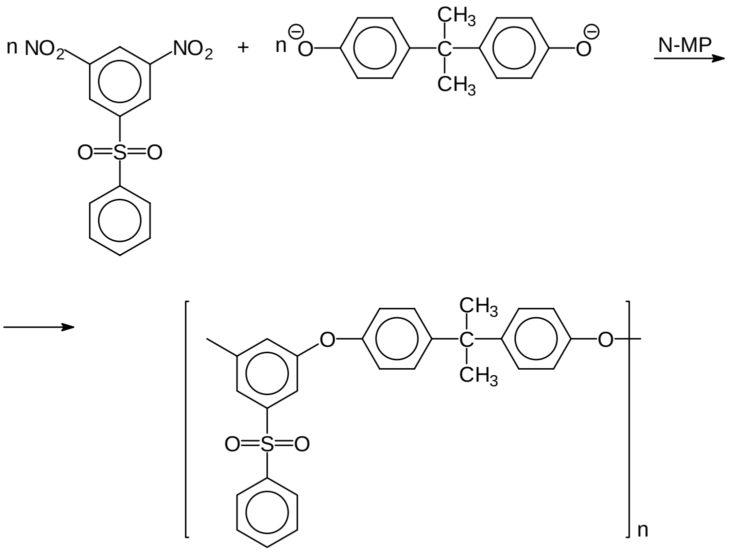
3.1. Monomers synthesis

The nitro groups in TNB may be replaced by aryloxy groups using aromatic nucleophilic nitro displacement [27,31] in accordance with Scheme 1. 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 (DNDAE) in high yields (60–95%) [13].

Conditions for the nitro group displacement in DNDAEs are harsher; the reaction proceeds at 150°C and leads to the



Scheme 3.

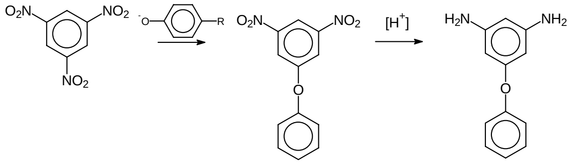


Scheme 4.

formation of 3,5-diaryloxy-substituted nitrobenzenes (DASNB) in yields of 50–70%.

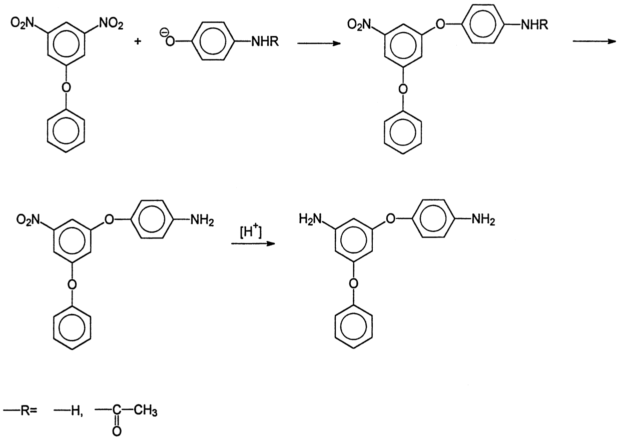
Replacement of the nitro groups in DASNBs proceeds at 200°C and leads to the formation of 1,3,5-triaryloxybenzenes (TAOB) in 25–30% yields.

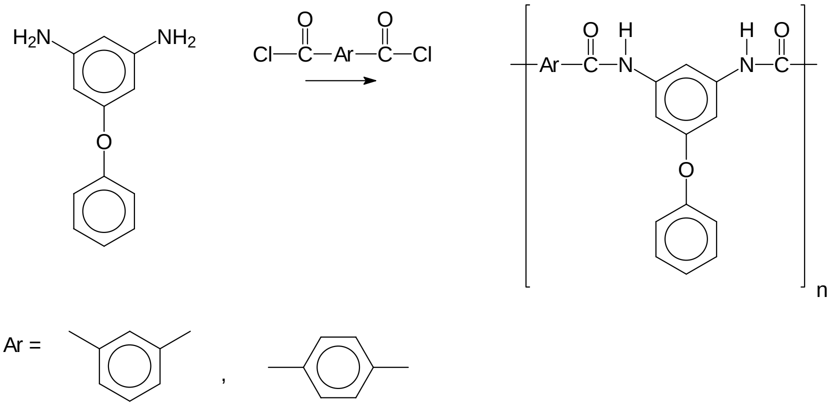
The mononitro substitution reaction on TNB was used to prepare new aryloxy-substituted dinitrocompounds [13], which were converted to the corresponding aryloxy-substituted diamines. The simplest dinitro compound and diamine thus obtained are 3,5-dinitrodiphenyl ether and 3,5-diaminodiphenyl ether:



The yields and some properties of the dinitro compound and diamine are given in Table 1.

