

Condensation monomers and polymers based on 2,4,6-trinitrotoluene

A L Rusanov, L G Komarova, D Yu Likhatchev, S A Shevelev, V A Tartakovskiy

Contents

I. Introduction	899
II. Synthesis of condensation monomers based on 2,4,6-trinitrotoluene and its derivatives	899
III. Synthesis of polymers based on 2,4,6-trinitrotoluene derivatives	903
IV. Conclusion	909

Abstract. The feasibility of conversion of 2,4,6-trinitrotoluene into condensation monomers (nitro compounds, diamines, *etc.*) and their applications in the synthesis of aromatic polymers has been analysed within the framework of a general problem of 2,4,6-trinitrotoluene conversion. The use of aromatic dinitro compounds and diamines for the preparation of oligomeric polyethers and polyamides (or polyimides), respectively, is considered. The possibility of the synthesis of polyamides and polyimides containing side aliphatic and aromatic groups and possessing better (in comparison with the corresponding unsubstituted polymers) characteristics is demonstrated. The bibliography includes 157 references.

I. Introduction

Aromatic condensation polymers belong to the most important class of thermostable high-molecular-mass compounds^{1–8} that have found wide application in the most advanced fields of science and technology.⁹ In this connection, a search for sources of raw materials for the synthesis of such polymers is the key problem, which determines further progress in this branch of chemistry.¹⁰ Of special interest is the development of methods for the synthesis of monomers from cheap and available raw materials, especially those based on compounds subject to utilisation, *e.g.*, the use of phosgene for the preparation of polycarbonates¹¹ or of dichlorodiphenyltrichloroethane (DDT) for the synthesis of a broad range of condensation polymers.^{12–16}

Large-scale investigations^{17–22} carried out in Russia over the past decade were aimed at the preparation of monomers and aromatic condensation polymers based on 2,4,6-trinitrotoluene

A L Rusanov, L G Komarova A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 119991 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 63 72. E-mail: alrus@ineos.ac.ru (A L Rusanov). Tel. (7-095) 135 93 27. E-mail: komarova@ineos.ac.ru (L G Komarova)

D Yu Likhatchev Materials Research Institute, UNAM, Circuito Exterior s/n, CU, Apdo Postal 70-360 Coyoacan, 04510 Mexico City, Mexico. Fax (52-555) 616 12 01. Tel. (52-555) 622 45 87. E-mail: likhach@servidor.unam.mx

S A Shevelev, V A Tartakovskiy N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation. Fax (7-095) 135 53 28. Tel. (7-095) 135 63 40. E-mail: shevelev@ioc.ac.ru (S A Shevelev). Tel. (7-095) 135 41 11. E-mail: secretary@ioc.ac.ru (V A Tartakovskiy)

Received 14 May 2003

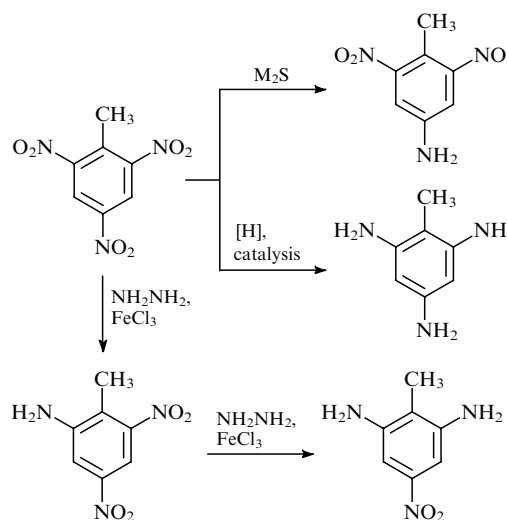
Uspekhi Khimii 72 (10) 1011–1024 (2003); translated by R L Birnova

(trotyl, TNT),²³ a reagent, cheap and available product contained in large amounts in out-of-date ammunition liable to liquidation.

The simplest TNT derivatives used as monomers in the synthesis of condensation polymers include aromatic dinitro compounds (monomers for aromatic oligo- and poly-ethers^{24,25}) and aromatic di- and triamines (monomers for aromatic polyamides and polyimides^{10,26–30}). Some transformations of TNT into condensation monomers are depicted in Scheme 1.

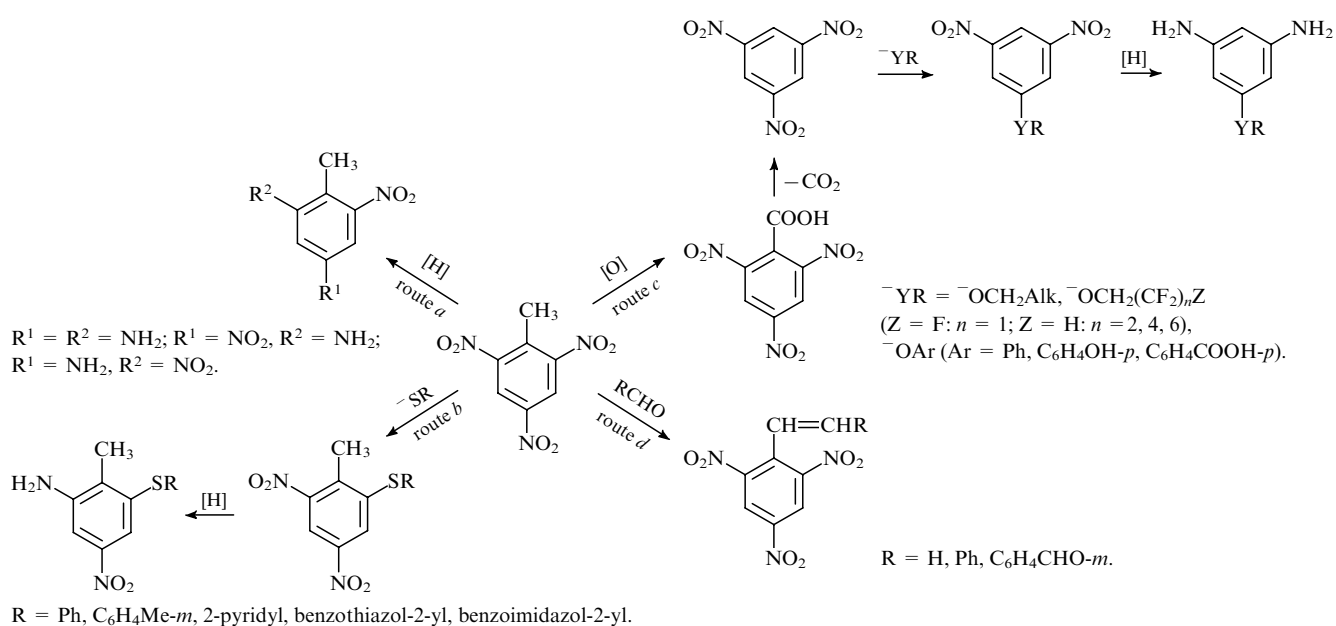
II. Synthesis of condensation monomers based on 2,4,6-trinitrotoluene and its derivatives

Complete or partial reduction of TNT is the simplest reaction in the series of TNT transformations (Scheme 1, route *a*). Monoaminodinitrotoluenes, diaminonitrotoluenes and 2,4,6-triaminotoluene (TAT) can be obtained depending on the method and conditions for TNT reduction.

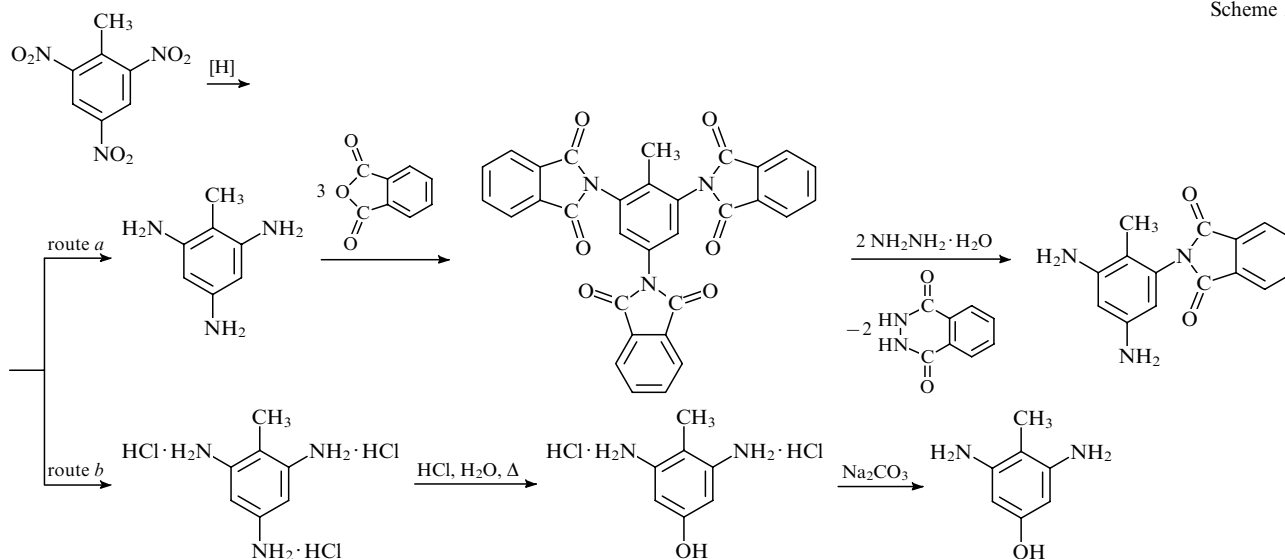


Thus reduction of TNT with sulfides of monovalent metals affords 4-amino-2,6-dinitrotoluene.³¹ Depending on the reaction conditions, the reduction of TNT with hydrazine hydrate in the presence of Raney nickel or iron chloride on activated charcoal yields either 2-amino-4,6-dinitrotoluene or 2,6-diamino-4-nitrotoluene.³² However, complete reduction of TNT resulting in TAT presents the greatest interest. Complete reduction of TNT to TAT is achieved by catalytic hydrogenation (Scheme 2, route *a*).³³ Electrochemical reduction of TNT in dilute HCl in the presence of TiCl₃ (Scheme 2, route *b*) leads to TAT · 3 HCl (yield 95%),¹⁸ which is much more resistant to oxidation than the free base.

Scheme 1



Scheme 2



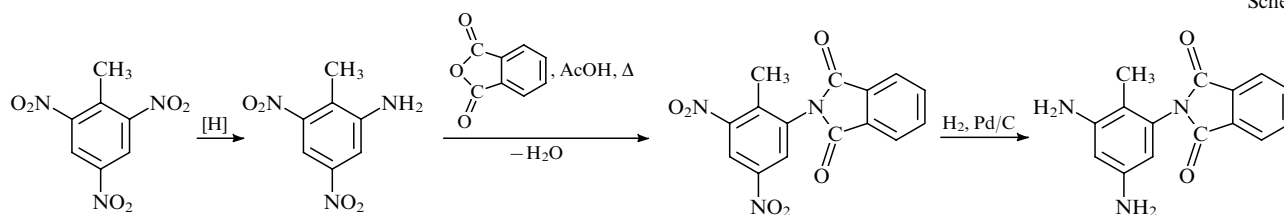
(a) catalytic hydrogenation, (b) electrochemical reduction, HCl (dilute), TiCl_3 .