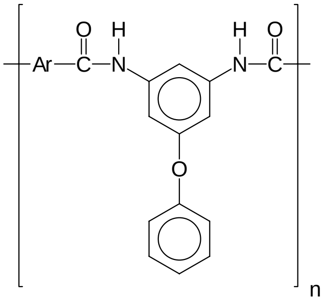
The nitro groups in DNDAE may be readily replaced with the residues of mono- and bis-phenols. The simplest DNDAE—3,5-dinitrodiphenyl ether—was reacted with 4-aminophenol or *p*-acetamidophenol with the formation of 3-nitro-5-4-amino(amido)phenoxydiphenyl ether; subsequent transformation of this product led to 3-amino-5-(4-aminophenoxy)diphenyl ether:

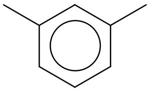
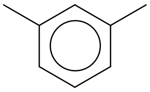
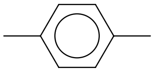
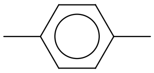




Scheme 5.

Table 4
Some properties of polyamides of general formula



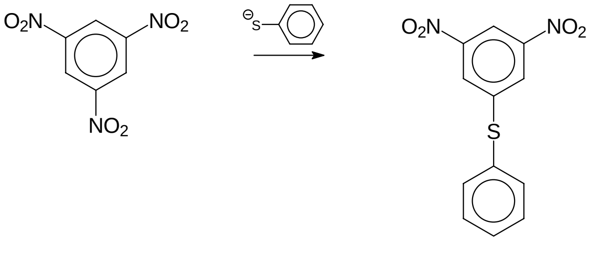
–Ar–	η_{red}, NMP, 0.5%, 25°C, dl/g	M_w[a]	T_g[b] (°C)	$T_{10\%}$[c] (°C)	Elementary analysis	
					Calculated %	Found %
	0.55[d]	23,000	252	356	C 72.70 H 4.28 N 8.48	C 72.51 H4.17 N 8.32
	0.46[e]	31,000	236	400	C 72.70 H 4.28 N 8.48	C 72 29 H 4.20 N 8.35C
	1.05[d]	58,000	275	400	C 72.70 H 4.28 N 8.48	C 72.54 H 4.36 N 8.29
	0.38[e]	17,000	246	350	C 72.70 H 4.28 N 8.48	C 72.31 H 4.30 N 8.41

[a] Measured using sedimentation method in NMP.
[b] Measured using thermomechanical method.
[c] Measured using dynamic thermogravimetric method (air, $\Delta T = 4.5$°C/min).
[d] Polyamides synthesised in NMP.
[e] Polyamides synthesised in chloroform with triethylamine.

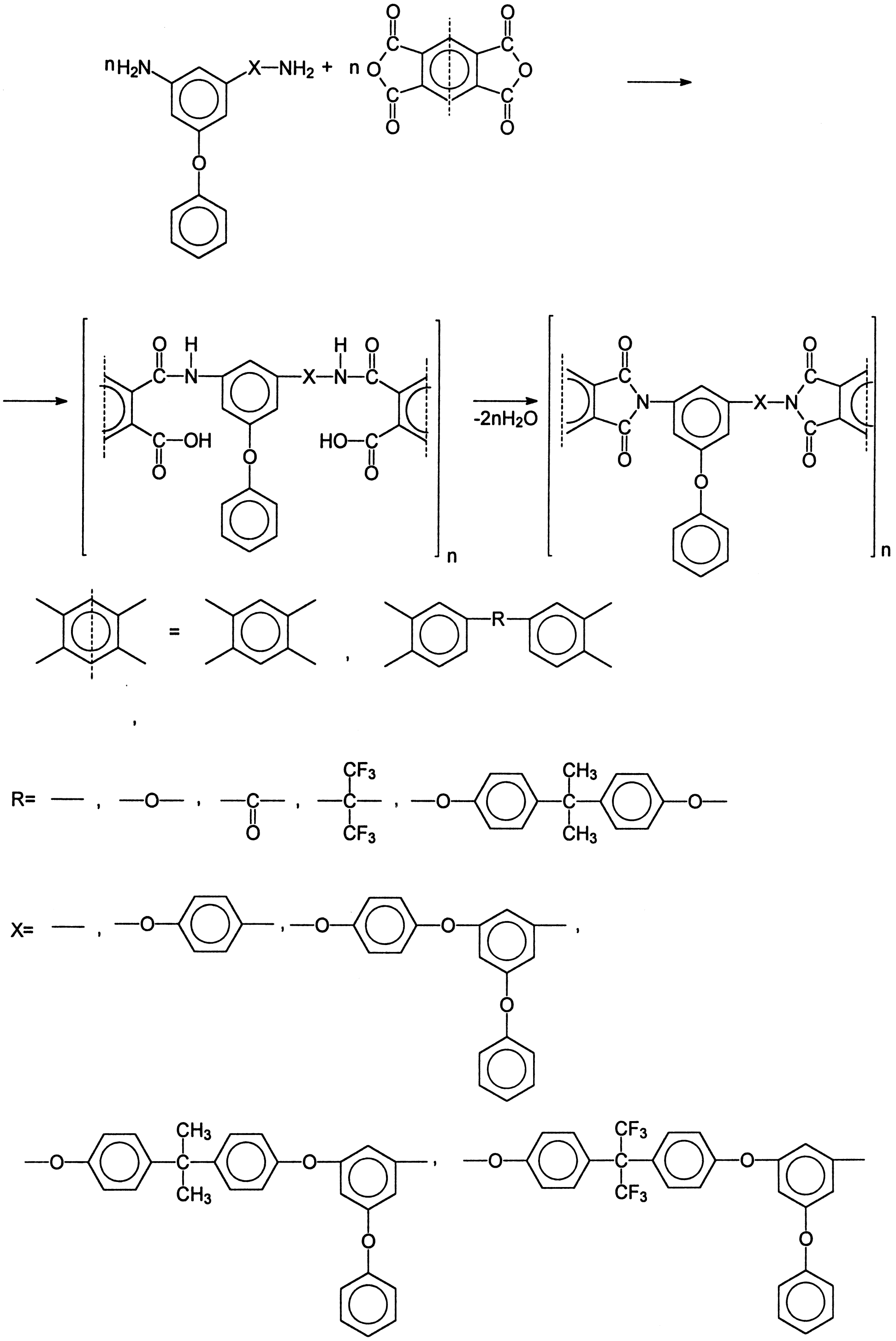
Yields and some properties of the intermediate and final compounds are given in Table 2. In contrast to the diamines listed in Table 1, 3-amino-5-(4-aminophenoxy)diphenyl ether contains an ether bond, which may be included in the polymer main chains.

Replacement of the nitro groups in DNDAEs 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. Preparation of these compounds was carried out in accordance with Scheme 2. Yields and some properties of the intermediate and final compounds are listed in Table 3.

The mono nitro substitution reaction on TNB was also used for the preparation of thiophenoxy substituted dinitrocompounds [15] and for the preparation of 3,5-dinitrodiphenylsulphide:

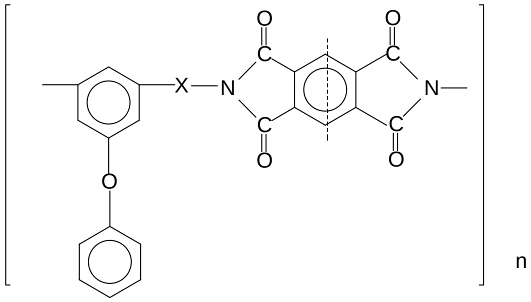


This compound was reduced with the formation of corresponding diamine; alternatively, the sulphide group of the compound was oxidised to the sulphone group and then 3,5-dinitrodiphenylsulphone was reduced to the corresponding



Scheme 6.

Table 5
Some properties of polyimides of general formula



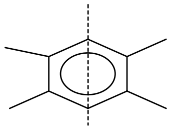
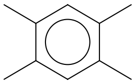
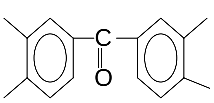
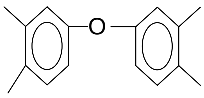
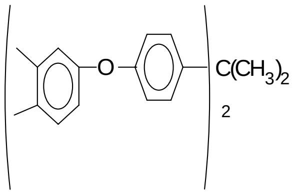
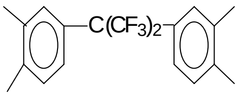
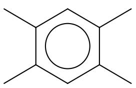
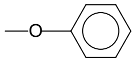
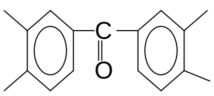
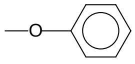
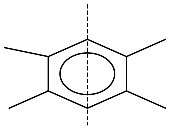
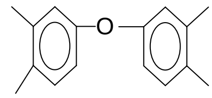
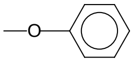
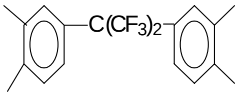
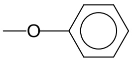
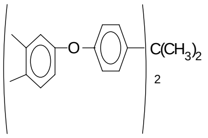
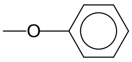
	–X–	η_{red}, dl/g NMP, 0.5%, 25°C	T_g, (°C)	$T_{10\%}$, (°C)	Elementary analysis	
					Calculated (%)	Found (%)
	–	0.66[a]	380	550	C 69.11 H 2.64 N 7.33	C 69.83 H 2.93 N 6.85
	–	0.35 15,000[b]	260	530	C 71.60 H 2.90 N 5.76	C 71.28 H 2.46 N 5.71
	–	0.83 48,000[b]	245	540	C 70.89 H 2.95 N 5.91	C 70.53 H 3.07 N 5.76
	–	0.30 44,000[b]	180	500	C 75.43 H 4.12 N 4.09	C 75.01 H 3.92 N 4.15
	–	0.70	260	530	C 59.23 H 4.490 N 4.46 F 19.09	C 58.91 H 4.40 N 4.37 F 18.73
		0.32[a]	278	550	C 70.89 H 2.95 N 5.91	C 70.75 H 2.90 N 5.89
		0.58[a]	230	510	C 72.67 H 3.12 N 4.84	C 72.18 H 3.06 N 4.75

Table 5 (*continued*)