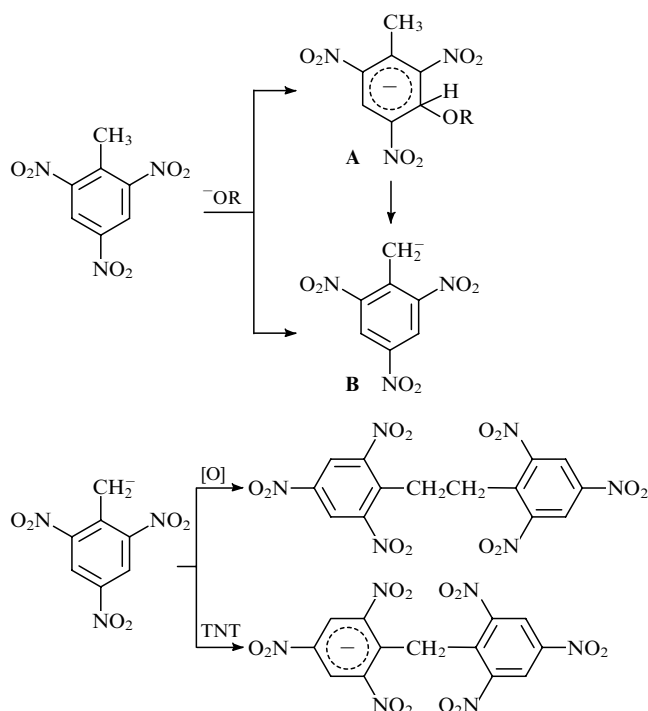
2,4,6-Triaminotoluene can be used for the synthesis of both polymers, *e.g.*, polyimides (PI) and a series of condensation monomers, substituted diamines in particular.^{34,35}

Thus partial hydrolysis of $\text{TAT} \cdot 3 \text{HCl}$ gave 2,6-diamino-4-hydroxytoluene,³⁵ whereas the reaction of TAT with a threefold molar excess of phthalic anhydride resulted in 2,4,6-triphthalimidotoluene, which was further converted into 2,4-diamino-6-phthalimidotoluene.³⁶ Since this procedure yields an isomer of 2,4-diamino-6-phthalimidotoluene (5%–10%) along with the main product, the pure monomer is prepared using the following reaction sequence (Scheme 3):³⁶

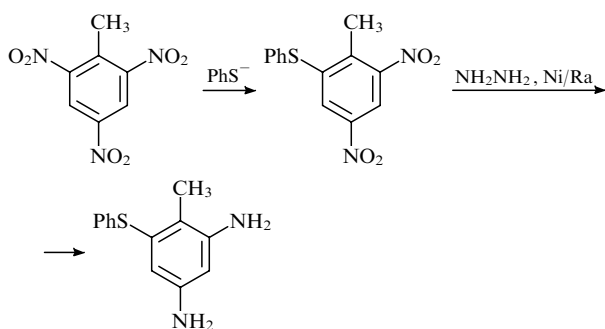
Yet another pathway for TNT conversion into condensation monomers (Scheme 1, route *b*) is based on the replacement of the nitro groups of TNT by nucleophiles under conditions of aromatic nucleophilic substitution.^{37–39} It is of note that reactions of TNT with bases are usually accompanied by the formation of an anionic 1,3- σ -complex **A**, which is further converted into a more stable 2,4,6-trinitrobenzyl anion **B** rather than the nitro groups being replaced.^{40,41} This anion can undergo further chemical transformations.

Scheme 3



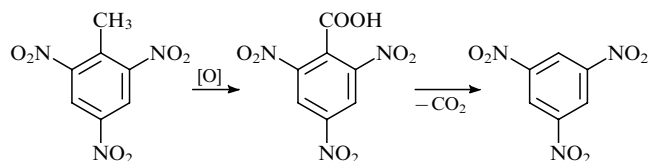


These processes can only be prevented if 'soft' nucleophiles, e.g., benzenethiols and their heterocyclic analogues are used or if the reactions are carried out in dipolar aprotic solvents of the amide type.^{42, 43} Thus reaction of TNT with benzenethiol in the presence of K_2CO_3 in *N*-methylpyrrolidone (*N*-MP) (50 °C, 2 h) leads to 2-methyl-3,5-dinitrodiphenyl sulfide (yield 72%); the reduction of the latter with hydrazine hydrate results in 3,5-diamino-2-methyldiphenyl sulfide (yield 86%).

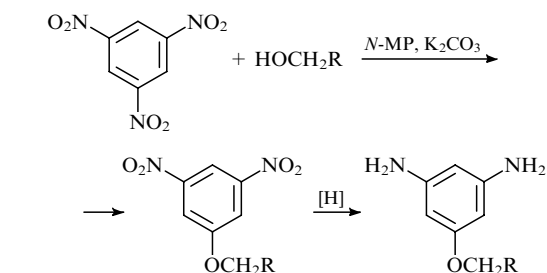


A broad range of condensation monomers was obtained following the route *c* (Scheme 1), which is based on the demethylation of TNT; this reaction yields 1,3,5-trinitrobenzene (TNB).

There are different ways to demethylate TNT; the most important includes the oxidation of the methyl group to the carboxy group and subsequent decarboxylation.^{44, 45}



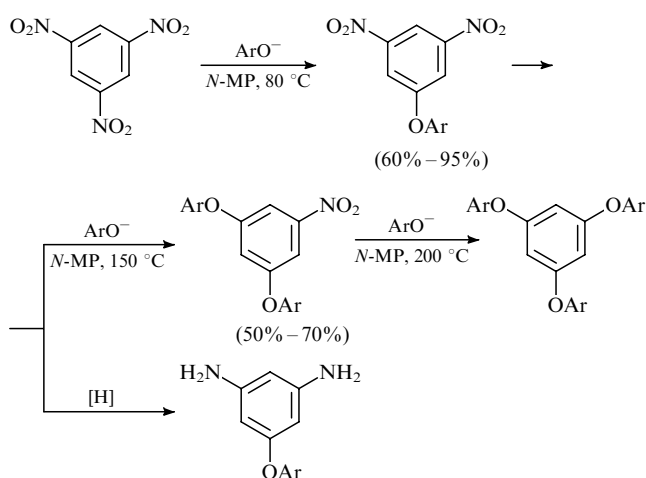
Aromatic nucleophilic substitution^{37–39} was used for the replacement of the nitro group in TNT by alkoxy-^{46–48} or perfluoroalkoxy groups.^{49–55}



$\text{R} = \text{H, Alk, (CF}_2\text{)}_n\text{X (X = F: } n = 1; \text{X = H: } n = 2, 4, 6\text{)}$.

The monosubstituted dinitro compounds thus obtained were reduced to the corresponding diamines.^{46, 51–53}

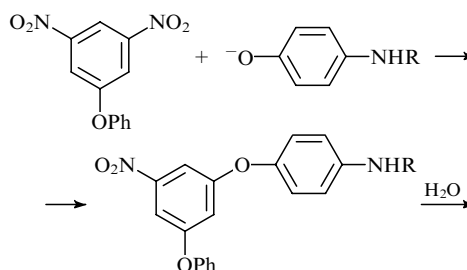
Considerable attention has been given to the replacement of the nitro groups in TNB by aryloxy groups.^{56–58} One, two or three nitro groups in TNB can be replaced using aromatic nucleophiles.

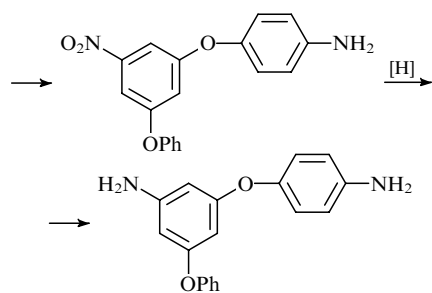


$\text{Ar} = \text{Ph, 2-MeC}_6\text{H}_4, 3\text{-MeC}_6\text{H}_4, 4\text{-XC}_6\text{H}_4$ (X = F, Br, I, OH, EtO, NH_2 , $\text{CH}_3\text{C(O)}$, COOH , NO_2), 3- ClC_6H_4 etc.

The replacement of the first nitro group in TNB occurs under mild conditions (80 °C) and gives high (60%–95%) yields of 3,5-dinitrodiaryl ethers^{56, 57} which are easily converted into the corresponding aryloxy-substituted diamines. The replacement of the nitro group in 3,5-dinitroaryl ethers requires more drastic conditions, viz., heating to 150 °C. The yield of 3,5-diaryloxy-substituted nitrobenzenes is 50%–70%. The formation of 1,3,5-triaryloxybenzenes as a result of replacement of the nitro group in 3,5-diaryloxy-substituted nitrobenzenes is possible only at 200 °C (yield 25%–30%).

The nitro group in 3,5-dinitrodiaryl ethers can easily be replaced by a mono- or bisphenolic residue. Thus 3,5-dinitrodiphenyl ether reacts with 4-amino- or 4-acetamidophenol to give 3-nitro-5-[4-amino(amido)phenoxy]diphenyl ether. Hydrolysis of 3-nitro-5-(4-acetamidophenoxy)diphenyl ether leads to 3-nitro-5-(4-aminophenoxy)diphenyl ether; subsequent reduction of the latter gives 3-amino-5-(4-aminophenoxy)diphenyl ether.⁵⁹

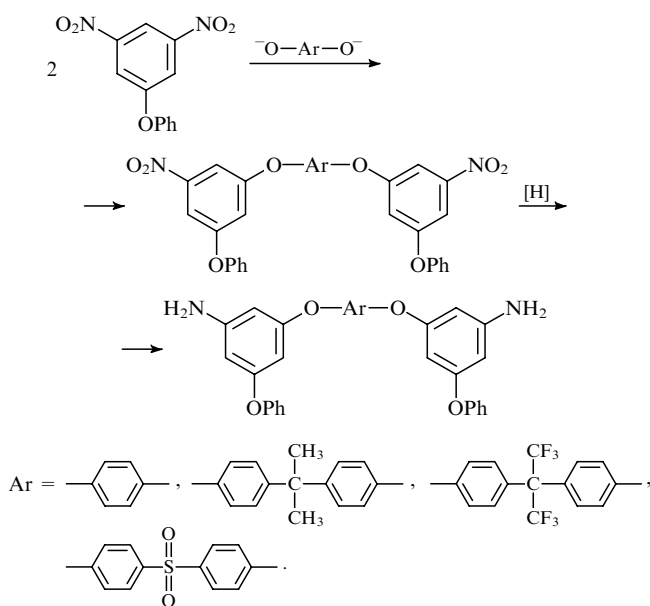




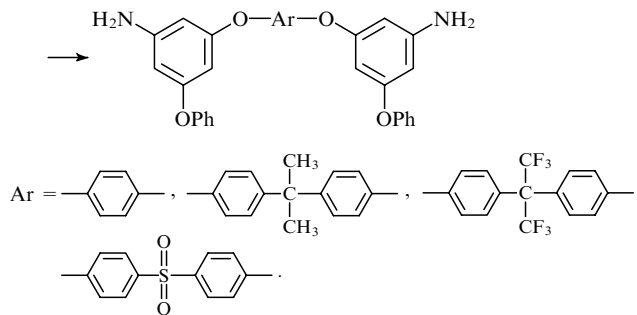
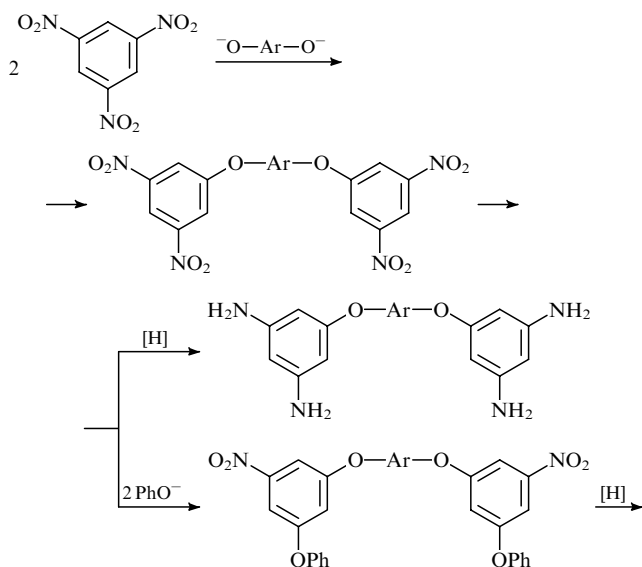
R = H, COCH₃.

It is noteworthy that 3-amino-5-(4-aminophenoxy)diphenyl ether contains an ether bond which can be incorporated into the main polymeric chain by polycondensation.