	–X–	η_{red}, dl/g NMP, 0.5%, 25°C	T_g, (°C)	$T_{10\%}$, (°C)	Elementary analysis	
					Calculated (%)	Found (%)
		0.47	220	520	C 72.09 H 3.19 N 4.95	C 71.73 H 3.10 N 4.83
		0.31	235	510	C 64.36 H 2.62 N 4.06 F 17.38	C 64.03 H 2.57 N 3.91 F 1748
		0.60	215	525	C 75.76 H 4.15 N 3.61	C 75.33 H 3.91 N 3.58

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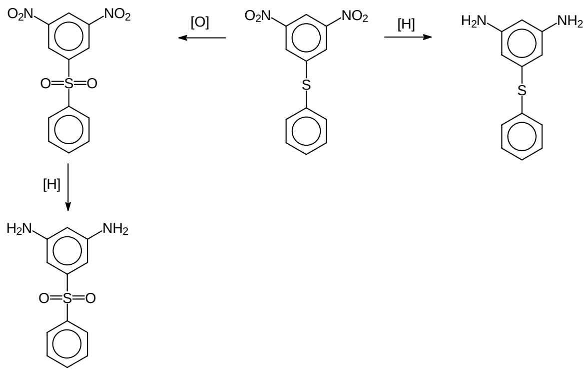
[a] Viscosity of polyamic acid.

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

3,5-diaminodiphenylsulphone:



Some properties of the dinitrocompounds and diamines containing phenylsulphide and phenylsulphone substituents are listed in Table 1.

3.2. Polymers synthesis

3.2.1. Aromatic oligoethers

The aromatic nucleophilic nitro displacement reaction may be used for the preparation of aromatic polyethers [27,28,31] but there are very few examples of such reactions [28]. Of especially great concern is the passivation of the second nitro group after reaction of the first one with the nucleophile. In addition, activators of the nitro groups are usually located in the *ortho*- or *para*-positions to the nitro groups. This is why it was of interest for us to use for the preparation of aromatic polyethers 3,5-dinitrodiphenylsulphone—TNT—based mononuclear compound containing an electron withdrawing activator in the *meta*-position towards nitro groups.

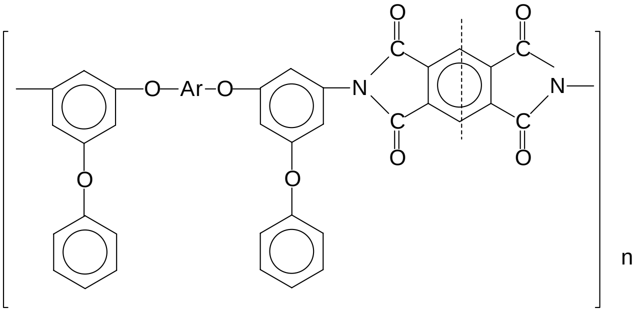
The model reaction between 3,5-dinitrodiphenylsulphone and two molecules of phenol was carried out in NMP at 150°C for 6 h in accordance with Scheme 3. The reaction led to the formation of 3,5-diphenoxydiphenylsulphone in 40% yield (after purification). This non-described previously compound melted at 100–102°C.

The synthesis of the corresponding polyether of 3,5-dinitrodiphenylsulphone and bis-phenol A was carried out under the same conditions in accordance with Scheme 4. Not surprisingly, the polyethers obtained have a rather low molecular weight product ($M_n = 1900$; $M_w = 2600$; $n = 5$) but this investigation has demonstrated the possibility of polyether preparation using mononuclear dinitrocompounds containing activators in the *meta*-position to the nitro groups.

3.2.2. Aromatic polyamides and polyimides

New substituted aromatic diamines, which were obtained, were used for the preparation of substituted condensation polymers. The 3,5-Diaminodiphenyl ether was used for the preparation of the corresponding polyamides; isophthalic and terephthalic acid dichlorides were used as derivatives of aromatic dicarboxylic acids. Synthesis of the polyamides was carried out in accordance with Scheme 5.

Table 6
Properties of polyimides of general formula



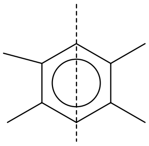
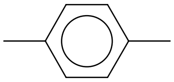
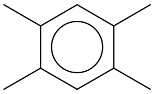
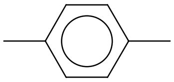
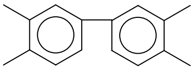
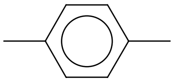
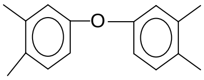
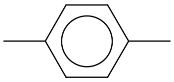
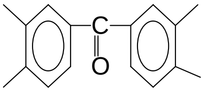
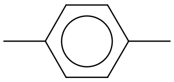
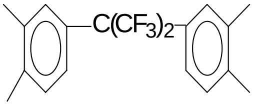
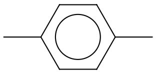
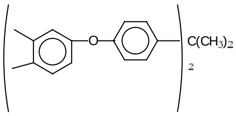
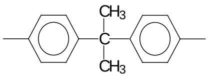
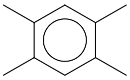
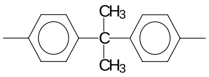
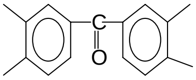
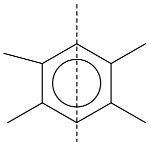
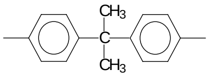
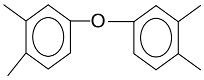
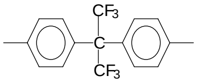
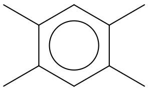
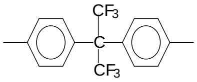
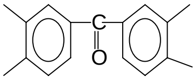
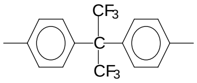
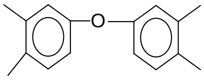
–Ar–		η_{red} NMP, 0.5%, 25°C, dl/g	T_g (°C)	$T_{10\%}$ (°C)	Elementary analysis	
					Calculated %	Found %
		–	210	520	C 72.95 H 3.37 N 4.25	C 7198 H 3.31 N 3.72
		0.37	213	550	C 78.62 H 3.73 N 3.98	C 78.19 H 3.58 N 4.05
		0.67 M_w47,000[a]	170	520	C 73.60 H 3.49 N 3.73	C 73.57 H 3.74 N 3.71
		1.00 M_w77,000[a]	190	520	C 74.01 H 3.44 N 3.73	C 73.57 H 3.74 N 3.71
		0.65	188	500	C 66.07 H 2.94 N 3.15 F 13.47	C 65.74 H 2.65 N3.01 F 13 72
		0.95	205	470	C 76.24 H 4.20 N 2.92	C 75.61 H 3.68 N 3.38
		0.42	195	470	C 75.76 H 4.15 N 3.61	C 75.11 H 3.98 N 3.55
		0.59	165	500	C 76.35 H 4.12 N 3.18	C 75.77 H 4.35 N 3.30

Table 6 (*continued*)

–Ar–		η_{red} NMP, 0.5%, 25°C, dl/g	T_g (°C)	$T_{10\%}$ (°C)	Elementary analysis	
					Calculated %	Found %
		0.50	165	490	C 76.03 H 4.18 N 3.22	C 75.42 H 4.46 N 3.13
		0.22	200	500	C 66.52 H 2.96 N 3.17 F 12.88	C 65.94 H 3.03 N3.50 F 12.63
		0.34	197	480	C 68.02 H 3.06 N 2.83 F 11.53	C 67.42 H 3.04 N 2.96 F 11.19
		0.26	182	510	C 67.63 H 3.10 N 2.87 F 11.67	C 66.77 H 3.14 N 2.96 F 11.16

[a] Measured, using sedimentation method in NMP.

For the preparation of polyamides two general methods were used:

- low temperature solution polycondensation in NMP;
- low temperature solution polycondensation in chloroform using triethylamine as the HCl acceptor.

The general properties of the polyamides obtained are given in Table 4. The polyamides obtained combine solubility in various organic solvents—NMP,DMAc,DMF, *m*-cresol etc. —with high glass transition (236–275°C) and degradation (350–400°C) temperatures.

Syntheses of phenoxy-substituted polyimides were carried out [17–19] in accordance with Scheme 6.

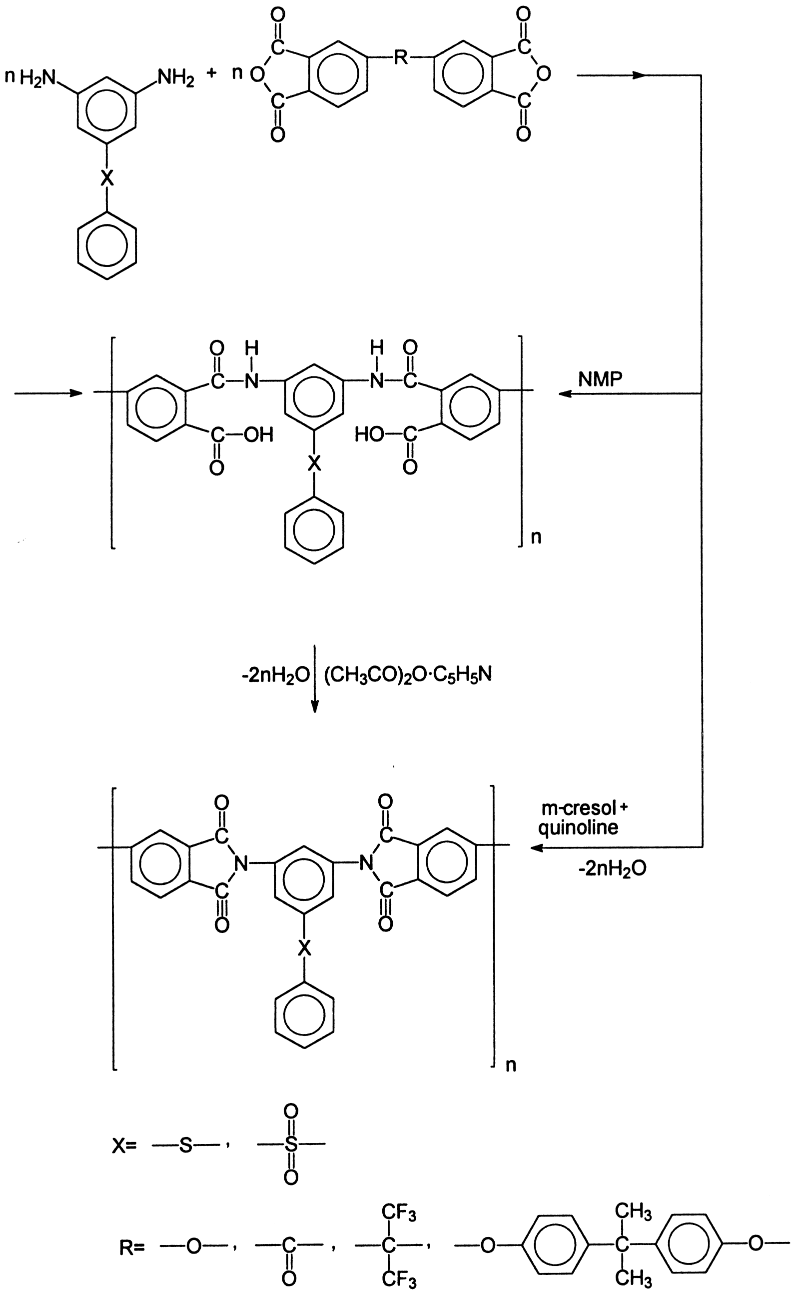
Syntheses of the polyimides were carried out using three different methods [30]:

- low-temperature solution polycondensation in NMP, followed by catalytic imidisation of the polyamic acids formed in using the pyridine:acetic anhydride (1:1) complex as catalyst (procedure 1);
- high-temperature solution polycondensation in NMP, using azeotrope-forming compounds (procedure 2);
- high-temperature solution polycondensation in *m*-cresol using isoquinoline as catalyst (procedure 3).

The structures of the polyimides obtained were confirmed using IR-spectroscopy. In the polyimide spectra there are absorption bands at 1780 and 1730 cm^{-1} related to the symmetrii and asymmetrii of the stretching vibration C=O of the imide group, the band at 1370 cm^{-1} related to the C–N bonds of the imide group, the band at 1100 and 720 cm^{-1} related to the vibrations of the imide structure. In addition, in all the phenoxy-substituted polyimide spectra there are bands at 1240–1250 cm^{-1} related to C_{ar}–O bonds. In comparison, the disappearence of absorption bands at 3100–3300 cm^{-1} (O–H stretching) and 1660 cm^{-1} (secondary amide groups) and the appearance of absorption bands at 1780, 1730, 1100 and 720 cm^{-1} indicate a complete imidisation.

Properties of the polyimides based on 3,5-diaminodiphenyl ether and 1-amino-3-phenoxy-5-(4-aminophenoxy)-benzene are given in Table 5.

As it may be seen from Table 5, all polyimides—with the exception of polypyromellitimides—are soluble in organic solvents—NMP, *m*-cresol and a mixture of TCE and phenol—indicating the positive influence of phenoxy substituents on polymer solubility. The reduced viscosity of the polyimide solutions were equal to 0.30–0.83 dl/g, the highest of them corresponding to $M_w = 48,000$ (measured using the sedimentation method in NMP); some of the polyimides demonstrate good film-forming properties. T_g values of the polyimides are in the range of 180–380°C and their 10% weight loss temperatures are 500–550°C, indicating large “use windows” between glass transition and degradation temperatures.



Scheme 7.

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.

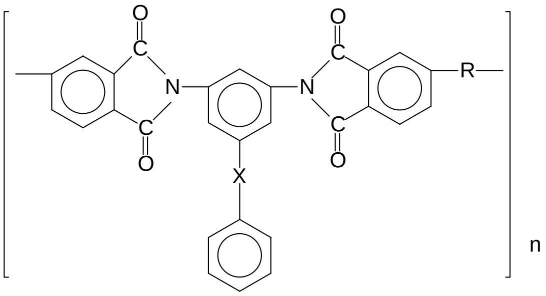
Polymers obtained using of 3,5-diaminodiphenyl ether may be considered as *m*-phenylenediamine—based polyimides containing phenoxy side groups. A comparison of these two polymer group properties has demonstrated that introduction of phenoxy substituents leads to an increase of the polymer solubility and decrease of their T_g values indicating that phenoxy side groups behave as chemical plasticisers. This conclusion is in agreement with prior work [1–7].

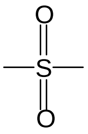
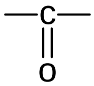
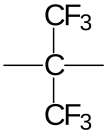
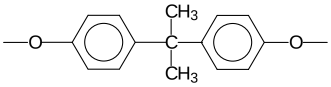
The properties of the polyimides based on bis-(3-amino-5-phenoxy)diphenyl ethers of hydroquinone and bisphenols are listed in Table 6.

As may be seen from Table 6, all polyimides—with the exception of polypyromellitimide based on bis-(3-amino-5-phenoxy)diphenyl ether of hydroquinone—are soluble in organic solvents. The reduced viscosity of the polyimide solutions in NMP were between 0.22–1.00 dl/g, the highest value corresponding to $M_w = 77,000$ (measured using the sedimentation method in NMP). Some of the polyimides demonstrate good film-forming properties.