The replacement of the nitro group in dinitrophenyl ethers by bisphenolic residues yields dinitro compounds and diamines which contain no less than two ether groups; these can potentially be incorporated into the main polymeric chain.^{60, 61}

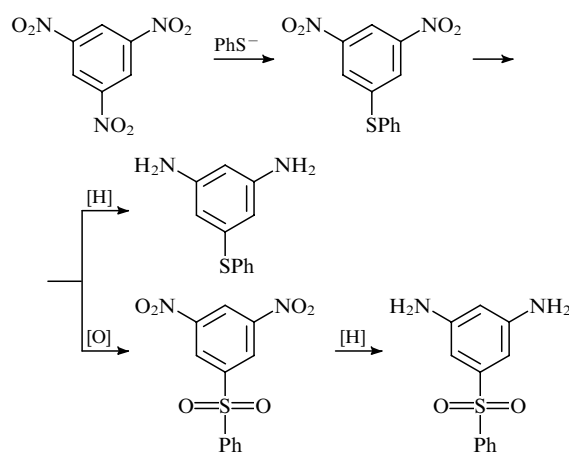


An alternative approach to the synthesis of such diamines includes the reaction of bisphenols with a twofold molar excess of TNB,⁵⁷ subsequent treatment of the tetranitro compounds formed with phenol and reduction of dinitro compounds to diamines.

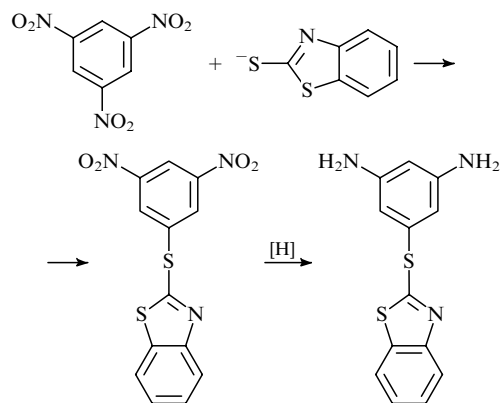


It is of note that the reduction of intermediate tetranitro compounds allows preparation of a novel type of aromatic tetraamines, viz., bis(3,5-diaminophenoxy)arylenes.

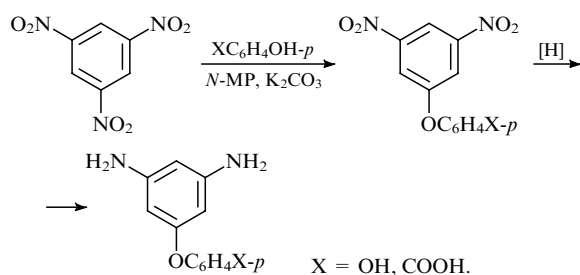
Monosubstitution of TNB is also employed in the synthesis of 3,5-dinitrodiphenyl sulfide;^{42, 62} its reduction gives the corresponding diamine. Oxidation of the sulfide group in 3,5-dinitrodiphenyl sulfide to the sulfonyl group and subsequent reduction of 3,5-dinitrodiphenyl sulfone yield 3,5-diaminodiphenyl sulfone.⁶²



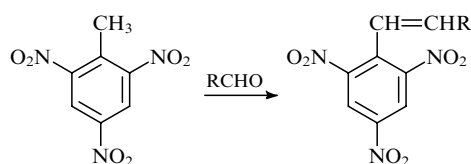
3,5-Diaminophenyl benzothiazol-2-yl sulfide was synthesised from TNB in addition to monomers containing a phenylthio group.⁶³ The former is prepared by treatment of TNB with 2-mercaptobenzothiazole (which is less expensive than benzenethiol) and subsequent reduction of the benzothiazol-2-yl 3,5-dinitrophenyl sulfide formed.



Monomers with functionalised aryl groups were synthesised besides dinitro compounds and diamines containing non-reactive aryl substituents.⁶⁴ Among the former, aromatic diamines containing free hydroxy and carboxy groups, e.g., 3,5-diamino-4'-hydroxy- and 3,5-diamino-4'-carboxydiphenyl ethers, present special interest.^{57, 64, 65}



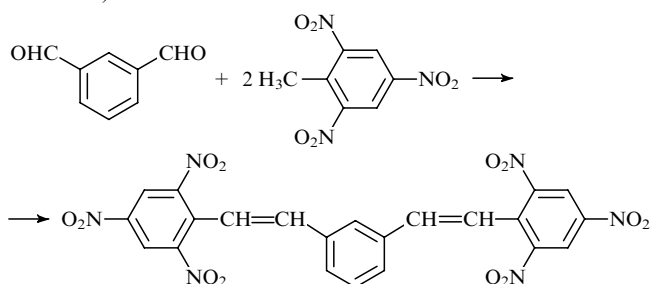
Yet another fairly interesting route of TNT conversion into condensation monomers includes reactions involving the methyl group (Scheme 1, route *d*). The methyl group of TNT, which is effectively activated by nitro groups, reacts easily with aldehydes to give trinitrophenyl-substituted alkenes.⁶⁶



$R = \text{H}, \text{Ph}.$

Such monomers can be converted into aromatic amines containing alkene substituents.

The reaction product of isophthalic aldehyde with a twofold molar excess of TNT⁶⁶ is a promising starting monomer for polycycloaddition reactions (*e.g.*, the Diels–Alder reaction^{67–70}).



III. Synthesis of polymers based on 2,4,6-trinitrotoluene derivatives

1. Polyamides and polyimides

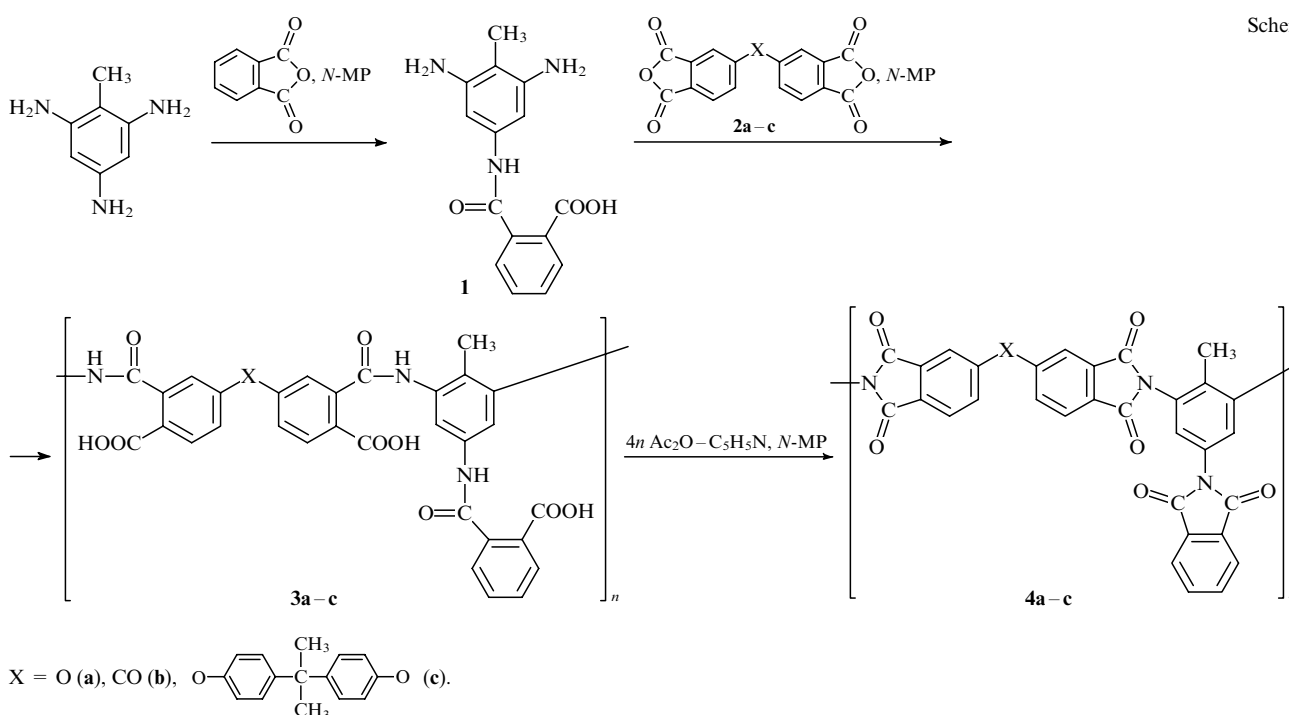
TAT presents the greatest interest among partial or complete reduction products of TNT. TAT-based phthalimido-substituted PI⁷⁵ were prepared by a selective polyacylation procedure.^{71–74}

The synthesis of phthalimido-substituted aromatic PI includes treatment of TAT with an equimolar amount of phthalic anhydride; this results in a mixture of mono-, bis- and tris(*o*-carboxybenzoyl)-substituted TAT derivatives with the predominance of the monoderivative **1**, which is due to a decrease in the activity of the free amino groups following monoacylation.⁷⁶

It is of note that the reaction of a free amino group in TAT with the carbonyl group of the substituent of the acylated amino group, due to their mutual *meta*-arrangement, is impeded in comparison with that in the reaction product of *o*-phenylenediamine with phthalic anhydride.⁷³

In order to obtain isomeric poly-*o*-carboxyamides **3a–c** (PCA) containing side *o*-carboxybenzamide groups, the acylation product of TAT with phthalic anhydride (a mixture of isomers) was treated with an equimolar amount of aromatic tetracarboxylic dianhydrides **2a–c** {3,3',4,4'-diphenyl oxide tetracarboxylic dianhydride (**2a**), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (**2b**) and 2,2-bis[3,4-dicarboxyphenyl]phenoxy]propane dianhydride (**2c**)} in *N*-MP at room temperature. The polyacylation process can be complicated due to the chemical heterogeneity of the TAT monoacylation products. Thus bis(*o*-carboxybenzoyl)triaminotoluene effects the polymeric chain termination, whereas non-acylated TAT favours the formation of branched and even cross-linked structures. Notwithstanding, homogeneous reaction solutions are formed in the synthesis of PCA **3a–c** with side *o*-carboxybenzamide substituents (Scheme 4).

Phthalimido-substituted polyimides **4a–c** are obtained from the corresponding PCA **3a–c** upon treatment with a fourfold excess of the pyridine–acetic anhydride mixture (1:1).⁷⁷ This is added to a solution of polycarboxyamide in *N*-MP at room temperature. The temperature is then increased to 100–110 °C and the reaction mass is kept at this temperature for 4 h. This reaction proceeds under homogeneous conditions and yields PI **4a–c** with a reduced viscosity (η_{red}) $\sim 0.3 \text{ dl g}^{-1}$ and molecular mass $\sim (22–105) \times 10^3$.



Scheme 4

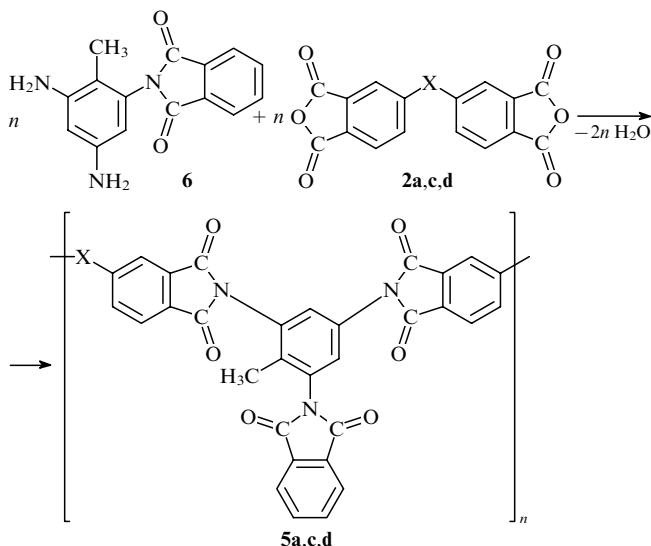
The imide structure of the products formed (the absorption maxima are around 720, 1370, 1720 and 1780 cm^{-1}) and the absence of non-cyclised units (within the limits of experimental error) were confirmed by the IR spectroscopic data.

All the PI synthesised are readily soluble in *N*-MP, DMF and a tetrachloroethane : phenol mixture (3 : 1). Good solubility of PI is due to the presence of methyl and phthalimide substituents and the isomeric character of the units in the polymer.

The softening temperatures (T_{soft}) of PI **4a–c** established by the thermomechanical method and the temperatures at which a 10% loss of the sample mass occurred ($T_{10\%}$) were determined by the dynamic thermogravimetric analysis (TGA) and found to be equal to 270–360 and 400–450 $^{\circ}\text{C}$, respectively.