All polyimides listed in Table 6 demonstrate low glass

Table 7
Some properties of polyimides of general formula



–X–	–R–	η_{red}, dl/g m.p. 25°C	$T_{10\%}$ (°C)	T_g (°C)	Elementary analysis	
					Calculated %	Found %
 $-SO_2-$	–O–	0.25	420	268	C 64.36 H 2.70 N 5.36 S 6.14	C 63.87 H 2.49 N 5.13 S 6.43
–S–	–O–	1.20	400	240	C 68.56 H 2.88 N 5.71 S 6.53	C 68.01 H 2.76 N 5.63 S 6.79
–S–	 $-CO-$	0.90	460	250	C 67.17 H 2.72 N 5.40 S 6.18	C 66.81 H 2.58 N 5.13 S 6.47
–S–	 $-C(CF_3)_2-$	0.79	415	220	C69.05 H 2.24 N 4.44 S 5.08 F 19.03	C 58.53 H 2.07 N 4.37 S 4.93 F 19.51
–S–		0.87	425	210	C 73.70 H 4.03 N 3.99 S 4.58	C 73.02 H 3.85 N 4.07 S 4.79

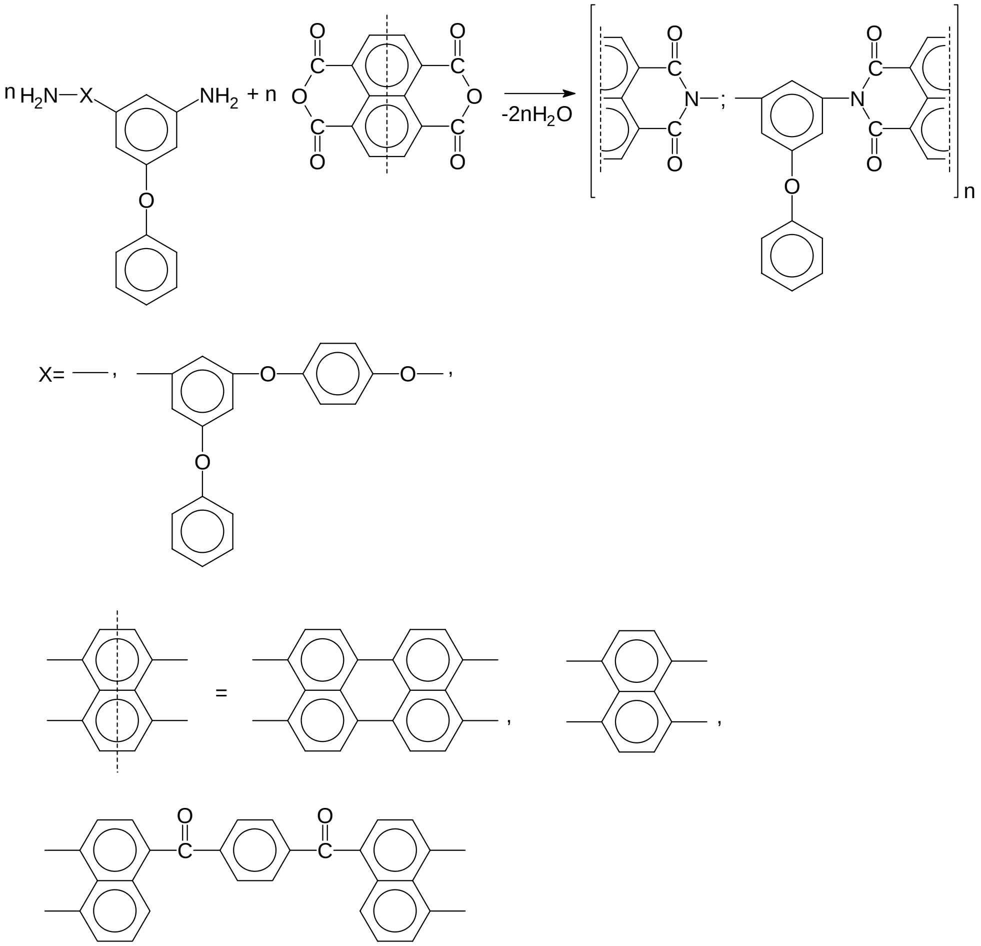
transition temperatures (165–213°C) and high degradation temperatures ($T_{10\%} = 470$–550°C) indicating their processability to form shaped articles.

The comparisons of polyimides based on different diamines obtained (Tables 5 and 6) indicated that the best solubility is typical for the polymers on the basis of bis-(3-amino-5-phenoxy)diphenyl ethers of bis-phenols. Some of these polyimides are soluble even in cyclohexanone. For these polymers, the lowest T_g values are also typical.

Polyimides containing phenylsulphide and phenylsulphone side groups [16] were obtained in accordance with Scheme 7. General properties of the polyimides thus obtained are listed in Table 7.

Comparison of the properties of the polyimides listed in Table 7 demonstrated that polyimides based on 3,5-diaminodiphenylsulphone have much lower reduced viscosity when compared with the related polyimide based on 3,5-diaminodiphenylsulphide. This difference is probably due to the negative influence of the electron-withdrawing phenylsulphone group on the nucleophilic reactivity of the amino groups.

Polyimides based on 3,5-diaminodiphenylsulphide demonstrated that solubility in organic solvents strongly depend on



Scheme 8.

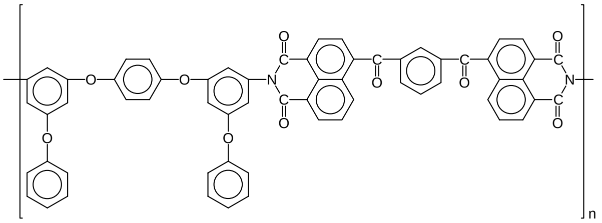
the nature of the dianhydride used, high enough η_{red} in NMP (0.79–1.20 dl/g) and moderate (210–250°C) T_g values combined with high (400–460°C) degradation temperatures.

Along with the polyimides containing five-membered imide rings (polyphthalimides) in the frame of the present investigation were synthesised polyimides containing six-membered naphthylimide cycles (polynaphthylimides and polyperyleneimides). These polymers are known to be more stable—hydrolytically and thermally—when compared with polyphthalimides [32–35].

Syntheses of phenoxy-substituted polynaphthylimides and polyperyleneimides were carried out in accordance with Scheme 8.

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 8.

As it may be seen from the data in Table 8, 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

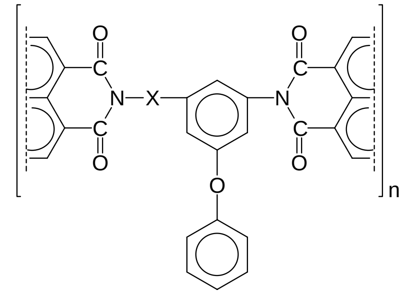


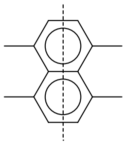
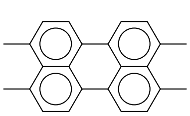
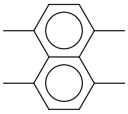
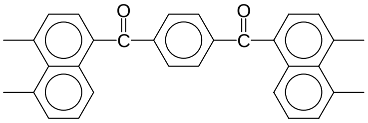
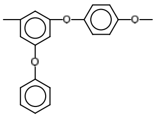
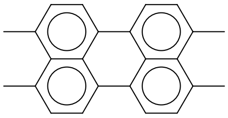
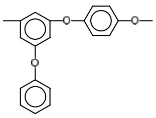
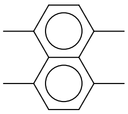
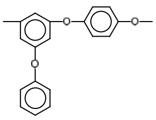
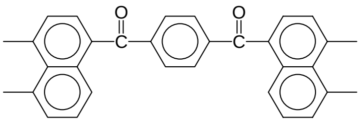
is soluble not only in NMP and a mixture of TCE and phenol (3:1), but also in DMF, $CHCL_3$ and DMAc (partially). Improved solubility of this polynaphthylimide when compared with polymers based on the same dianhydride and common aromatic diamines [36] demonstrates the influence of bis-(3-amino-5-phenoxy)diphenyl ether of the hydroquinone structure on the solubility of the polymers.

4. Conclusions

New aromatic dinitrocompounds containing phenoxy-,

Table 8
Properties of polynaphthylimides and polyperylenimides of general formula



–X–		η_{red} (TCE: phenol dl/g	T_g, (°C)	Tdegr. (5%) °C	Elementary analysis	
					Calculated %	Found %
–		0.23	–		C 77.69 H 2.90 N 5.03	C 77.52 H 2.58 N 4.97
–		0.20	–	500	C 72.22 H 2.80 N 6.48	C 71.93 H 2.47 N 6.01
–		0.89	315	470	80.23 H 3.37 N 4.25	C 80.03 H 3.13 N 4.05
		0.23	–	475	C 77.88 H 3.39 N 3.36	C 77.61 H 3.22 N 3.25
		0.37	260	480	C 74.57 H 3.41 N 3.95	C 74.38 H 3.17 N 3.67
		0.45	250	480	C 79.65 H 3.67 N 3.00	C 79.27 H 3.53 N 2.87

thiophenoxy- and phenylsulphone side groups were obtained on the basis of 1,3,5-trinitrobenzene—a simplest derivative of 2,4,6-trinitrotoluene—using aromatic nucleophilic nitro displacement reactions. Hydrogenation of the dinitrocompounds thus obtained led to the formation of the corresponding diamines.

Dinitrocompounds containing strong electron-withdrawing groups in the *meta* position were used for the preparation of oligomeric polyethers. The diamines obtained were reacted with aromatic dicarboxylic acid dichlorides and aromatic tetracarboxylic acid dianhydrides. The resulting polyamides and polyimides containing phenoxy-, thiophenoxy- and phenylsulphone side groups demonstrated improved solubility and increased "windows" between softening and degradation temperatures when compared with related non-substituted polymers.

Acknowledgements

The authors would like to thank the International Science and Technology Center for the financial support of this work (grant No. 419).

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