The stable monomer TAT · 3 HCl is used for the synthesis of aromatic PI along with the easily oxidisable free base TAT. In the case of the former, it is first converted into a free base. To this end, a TAT · 3 HCl suspension is treated with pyridine whereupon solubilisation of the starting material occurs, which is followed by subsequent processing according to the procedure of PI synthesis from the free base (TAT) (see Scheme 4).

The polyimides **5a,c,d** having similar but more ordered structures were prepared by the reaction of 2,4-diamino-6-phthalimidotoluene (**6**) with aromatic tetracarboxylic dianhydrides **2a,c,d**.³⁶

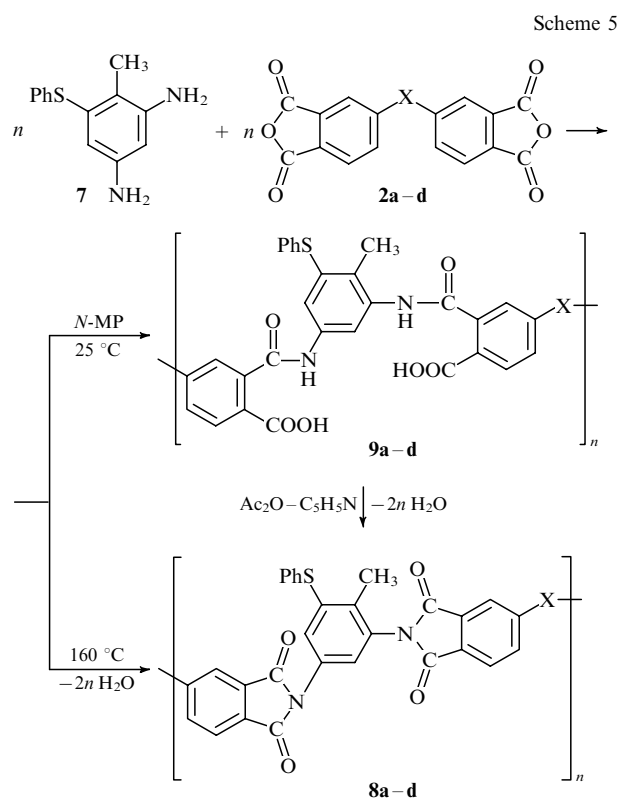


X = O (**a**), $\text{OC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}$ (**c**), $\text{C}(\text{CF}_3)_2$ (**d**).

Polyimides **5** are synthesised by high-temperature polycyclocondensation in *m*-cresol using quinoline as a catalyst. This reaction proceeds under homogeneous conditions; the reaction products contain no non-cyclised fragments (IR spectroscopic data). All the PI synthesised are soluble in *N*-MP, *m*-cresol and butyrolactone. Polyimide **5c** is soluble in both the aforementioned solvents and THF, chloroform and cyclohexanone, and PI **5d** is also soluble in acetone. This is due to the presence in PI **5c,d** of phthalimide and methyl substituents, *m*-phenylene fragments and 'hinged' hexafluoroisopropylidene groups.

According to the data from thermomechanical analysis, T_{soft} of the polymers **5a,c,d** are 275–350 $^{\circ}\text{C}$, and $T_{10\%} = 415\text{--}465$ $^{\circ}\text{C}$ (data from TGA in air at a heating rate of 4.5 $^{\circ}\text{C min}^{-1}$). A comparison of PI synthesised from diamine **6** in accordance with Schemes 2 and 3 demonstrated that their thermal characteristics and solubilities differ slightly from one another, presumably due to the difference in their isomeric compositions.

The reaction of 3,5-diamino-2-methyldiphenyl sulfide (**7**) with aromatic tetracarboxylic dianhydrides **2a–d** is carried out in accordance with the following scheme (Scheme 5):



R = O (**a**), CO (**b**), $\text{OC}_6\text{H}_4\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{O}$ (**c**), $\text{C}(\text{CF}_3)_2$ (**d**).

Two approaches were used in the synthesis of PI **8a–d**: (1) the reaction of the diamine **7** with aromatic tetracarboxylic dianhydrides in *N*-MP at room temperature, which yields PCA **9a–d**, with subsequent imidisation of these polymers using the pyridine–acetic anhydride mixture (1 : 1); (2) high-temperature (160 $^{\circ}\text{C}$) polycyclocondensation of the starting monomers in *m*-cresol catalysed by quinoline.

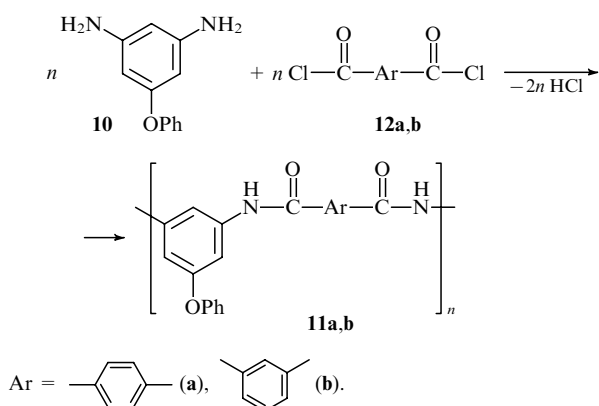
In virtually all cases, the PI **8a–d** prepared in *m*-cresol were characterised by higher values of η_{red} in comparison with the polymers of the same structures prepared in *N*-MP. For example, the η_{red} values for PI **8c** prepared in *m*-cresol and *N*-MP are equal to 0.80 and 0.30 dl g^{-1} , respectively.

High solubility in *N*-MP, DMF and *m*-cresol is a distinguishing feature of the PI under study. The polyimide **8d** is also soluble in THF, cyclohexanone, chloroform, dichloromethane and even in acetone. The presence of phenylthio substituents is one of the factors which determine high solubility of PI **8**, which is in keeping with the published data.^{78–80}

Studies of the effects of methyl substituents on the properties of PI by comparing characteristics of polymers based on 3,5-diamino-2-methyldiphenyl (**7**) and 3,5-diaminodiphenyl sulfide have shown that methyl-substituted PI possess higher solubilities. The softening temperatures of the methyl-substituted PI are 250–285 $^{\circ}\text{C}$, *i.e.*, somewhat higher than those of the corresponding PI devoid of methyl groups. On the contrary, the decomposition temperatures of methyl-substituted PI are lower (310–370 $^{\circ}\text{C}$) than those of PI containing no methyl groups.¹⁴

Considerable attention has been given to the synthesis of heterochain polymers containing no methyl groups, especially to the synthesis of polymers based on aromatic diamines containing a phenoxy substituent, which affects favourably the solubility of aromatic condensation polymers.^{78–85} For example, polyamides **11a,b** (PA) were prepared on the basis of 3,5-diaminodiphenyl ether (**10**). (Some aromatic PA are widely known owing to their excellent thermal and mechanical properties.^{86–88}) These PA were

synthesised using terephthalic (**12a**) and isophthalic (**12b**) acid dichlorides.^{89, 90}



The synthesis of PA **11a,b** was carried out using two different approaches: (1) low-temperature polycondensation in *N*-MP^{86,90} and (2) low-temperature polycondensation in chloroform in the presence of triethylamine as an HCl acceptor.⁸⁶⁻⁹⁰

The polyamides **11a,b** are readily soluble in organic solvents [*N*-MP, dimethylacetamide (DMAA), DMF, *m*-cresol, etc.]; their decomposition temperatures are 350–400 °C. These characteristics are in good agreement with those obtained in earlier studies on aromatic PA containing phenoxy substituents.^{80, 83} Glass-transition temperatures of the PA synthesised (236–275 °C) are lower than those of unsubstituted PA with similar structures.^{86, 87} This suggests that phenoxy substituents exert a plastifying effect.

Considerable attention has been given to the synthesis of PI containing aromatic substituents. The interest in substituted PI is due to the poor processability of unsubstituted PI.^{26-30, 91, 92} Among PI containing aromatic substituents, phenoxy-substituted polymers are especially popular. Such PI were prepared^{58-61, 90, 93, 94} by treatment of phenoxy-substituted amines **10, 13-16** with tetracarboxylic dianhydrides (Scheme 6).

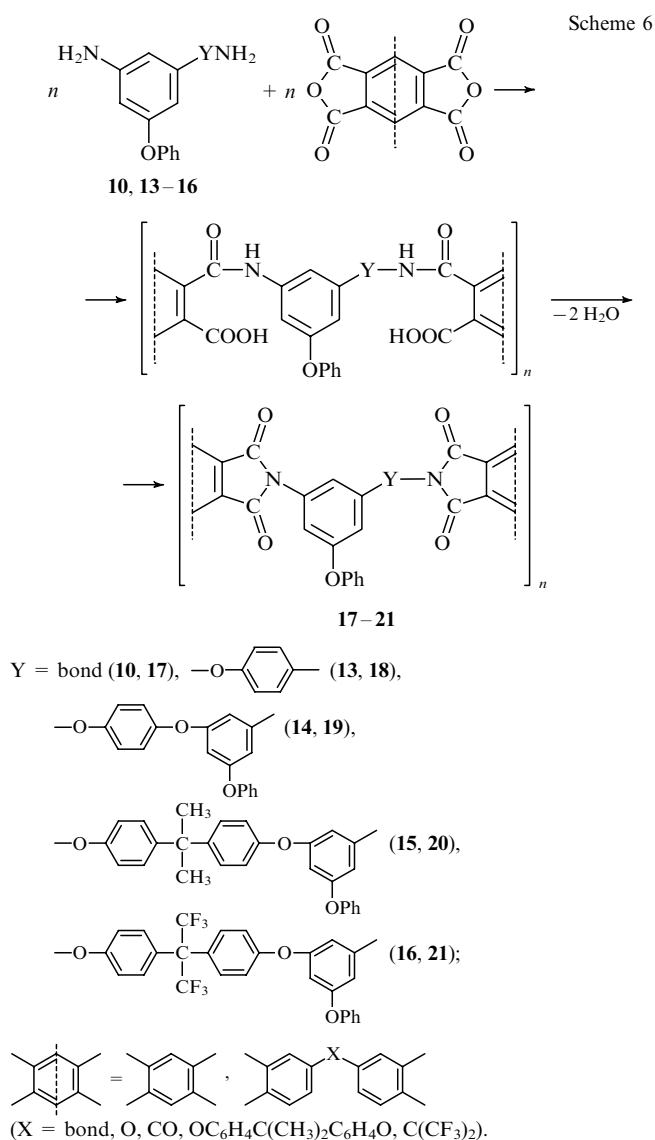
The PI **17-21** can be prepared by three routes:⁹⁵ (1) low-temperature polycondensation in *N*-MP with subsequent catalytic imidisation of the PCA formed in the reaction solution in the presence of pyridine–acetic anhydride (1 : 1); (2) high-temperature polycondensation in *N*-MP in the presence of azeotrope-forming compounds; (3) high-temperature polycondensation in *m*-cresol catalysed by isoquinoline.

A comparison of PI prepared by three different methods has demonstrated that high-molecular-mass polymers are formed in nearly all cases.

Polyimides **17** and **18** except for those PI based on pyromellitic dianhydride are soluble in *N*-MP, *m*-cresol and a tetrachloroethane–phenol mixture, which suggests a favourable influence of the phenoxy substituents on the solubility of the polymers. The values of η_{red} for these polymers in *N*-MP are equal to 0.30–0.83 dl g⁻¹ ($M_w \leq 48\,000$). Some PI demonstrate good film-forming properties. The softening temperatures (T_{soft}) (180–380 °C) and $T_{10\%}$ (500–550 °C) of the polymers **17** and **18** differ significantly from one another.

Polymers **17** based on 3,5-diaminodiphenyl ether (**10**) may be considered as PI analogues based on *m*-phenylenediamine. A comparison of properties of these two groups of polymers suggests that the introduction of phenoxy substituents leads to an increase in the solubility of the polymers and a decrease in their glass-transition temperatures, indicating that phenoxy groups behave as chemical plasticisers. This finding is in good agreement with the literature data.^{78-84, 96-101}

Polyimides **19-21** have $\eta_{\text{red}} = 0.22-1.00$ dl g⁻¹ (*N*-MP) and M_w up to 77 000 (*N*-MP, sedimentation data). With the exception of polypyromellitimide, these polymers are soluble in organic solvents. Some of them form films. The polymers **19-21** prepared

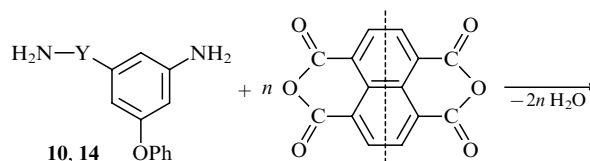


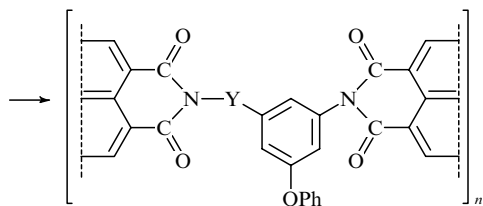
in accordance with Scheme 6 have low softening temperatures (165–213 °C) and high decomposition temperatures ($T_{10\%} = 470-550$ °C), which determines their processability into articles using solvent-free methods.

A comparison of various characteristics of these PI has shown that polymers **19** based on bis(3-amino-5-phenoxy)diphenyl bisphenol ethers manifest the best solubility; some of them are soluble even in cyclohexanone. They also have the lowest T_{soft} .

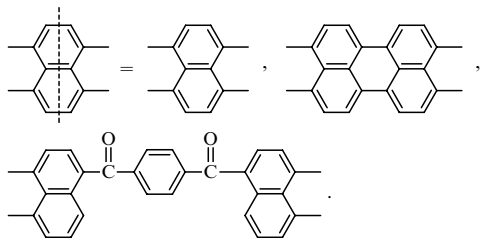
In addition to PI containing five-membered imide rings, PI with six-membered imide rings, *viz.*, polynaphthylimides and polyperyleneimides, have been synthesised; the latter are known to be more hydrolytically stable and thermostable than polynaphthylimides.¹⁰²⁻¹⁰⁵

The synthesis of phenoxy-substituted polynaphthylimides and polyperyleneimides^{90, 106} was carried out as follows:



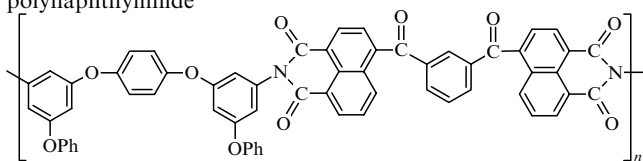


Y = bond (**10**), $-\text{O}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_3(\text{OPh})-\text{C}_6\text{H}_3(\text{OPh})-\text{O}-$ (**14**);

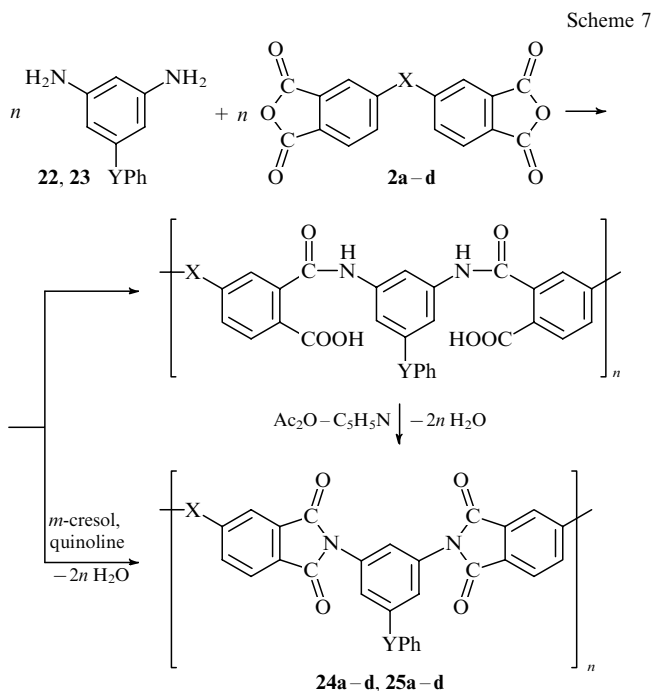


All these reactions were carried out in phenolic solvents (*m*-cresol, *m*- or *p*-chlorophenols) under high-temperature polycondensation conditions using benzoimidazole and/or benzoic acid as a catalyst. The polymerisation process is homogeneous in all cases and yields deeply coloured polymers.

Some of the polymers synthesised are well soluble in organic solvents and possess good thermal characteristics. Thus the polynaphthylimide



is soluble not only in *N*-MP and the tetrachloroethane–phenol mixture (3 : 1), but also in DMF, chloroform and, partially, in



Y = S (**22, 24**), SO₂ (**23, 25**);

X = O (**a**), CO (**b**), OC₆H₄C(CH₃)₂C₆H₄O (**c**), C(CF₃)₂ (**d**).

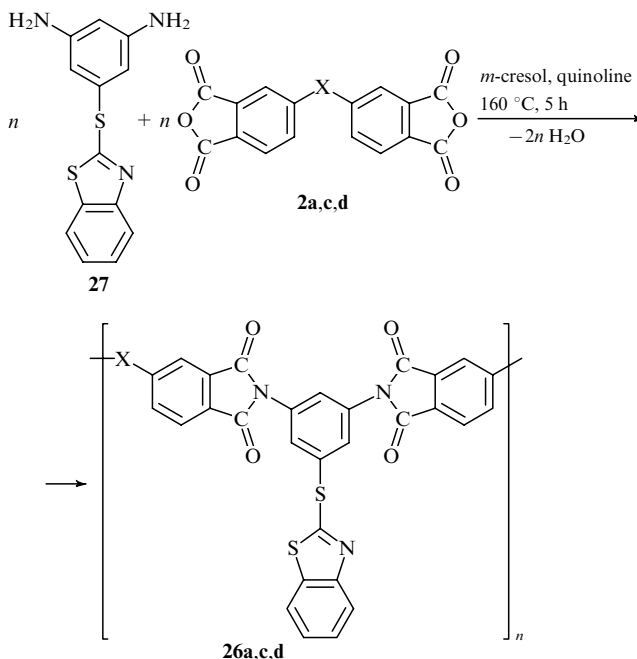
DMA. Enhanced solubility of this polynaphthylimide in comparison with the polymers prepared from the same dianhydrides and aromatic diamines containing no phenoxy substituents^{105,107} demonstrates a positive influence of the hydroquinone bis(3-amino-5-phenoxy)diphenyl ether structure on the solubility of the polymers.

Polyimides containing phenylthio- and phenylsulfonyl side groups^{62,94} were prepared from the diamines **22** and **23** in accordance with Scheme 7.

The polyimides **25a–d** based on 3,5-diaminodiphenyl sulfone (**23**) are characterised by lower η_{red} values (0.25 dl g⁻¹) than PI **24a–d** based on 3,5-diaminodiphenyl sulfide (**22**) (0.79–1.20 dl g⁻¹). This difference may be due to the negative effect of the electron-withdrawing phenylsulfonyl group on the reactivity of the amino groups.

The solubility of the PI **24a–d** in organic solvents strongly depends on the nature of the dianhydride used. The values of η_{red} of the polymers in *N*-MP are fairly high (0.79–1.20 dl g⁻¹), while moderate softening temperatures (210–250 °C) combine with high decomposition temperatures (400–460 °C).

The polyimides **26a,c,d** containing benzothiazol-2-ylthio groups were prepared by high-temperature polycyclocondensation of the diamine **27** with the dianhydrides **2a,c,d** in *m*-cresol.¹⁰⁸



X = O (**a**), OC₆H₄C(CH₃)₂C₆H₄O (**c**), C(CF₃)₂ (**d**).

All the PI **26** were synthesised under homogeneous conditions. These polymers have $\eta_{\text{red}} = 0.29\text{--}0.42$ dl g⁻¹, $T_{\text{soft}} = 215\text{--}265$ °C and $T_{10\%} = 325\text{--}400$ °C. The polymer **26a** is soluble in *N*-MP, the PI **26c**, in *N*-MP and THF and the PI **26d** is soluble in *N*-MP, THF and chloroform. The positive influence of benzothiazol-2-yl side groups on the solubility of the polymers has been observed previously.^{109,110}

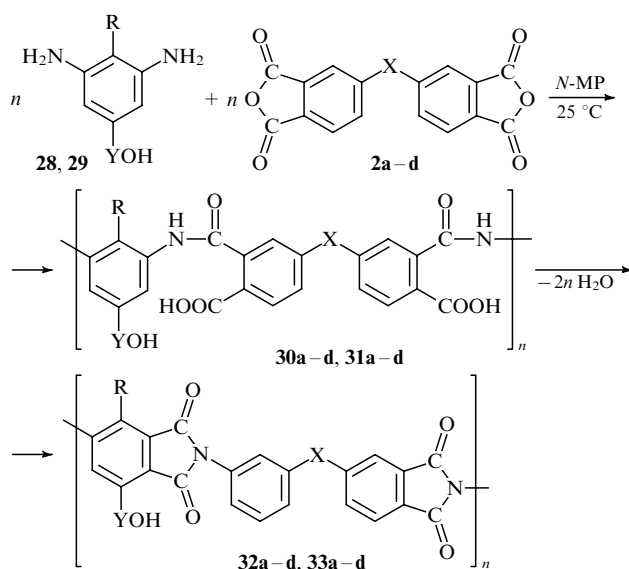
PI containing functional side groups, first of all, hydroxy groups, were synthesised along with PI prepared from TNT derivatives devoid of reactive substituents.^{65,111}

Recently,^{112–119} PI containing free hydroxy groups have attracted the keen attention of investigators because of the possibility of forming hydrogen bonds, which increases the glass-transition temperatures of the polymers, favours their solubilities in amide solvents and enhances moisture absorption.¹¹⁶

It is noteworthy that hydroxy groups can be used as the reaction centres for the introduction of other side groups, *e.g.*,

unsaturated substituents able to form crosslinked structures;¹¹⁷ chromophores imparting nonlinear optical properties to the PI^{120–122} and thermally unstable side groups prone to thermal decomposition with the formation of low-permittivity nanofoams.^{123–125}

Polyimides based on 3,5-diamino-4'-hydroxydiphenyl ether (**28**), 2,6-diamino-4-hydroxytoluene (**29**) and the tetracarboxylic dianhydrides **2a–d** were prepared in two steps.



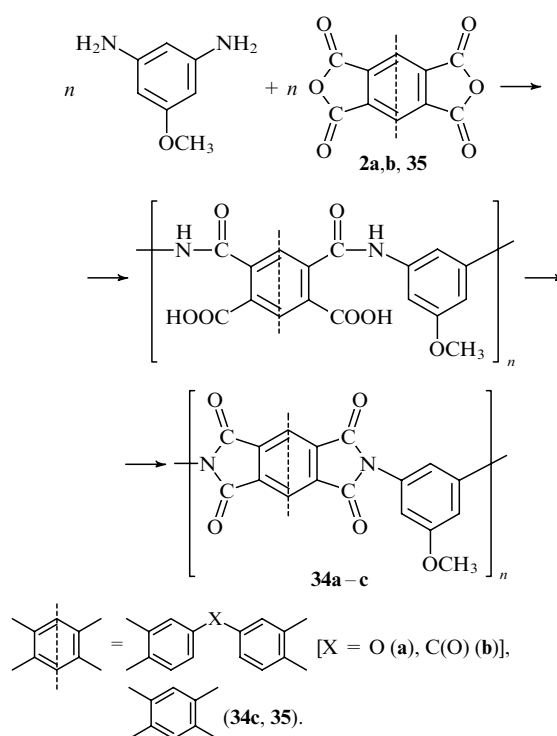
28, 30, 32: R = H, Y = $-\text{O}-\text{C}_6\text{H}_4-$; **29, 31, 33:** R = CH₃, Y = bond;
X = O (**a**), CO (**b**), OC₆H₄C(CH₃)₂C₆H₄O (**c**), C(CF₃)₂ (**d**).

The first step includes the preparation of PCA **30a–d** and **31a–d** in *N*-MP under mild conditions (25 °C). The second step, *viz.*, polycyclisation of PCA, is carried out in the absence of the pyridine–acetic anhydride mixture to prevent acylation of the hydroxy groups. After addition of toluene to the reaction mixture (for azeotropic distillation of water), the reaction temperature is raised to 180 ± 10 °C and the solution is kept at this temperature for 6 ± 1 h. This method has recently found wide acceptance in PI synthesis.^{95, 126} Cyclisation of PCA **30a–d** and **31a–d** from all the aromatic tetracarboxylic dianhydrides **2a–d** occurs under homogeneous conditions and yields PI **32a–d** and **33a–d** with moderate viscosities ($\eta_{\text{red}} = 0.28\text{--}0.80\text{ dl g}^{-1}$) and high degrees of cyclisation.

All the PI synthesised represent amorphous polymers with glass-transition temperatures of 223–369 °C typical of flexible-chain PI and decomposition temperatures of 378–439 °C. They are well soluble in organic solvents; the PI based on the dianhydride **2d** manifest the best solubility.

The introduction of alkoxy substituents into the PI macromolecules enhances their solubilities. It is known that the presence of methoxy substituents in PI macromolecules increases their solubilities in organic solvents.⁹⁶ The methoxy-substituted PI are prepared starting from 3,5-diaminoanisole.⁴⁶

The PI **34a–c** were synthesised by the reaction of 3,5-diaminoanisole with dianhydrides **2a,b** and pyromellitic dianhydride (**35**) using three different procedures:^{90–92} low-temperature condensation of 3,5-diaminoanisole with tetracarboxylic dianhydrides in amide solvents followed by thermal (route 1) or catalytic (route 2) imidisation of the PCA formed in the presence of the pyridine–acetic anhydride mixture (1 : 1) and high-temperature (150–180 °C) condensation in *m*-cresol in the presence of a catalyst (quinoline, isoquinoline or benzoic acid) (route 3).



The reaction of 3,5-diaminoanisole with tetracarboxylic dianhydrides in amide solvents (*e.g.*, *N*-MP) is carried out at room temperature. This reaction proceeds in a homogeneous system and yields PCA with relatively high η_{red} (0.47–1.12 dl g⁻¹).

Catalytic imidisation affords PI more soluble in comparison with polymers synthesised by solid-phase methods;⁹⁶ therefore, this approach presents the greatest interest. Catalytic imidisation is performed by adding the pyridine–acetic anhydride mixture to a prepolymer solution and stirring the boiling reaction mixture for several hours. In all cases studied, the imidisation was accompanied by precipitation of the polymer from the reaction mass in the form of a swollen gel. It is noteworthy that this does not prevent the cyclisation of the *o*-carboxamide fragments into imide fragments with a high degree of conversion.

Polypyromellitimide **34c** does not soften unless the decomposition temperature is reached. The softening temperatures of polyimides **34a,b** are 300 and 310 °C, respectively.

Depending on the structure of the central fragment of the dianhydride, the thermal stabilities of the PI synthesised decrease in the following order: **34c** > **34b** > **34a**. This is consistent with the generally accepted viewpoint on the correlation between the structures of the polymers and their thermal stabilities.^{127, 128}

Dynamic TGA studies of thermal stabilities of PI prepared (air, heating rate 4.5 °C min⁻¹) have shown that $T_{10\%}$ depends only insignificantly on the polymer structure: $T_{10\%}$ is ~ 400 °C for all the PI studied. The relatively low thermal stabilities of the polymers **34a–c** can be attributed to the presence of the methoxy groups.

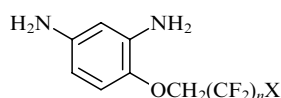
The polyimides **34b,c** are insoluble in amide-type (including *N*-MP) or any other solvents; only the PI **34a** is soluble in *m*-cresol and the tetrachloroethane–phenol mixture (3 : 1). Presumably, the ‘hinged’ groups have a more pronounced effect on the solubility of the polymers than methoxy substituents.

The high solubility of the polymer **34a** in phenolic solvents has made it possible to obtain virtually colourless films with a tensile strength of 114 MPa (at 25 °C) and elongation at rupture of 9%.

An attempt to synthesise the PI **34a** by high-temperature condensation in *m*-cresol was less successful, although this was performed in a homogeneous medium. The η_{red} value of the polymer **34a** thus prepared is much lower than that of the corresponding polymer obtained by catalytic cyclisation of PCA.

Polymers containing perfluoroalkyl side groups also present substantial interest.^{49–51} Such polymers have found wide application in aerospace and electronic engineering owing to their high thermal stabilities, mechanical strengths and good insulating characteristics.^{129–133} These technological fields have a continuing demand for transparent PI (coating of solar batteries) and low-permittivity PI (reduction of delay periods in electric circuits). The optoelectronic industry requires PI transparent at the wavelengths exceeding that of the visible light and possessing controllable refraction indices. Introduction of fluorine into polyimide materials is one of the most efficient approaches to the synthesis of such PI.^{134–136} The introduction of side fluoroalkoxy groups into the starting monomers is also widely used.

The synthesis of fluorinated PI based on diamines of the general formula

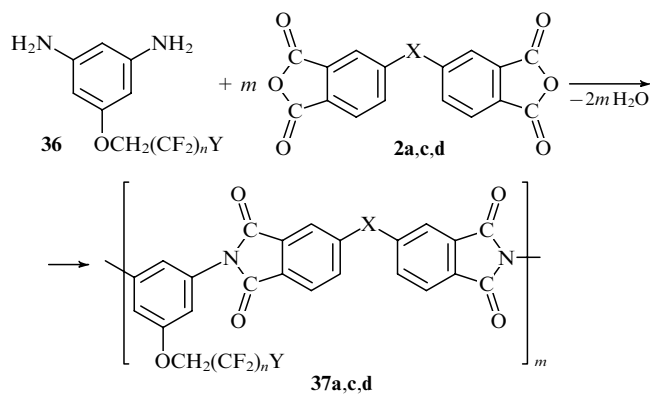


X = F: $n = 3, 6, 7$; X = H: $n = 10$.

has been described.¹³⁷

However, the values of η_{red} of the polymers thus prepared were relatively low and decreased with an increase in the length of the fluoroalkoxy group. This may be due to two reasons, viz.: (1) a decrease in the reactivities of fluorinated diamines as nucleophiles due to the presence of electron-withdrawing fluoroalkoxy groups; (2) the steric hindrance of the amino group in the *ortho*-position relative to the bulky fluoroalkoxy group. This circumstance has stimulated the search for new ways to synthesise fluorinated PI.

Some novel representatives of such PI were synthesised from perfluoroalkoxy-substituted *m*-phenylenediamines **36** based on TNT and various aromatic tetracarboxylic dianhydrides.^{51–54}



Y = F: $n = 1$; Y = H: $n = 2, 4, 6$;
X = O (**a**), OC₆H₄C(CH₃)₂C₆H₄O (**c**), C(CF₃)₂ (**d**).

This reaction is carried out in *m*-cresol in the presence of isoquinoline (160 °C, 5 h). The homogeneous reaction conditions favour the preparation of PI completely soluble in *N*-MP. Depending on their structures, such PI are also soluble in other organic solvents. Thus the polymers **37c** are soluble in chlorinated solvents but are insoluble in acetone, whereas the PI **37d** are soluble in acetone, but not in chlorinated hydrocarbons. High solubility of the PI **37** may be due to the presence of side perfluoroalkoxy and bridging groups^{96,136} as well as to the amorphous structure of these compounds (X-ray diffraction data).

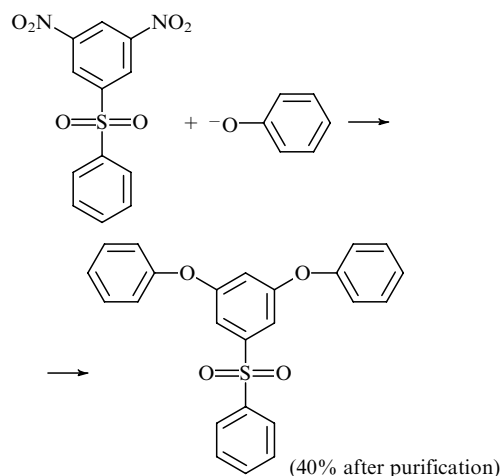
Virtually all PI **37** are high-molecular-mass compounds with $T_{soft} = 155–265$ °C (thermomechanical analysis data) and

$T_{10\%} = 400–430$ °C, which exceed those of the methoxy-substituted PI **35**. It should be noted that T_{soft} of the polymers **37** decreases with an increase in the length of the fluoroalkoxy group. Colourless strong elastic films were cast from solutions of the PI **37** in THF. Pressing of these PI at temperatures exceeding T_{soft} by 100 °C at 10 MPa produced transparent yellowish articles. The polymers **37** possess relatively low refraction indices and dielectric constants (ϵ), which is in good agreement with the known data.^{124,137}

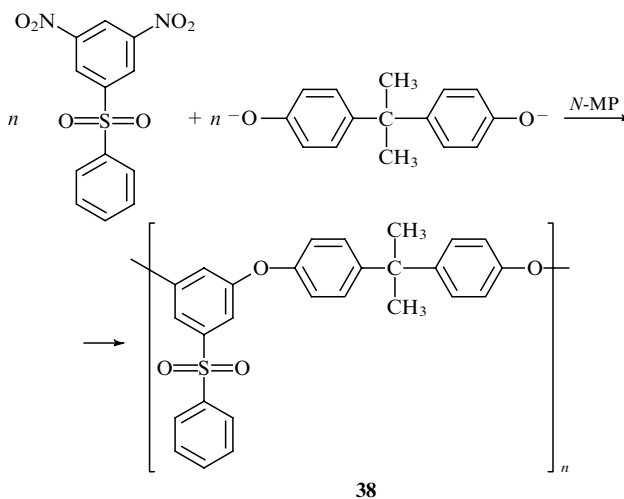
2. Aromatic oligo- and polyethers

Aromatic nucleophilic substitution of nitro groups can be employed for the preparation of aromatic polyethers,^{24,25,138} although there are few examples of such reactions.¹³⁸ A serious problem in the synthesis of polyethers from mononuclear dinitro compounds is passivation of the second nitro group following replacement of the first nitro group by a nucleophile. What is also essential is that nitro group activators usually occupy the *ortho*- and *para*-positions. Therefore, the possibility of using 3,5-dinitrodiphenyl sulfone, a TNT-based mononuclear compound containing an electron-withdrawing activating group in the *meta*-position with respect to the nitro groups, in the synthesis of aromatic polyethers is of interest for investigators.⁹⁰

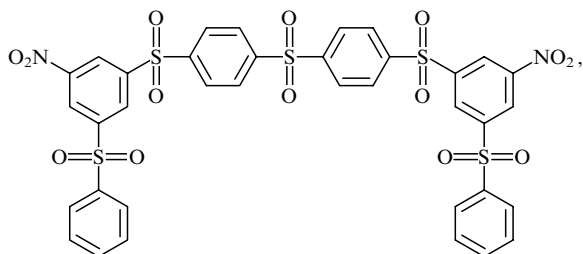
The model reaction of 3,5-dinitrodiphenyl sulfone with phenol was carried out in *N*-MP (150 °C, 6 h).



The synthesis of the polyether **38** based on 3,5-dinitrodiphenyl sulfone and bisphenol A was carried out under identical conditions.



Although the polyether formed has low molecular mass ($n = 5$, $M_n = 1900$, $M_w = 2600$), this reaction has demonstrated the feasibility of polyether synthesis from mononuclear dinitro compounds containing an activating group in the *meta*-position with respect to the nitro groups, which is in agreement with the earlier data.¹³⁹ It seems therefore expedient to use the dinitro-compound,



which represents the reaction product of 4,4'-dimercaptodiphenyl sulfide with a twofold molar excess of 3,5-dinitrodiphenyl sulfone and subsequent oxidation of the sulfide groups to the sulfonyl groups, as a starting monomer for the synthesis of high-molecular-mass polyethers.

IV. Conclusion

The development of condensation monomers and polymers based on TNT and its derivatives offers a solution for two different problems, *viz.*, utilisation of TNT and design of cheap and accessible PI with enhanced processability into articles.

Taking into account the increasing interest in dendritic polymers in the past two decades,^{140–151} it may be expected that the progress in the chemistry of monomers and polymers based on TNT will be associated with the synthesis of such polymers. It should be noted that TAT is an ideal trifunctional core for the synthesis of novel representatives of dendritic PA and PI, while 1,4-bis(3,5-diaminophenoxy)benzene can serve as a tetrafunctional core for the preparation of dendritic PA and PI.

The A₂B-type monomers derived from TNT^{152, 153} can find application in the synthesis of superbranched polymers.^{154–157} In particular, 3,5-diamino-4'-carboxydiphenyl ether can be used for the preparation of superbranched aromatic PA containing peripheral amino groups, whereas 3,5-dinitro-4'-hydroxydiphenyl ether is a promising starting material for the synthesis of superbranched aromatic polyethers based on aromatic nucleophilic nitrosubstitution.

The novel architecture of these polymers determines their novel properties which in turn opens up new areas for their application.

This review has been written with financial support of the International Science and Technology Center (Grant No. 419).

References

- H Lee, D Stoffey, K Neville, in *New Linear Polymers* (New York: McGraw-Hill, 1967)
- A H Frazer, in *High Temperature Resistant Polymers* (New York: Wiley-Interscience, 1968)
- V V Korshak, in *Termostoikie Polimery* (Thermally Stable Polymers) (Moscow: Nauka, 1969) p. 411
- R T Cotter, M Matzner, in *Ring-Forming Polymerization Pt. B-2* (New York: Academic Press, 1972) p. 568
- Z Yedlinski (Ed.), in *Advances in the Chemistry of Thermally Stable Polymers* (Warszawa: Polish Scientific Publishers, 1977) p. 156
- P E Cassidy, in *Thermally Stable Polymers* (New York: Marcel Dekker, 1980) p. 163
- J P Critchley, W W Wright, in *Heat-Resistant Polymers* (New York: Plenum, 1983) p. 259
- K U Buellen *Spezialplaste* (Berlin: Akademie-Verlag, 1978)
- R R Luise, in *Applications of High Temperature Polymers* (New York: CRC Press, 1996) p. 272
- J Stille, T Campbell (Eds) *Condensation Monomers* (New York: Wiley-Interscience, 1972)
- H Schnell *Chemistry and Physics of Polycarbonates* (New York: Wiley-Interscience, 1964)
- V V Korshak, A L Rusanov, S Kh Fidler, D S Tugushi, R G Kakauridze, Yu N Margalitadze, S N Zinov'ev *Plastmassy* (10) 28 (1984)
- E R Kekharsaeva, E B Shustov, A K Mikitaev, V T Dorofeev *Plastmassy* (2) 9 (1985)
- V V Korshak, A L Rusanov *Usp. Khim.* **58** 1006 (1989) [*Russ. Chem. Rev.* **58** 588 (1989)]
- A L Rusanov, in *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii (Itogi Nauki i Tekhniki)* [The Chemistry and Technology of Polymers (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1990) Vol. 26, p. 3
- A L Rusanov *Prog. Polym. Sci.* **19** 589 (1994)
- V A Tartakovskiy, S A Shevelev, M D Dutov, A Kh Shakhnes, A L Rusanov, L G Komarova, A M Andrievskiy *Konversiya* 7 (1994)
- V A Tartakovskiy, S A Shevelev, M D Dutov, A Kh Shakhnes, A L Rusanov, L G Komarova, A M Andrievskiy, in *Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems (NATO ASI Series)* (Ed. H Krause) (Dordrecht, Boston, London: Kluwer Academic, 1997) p. 137
- V A Tartakovskiy, S A Shevelev, A L Rusanov, in *Proceedings of the 218th ACS National Meeting, New Orleans, LA, 1999* p. 27
- S A Shevelev, V A Tartakovskiy, A L Rusanov, in *Combustion of Energetic Materials* (Eds K K Kuo, L T DeLuca) (New York: Begell House, 2002) p. 62
- A L Rusanov, L G Komarova, M P Prigozhina, V A Tartakovskiy, S A Shevelev, M D Dutov, in *Combustion of Energetic Materials* (Eds K K Kuo, L T DeLuca) (New York: Begell House, 2002) p. 1031
- A L Rusanov, L G Komarova, V A Tartakovskiy, S A Shevelev, in *Recent Progress in Polycondensation* (Ed. T Matsumoto) (Kerala: Research Signpost, 2002) p. 117
- V L Zbarskii, V F Zhilin, in *Toluol i Ego Nitroproizvodnyye* (Toluene and Its Nitro-Derivatives) (Moscow: Editorial, 2000) p. 165
- T Takekoshi *Polym. J.* **19** 191 (1987)
- A L Rusanov, T Takekoshi *Usp. Khim.* **60** 1449 (1991) [*Russ. Chem. Rev.* **60** 738 (1991)]
- N A Adrova, M I Bessonov, L A Laius, A P Rudakov, in *Poliimidy — Novyi Klass Termostoikikh Polimerov* (Polyimides as a New Class of Thermally Stable Polymers) (Leningrad: Nauka, 1968) p. 211
- M I Bessonov, M M Koton, V V Kudryavtsev, L A Laius, in *Poliimidy — Klass Termostoikikh Polimerov* (Polyimides as a Class of Thermally Stable Polymers) (Leningrad: Nauka, 1983) p. 307
- K Mittal (Ed.), in *Polyimides: Synthesis, Characterization and Applications* Vol. 1 (New York, London: Plenum, 1984) p. 3
- K Mittal (Ed.) *Polyimides: Synthesis, Characterization and Applications* Vol. 2 (New York, London: Plenum, 1984) p. 617
- V V Korshak, A L Rusanov, I Batirov, in *Novoe v Oblasti Termostoikikh Poliimidov* (The New in Thermally Stable Polymers) (Dushanbe: Donish, 1986) p. 102
- A Mitchel, R D Sunner, in *Proceedings of the 24th Conference of ICT, Karlsruhe, 1993* p. 38
- A L Rusanov, V A Tartakovskiy, S A Shevelev, V I Savchenko, in *Proceedings of Global Demilitarization Symposium and Exhibition, Lexington, KY, 2002* p. 20
- E F Litvin, V Z Sharf *Russ. Khim. Zh.* **44** 90 (2000)^a
- S A Shevelev, A Kh Shakhnes, B I Ugrak, S S Vorob'ev *Synth. Commun.* **31** 2557 (2001)
- A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, A Kh Shakhnes, S S Vorob'ev *Vysokomol. Soedin., Ser. B* **43** 1430 (2001)^b
- A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, V I Gulevskaya, A Kh Shakhnes, E F Litvin, L M Kozlova, V Z Sharf *Vysokomol. Soedin., Ser. B* **44** 1276 (2002)^b
- J F Bunnett, R E Zahler *Chem. Rev.* **49** 273 (1951)
- H Feuer (Ed.) *The Chemistry of the Nitro and Nitroso Groups* Vol. 1 (New York: Wiley, 1969)

39. J March *Advanced Organic Chemistry. Reactions, Mechanisms and Structures* Vol. 3 (Third Ed.) (New York: Wiley, 1985)
40. F Terrier *Chem. Rev.* **82** 77 (1982)
41. G A Artamkina, M P Egorov, I P Beletskaya *Chem. Rev.* **82** 427 (1982)
42. S A Shevelev, M D Dutov, O V Serushkina *Izv. Akad. Nauk, Ser. Khim.* 2528 (1995)^c
43. A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, M D Dutov, O V Serushkina *Vysokomol. Soedin., Ser. B* **44** 2039 (2002)^b
44. W E Garner, C L Alberney *Proc. Roy. Soc.* **99** 213 (1921)
45. BRD P. 3 035 030; *Chem. Abstr.* **95** 24 518 (1981)
46. A L Rusanov, L G Komarova, A M Trushkin, S A Shevelev, M D Dutov, O V Serushkina, A M Andrievskiy *Vysokomol. Soedin., Ser. B* **35** 883 (1993)^b
47. A Albert *J. Chem. Soc.* 244 (1942)
48. P T Izzo *J. Org. Chem.* **24** 2026 (1959)
- doi> 49. S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov, A L Rusanov *Mendeleev Commun.* 69 (1998)
50. S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov, A L Rusanov *Izv. Akad. Nauk, Ser. Khim.* 1667 (1998)^c
51. S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov, A L Rusanov, L G Komarova, M P Prigozhina, A A Askadskiy *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **39** (2) 851 (1998)
- doi> 52. A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov *High Perform. Polym.* **11** 395 (1999)
53. A L Rusanov, L G Komarova, M P Prigozhina, A A Askadskiy, V V Kazantseva, S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov *Vysokomol. Soedin., Ser. A* **41** 1357 (1999)^b
54. A L Rusanov, L G Komarova, M P Prigozhina, A A Askadskiy, S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov, in *Polyimides and High Performance Polymers* (Eds M J M Abadie, B Sillion) (Amsterdam: Elsevier, 2001) p. 89
55. A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, M D Dutov, M A Korolev, O Yu Sapozhnikov, in *Proceedings of the 7th International Conference on Polymers in Electronic Packaging, McAfee, 2000* p. 1
56. S A Shevelev, M D Dutov, I A Vatsadze, O V Serushkina, M A Korolev, A L Rusanov *Izv. Akad. Nauk, Ser. Khim.* 393 (1995)^c
- doi> 57. S A Shevelev, M D Dutov, I A Vatsadze, O V Serushkina, A L Rusanov, A M Andrievskiy *Mendeleev Commun.* 157 (1995)
58. A L Rusanov, L G Komarova, M P Prigozhina, T S Sheveleva, A A Askadskiy, K A Bychko, S A Shevelev, M D Dutov, I A Vatsadze, O V Serushkina *Vysokomol. Soedin., Ser. A* **38** 1462 (1996)^b
59. A L Rusanov, L G Komarova, M P Prigozhina, T S Sheveleva, A A Askadskiy, S A Shevelev, M D Dutov, I A Vatsadze *Vysokomol. Soedin., Ser. B* **38** 2060 (1996)^b
60. Russ. P. 2 072 350; *Chem. Abstr.* **128** 48 636 (1998)
61. A L Rusanov, L G Komarova, M P Prigozhina, T S Sheveleva, A A Es'kov, S A Shevelev, M D Dutov, I A Vatsadze *Vysokomol. Soedin., Ser. A* **39** 1701 (1997)^b
62. A L Rusanov, M P Prigozhina, L G Komarova, T S Sheveleva, S A Shevelev, M D Dutov, O V Serushkina *Vysokomol. Soedin., Ser. A* **41** 70 (1999)^b
63. S A Shevelev, M D Dutov, O V Serushkina *Izv. Akad. Nauk, Ser. Khim.* 25 (1995)^c
64. Russ. P. 2 062 267; *Chem. Abstr.* **126** P89 135 (1997)
65. M Abadie, I Izri, T S Sheveleva, A L Rusanov, L G Komarova, Ya S Vygodskii, S A Shevelev, M D Dutov, I A Vatsadze, in *Proceedings of the 4th European Technical Symposium on Polyimides and High Performance Polymers, Montpellier, 1996* p. 163
- doi> 66. V V Rozhkov, A M Kuvshinov, V I Gulevskaya, I I Chervin, S A Shevelev *Synthesis* 2065 (1999)
67. A S Onishchenko *Dienoviy Sintez* (Diene Synthesis) (Moscow: Izd. Akad. Nauk SSSR, 1963)
68. A Vasserman *Reaktsiya Dil'sa - Al'dera* (Diels - Alder Reaction) (Eds L M Kogvan, O N Temkin) (Moscow: Mir, 1968)
69. O Diels, K Alder *Liebigs Ann. Chem.* **460** 98 (1928)
70. J G Martin, R K Hill *Chem. Rev.* **61** 537 (1961)
71. V V Korshak, A L Rusanov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2518 (1968)^c
72. V V Korshak, A L Rusanov, R D Katsarava *Vysokomol. Soedin., Ser. A* **16** 722 (1974)^b
73. V V Korshak, A L Rusanov, I Batirov, R D Katsarava, F F Nijazi *Faserforsch. Textiltech. B* **29** 649 (1978)
74. V V Korshak, A L Rusanov, Z B Shifrina, Yu N Margalitadze, S Kh Fidler, B R Livshits, T V Lekae *Dokl. Akad. Nauk SSSR* **289** 367 (1986)^d
75. A L Rusanov, L G Komarova, M P Prigozhina *Vysokomol. Soedin., Ser. B* **44** 2228 (2002)^b
76. D A Bochvar, I V Stankevich, V V Korshak, A L Rusanov *Dokl. Akad. Nauk SSSR* **184** 95 (1969)^d
- doi> 77. J V Bower, L W Frost *J. Polym. Sci., Part A: Gen. Pap.* **1** 3135 (1963)
- doi> 78. J de Abajo, E Gujarrro, F J Serna, J G de la Campa *J. Polym. Sci., Part A: Polym. Chem.* **24** 483 (1986)
- doi> 79. A Meléndez, J de la Campa, J de Abajo *Polymer* **29** 1142 (1988)
- doi> 80. M-A Kakimoto, M Yoneyama, Y Imai *J. Polym. Sci., Part A: Polym. Chem.* **26** 149 (1988)
- doi> 81. H R Kricheldorf, Yu Engelhardt *Makromol. Chem.* **190** 2939 (1989)
- doi> 82. H R Kricheldorf, Yu Engelhardt *Makromol. Chem.* **191** 2017 (1990)
83. H R Kricheldorf, B Schmidt *Macromolecules* **25** 5471 (1992)
84. H R Kricheldorf, B Schmidt, R Burger *Macromolecules* **25** 5465 (1992)
- doi> 85. T Ichino, S Sasaki, T Matsuura, S Nishi *J. Polym. Sci., Part A: Polym. Chem.* **28** 323 (1990)
86. L B Sokolov, I D Gerasimov, V M Savinov, V K Belyakov, in *Termostoikiye Aromaticheskie Poliamidy* (Thermally Stable Aromatic Polyamides) (Moscow: Khimiya, 1975) p. 253
87. P W Morgan *Condensation Polymers: by Interfacial and Solution Methods* (New York, London, Sidney: Interscience, 1965)
88. J Preston, in *Encyclopedia of Polymer Science and Engineering* Vol. 11 (Second Ed.) (Ed. J I Kroschwitz) (New York: Wiley, 1988)
89. A L Rusanov, M P Prigozhina, L G Komarova, S A Shevelev, M D Dutov, I A Vatsadze *Vysokomol. Soedin., Ser. B* **42** 880 (2000)^b
- doi> 90. A L Rusanov, V A Tartakovskiy, S A Shevelev, M D Dutov, I A Vatsadze, O V Serushkina, L G Komarova, M P Prigozhina, E G Bulycheva, L B Elshina *Polymer* **41** 5021 (2000)
91. C E Sroog *Prog. Polym. Sci.* **16** 561 (1991)
92. V V Korshak, A L Rusanov, G V Kazakova, N S Zabel'nikov, G S Matvelashvili *Vysokomol. Soedin., Ser. A* **30** 1795 (1988)^b
93. A L Rusanov, L G Komarova, T S Sheveleva, M P Prigozhina, S A Shevelev, M D Dutov, I A Vatsadze, O V Serushkina *React. Funct. Polym.* **30** 279 (1996)
94. A L Rusanov, L G Komarova, T S Sheveleva, M P Prigozhina, S A Shevelev, M D Dutov, I A Vatsadze *Macromol. Symp.* **122** 123 (1997)
95. A L Rusanov, E G Bulycheva, G S Matvelashvili, G V Kazakova *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **35** (1) 370 (1994)
96. F W Harris, L H Lanier, in *Structure-Solubility Relationships in Polymers* (Eds F W Harris, R B Seymour) (New York, San Francisco, London: Academic Press, 1977) p. 193
97. D J Kumar *J. Polym. Sci., Polym. Chem. Ed.* **22** 3439 (1984)
98. F W Harris, S L C Hsu, C C Tso *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **31** (1) 342 (1990)
99. F W Harris, S-H, Lin, F L, S Z D Cheng *Polymer* **37** 5049 (1996)
- doi> 100. I K Spiliopoulos, J A Mikroyannidis *Polymer* **37** 3331 (1996)
- doi> 101. S Tamai, W Yamashita, A Yamaguchi *J. Polym. Sci., Part A: Polym. Chem.* **36** 971 (1998)
102. V V Korshak, A L Rusanov, I Batirov *Dokl. Akad. Nauk SSSR* **240** 88 (1978)^d
103. A L Rusanov *Usp. Khim.* **61** 815 (1992) [*Russ. Chem. Rev.* **61** 449 (1992)]
104. A L Rusanov *Adv. Polym. Sci.* **111** 116 (1994)
105. A L Rusanov, L B Elshina, E G Bulycheva, K Muellen *Vysokomol. Soedin., Ser. A* **41** 7 (1999)^b

106. A L Rusanov, E G Bulycheva, L B Elshina, S A Shevelev, M D Dutov, I A Vatsadze *Vysokomol. Soedin., Ser. A* **42** 1287 (2000)^b
107. A L Rusanov, E G Bulycheva, in *Proceedings of the 2nd European Technical Symposium on Polyimides and High Performance Polymers, Montpellier, 1991* p. PI-12
108. A L Rusanov, L G Komarova, M P Prigozhina, S A Shevelev, M D Dutov, O V Cerushkina *Vysokomol. Soedin., Ser. B* **42** 705 (2000)^b
- [doi>](#) 109. A E Lozano, J G De la Campa, J De Abajo, J Preston *Polymer* **35** 872 (1994)
110. J A Mikroyannidis *Macromolecules* **28** 5177 (1995)
111. M Abadie, I Izri-Zinina, T S Sheveleva, L G Komarova, A L Rusanov, Ya S Vygodskii, S A Shevelev, M D Dutov, I A Vatsadze *Vysokomol. Soedin., Ser. A* **39** 922 (1997)^b
- [doi>](#) 112. Q Jin, T Yamashita, K Hori *J. Polym. Sci., Part A: Polym. Chem.* **32** 503 (1994)
113. D N Khanna, W H Mueller *Polym. Eng. Sci.* **29** 954 (1989)
114. T Omota, K Koseki, T Yamaoka *Macromolecules* **23** 4788 (1990)
- [doi>](#) 115. Y Oishi, M Shirazaki, M Kakimoto, Y Imai *J. Polym. Sci., Part A: Polym. Chem.* **31** 293 (1993)
- [doi>](#) 116. T M Moy, J E McGrath *J. Polym. Sci., Part A: Polym. Chem.* **32** 1903 (1994)
- [doi>](#) 117. B-C Ho, Y-S Lin, Y-D Lee *J. Appl. Polym. Sci.* **53** 1513 (1994)
118. M Ueda, T Nakayama *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **37** (1) 146 (1996)
- [doi>](#) 119. H-S Yu, T Yamashita, K Horie *Macromolecules* **29** 1144 (1996)
- [doi>](#) 120. T-A Chen, A K-Y Jen, Y Cai *J. Am. Chem. Soc.* **117** 7295 (1995)
- [doi>](#) 121. T-A Chen, A K-Y Jen, Y Cai *Macromolecules* **29** 535 (1996)
- [doi>](#) 122. C Samyn, T Verbiest, A Persoon *Macromol. Rapid Commun.* **21** 1 (2000)
123. J L Hedrick, K R Carter, J W Labadie, R D Miller, W Volksen, C J Hawker, D Y Yoon, T P Russell, J E McGrath, R M Briber *Adv. Polym. Sci.* **141** 1 (1999)
- [doi>](#) 124. A L Rusanov, T A Stadnik, K Müllen *Usp. Khim.* **68** 760 (1999) [*Russ. Chem. Rev.* **68** 685 (1999)]
- [doi>](#) 125. J L Hedrick, J F Labadie, W Volksen, J G Hilborn. *Adv. Polym. Sci.* **147** 61 (1999)
- [doi>](#) 126. T M Moy, M Konas, J E McGrath *J. Polym. Sci., Part A: Polym. Chem.* **32** 2377 (1994)
- [doi>](#) 127. Z B Shifrina, A L Rusanov *Usp. Khim.* **65** 648 (1996) [*Russ. Chem. Rev.* **65** 599 (1996)]
128. V V Korshak *Khimicheskoe Stroenie i Temperaturnye Kharakteristiki Polimerov* (Chemical Structure and Temperature Characteristics of Polymers) (Moscow: Nauka, 1970)
129. S Feger, M M Khojasteh, J E McGrath (Eds) *Polyimides: Materials, Chemistry and Characterization* (Amsterdam: Elsevier, 1989)
130. D Wilson, H D Stenzenberger, P M Hergenrother (Eds) *Polyimides* (New York: Chapman and Hall, 1990)
131. M J M Abadie, B Sillion (Eds) *Polyimides and Other High Temperature Polymers* (Amsterdam: Elsevier, 1991)
132. M K Ghosh, K L Mittal (Eds) *Polyimides: Fundamentals and Applications* (New York: Marcel Dekker, 1996)
133. D L Goff, E L Yuan, H Long, H J Neuhaus, in *Polymers for Electronic Packaging and Interconnection (Am. Chem. Soc., Symp. Ser. 407)* (Eds J H Lupinski, R S Moore) (Washington, DC: American Chemical Society, 1989) p. 93
134. A K St Clair, T L St Clair, K I Shevket *Polym. Mater. Sci. Eng.* **51** 62 (1984)
135. S Sasaki, S Nishi, in *Polyimides: Fundamentals and Applications* (Eds M K Ghosh, K L Mittal) (New York: Marcel Dekker, 1996) p. 71
136. A K St Clair, T L St Clair, E N Smith, in *Structure–Solubility Relations in Polymers* (Eds F W Harris, R B Seymour) (New York: Academic Press, 1977) p. 199
- [doi>](#) 137. T Ichino, S Sasaki, T Matsuura, S Niski *J. Polym. Sci., Part A: Polym. Chem.* **28** 323 (1990)
- [doi>](#) 138. E Radlmann, W Schmidt, G E Nischk *Makromol. Chem.* **130** 45 (1969)
139. I S Chang, S Y Kim, in *Proceedings of Conference ‘Polycondensation-2000’, Tokyo, 2000* p. 94
140. D A Tomalia, A M Naylor, W A Goddard III *Angew. Chem., Int. Ed. Engl.* **29** 138 (1990)
141. A M Muzafarov, E A Rebrov, V S Papkov *Usp. Khim.* **60** 1596 (1991) [*Russ. Chem. Rev.* **60** 807 (1991)]
142. J M J Frechet *Science* **263** 1710 (1994)
- [doi>](#) 143. B J Voit *Acta Polym.* **46** 87 (1995)
144. G R Newcome, C N Moorefield, F Vogtle *Dendritic Molecules: Concepts, Synthesis, Perspectives* (New York: VCH, 1996)
- [doi>](#) 145. F W Zeng, S C Zimmerman *Chem. Rev.* **97** 1681 (1997)
- [doi>](#) 146. H Frey *Angew. Chem., Int. Ed.* **37** 2193 (1998)
147. M Fisher, F Vogtle *Angew. Chem., Int. Ed.* **38** 885 (1999)
- [doi>](#) 148. J-P Majoral, A-M Caminade *Chem. Rev.* **99** 845 (1999)
149. C J Hawker *Adv. Polym. Sci.* **147** 113 (1999)
- [doi>](#) 150. I P Beletskaya, A V Chuchurjukin *Usp. Khim.* **69** 699 (2000) [*Russ. Chem. Rev.* **69** 639 (2000)]
151. A M Muzafarov, E A Rebrov *Vysokomol. Soedin., Ser. A* **42** 2015 (2000)^b
152. P J Flory *Chem. Rev.* **39** 137 (1946)
153. P J Flory *Principles of Polymer Chemistry* (Ithaca: Cornell University Press, 1953)
- [doi>](#) 154. M N Bochkarev, M A Katkova *Usp. Khim.* **64** 1106 (1995) [*Russ. Chem. Rev.* **64** 1035 (1995)]
155. E Malmstrom, A Hult *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **37** 555 (1997)
- [doi>](#) 156. Y H Kim *J. Polym. Sci., Part A: Polym. Chem.* **36** 1685 (1998)
- [doi>](#) 157. M Jikei, M Kakimoto *Prog. Polym. Sci.* **26** 1233 (2001)

^a — *Mendeleev Chem. J. (Engl. Transl.)*

^b — *Polym. Sci. (Engl. Transl.)*

^c — *Russ. Chem. Bull., Ent. Ed. (Engl. Transl.)*

^d — *Dokl. Chem. (Engl. Transl.)*