Polymers from Aromatic Nitriles and Amines: Polybenzimidazoles and Related Polymers

D. I. PACKHAM, J. D. DAVIES and H. M. PAISLEY

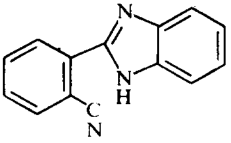
The synthesis of polybenzimidazoles and related products by the condensation of aromatic nitriles with amines is described. The alkoxide catalysed reaction of phthalonitrile with 3,3′,4,4′-tetra-aminodiphenyl and 3,3′,4,4′-tetra-aminodiphenyl ether affords low molecular weight polybenzimidazoles. Chain termination reactions that favour the formation of low molecular weight products are discussed. Condensation of 1,2,4,5-tetracyanobenzene with the tetra-amines gave polymers with structural similarities to the polybenzoylenebenzimidazoles.

As part of our study on the synthesis of macrocyclic compounds and heterocyclic polymers we have examined in detail the condensation reactions of aromatic and heterocyclic nitriles with amines. In recent publications we reported the preparation of two new classes of thermally stable polymers, the macrocyclic polymers[1] and the poly[benzo*bis*(aminoiminopyrrolenines)][2]. These polymers were formed by the condensation of suitable tetranitriles, e.g. 1,2,4,5-tetracyanobenzene (pyromellitonitrile) with *meta* or *para* substituted aromatic or heterocyclic diamines. We now describe the synthesis of other polymers by the alkoxide catalysed reaction of nitriles with aromatic tetra-amines. Where the amino groups are in *ortho* pairs the polymer structures are related to the polybenzimidazoles[3] and the polybenzoylene benzimidazoles[4].

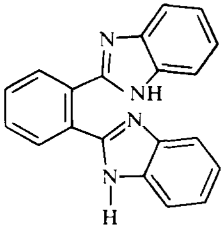
RESULTS AND DISCUSSION

Condensation of phthalodinitrile with amines

Model reactions—Depending on the molar ratio of the reactants and the reaction conditions, phthalonitrile will condense with *meta* or *para* substituted aromatic diamines in hydroxylic solvents containing sodium alkoxide as catalyst to give either the macrocyclic compounds or the *bis-iso*indolyl derivatives previously described[2, 5, 6]. In contrast the products of the reaction of *o*-phenylene diamine with phthalonitrile in refluxing 2-methoxyethanol containing sodium methoxyethanolate catalyst were found to be (2′-benzimidazolyl)2-cyanobenzene (I) and 1,2-*bis*(2′-benzimidazolyl)benzene (II).



I



II

The synthesis of benzimidazoles by the condensation of *o*-diamines with acids, acid chlorides, anhydrides or esters has been described by Phillips[7]. The preparation of benzimidazoles by the reaction of nitriles with *o*-phenylene diamine (under acid conditions) was reported by Holljes and Wagner[8], who concluded that the reaction occurred only under acid conditions. Whilst frequently this may be so, phthalonitrile represents a special case where the benzimidazolylcyanobenzene and *bis*benzimidazolylbenzene may be obtained in good yield under essentially alkaline conditions. This reaction appears to be peculiar to the *ortho* dinitrile since under the same alkaline conditions *meta* and *tere*phthalonitrile were extremely slow to react with the aromatic *ortho* diamines. Only 2% reaction occurred between *tere*phthalonitrile and *o*-phenylene diamine after 24 h in refluxing 2-methoxyethanol.

Polymerization reactions—Phillips' synthesis of benzimidazoles was extended by Brinker and Robinson[9] to the preparation of aliphatic polybenzimidazoles and to the aromatic series by Marvel and others[3]. More recently Iwakura, Uno and Imai[10] used polyphosphoric acid as the reaction medium for the preparation of polybenzimidazoles from aromatic tetra-amines and acid derivatives including nitriles.

The condensation of phthalonitrile with suitable tetra-amines, e.g. 3,3′,4,4′-tetra-aminodiphenyl or 3,3′,4,4′-tetra-aminodiphenyl ether in refluxing 2-methoxyethanol containing sodium methoxyethanolate proceeded smoothly with the evolution of ammonia. Soluble, white to buff coloured polymeric products of low molecular weight were obtained. As the reaction of phthalonitrile with *o*-phenylene diamine afforded the benzimidazoles it was reasonable to assign structure III (*Figure 1*) to the polymers. The infra-red spectra of the products supported this view.

Despite variations in the reaction conditions, only relatively low molecular weight products (up to $\bar{M}_n$ 5 900) were obtained. A consideration of the condensation mechanism shows that some chain termination reactions, responsible for limiting the molecular weight of the product, are possible. By analogy with the formation of *o*-cyanobenzimidazole from phthalonitrile and *o*-phenylene diamine it may be concluded that the first step in the reaction of phthalonitrile with tetra-aminodiphenyl is the formation of 2(2′-cyanophenyl)5(3″,4″-diaminophenyl)benzimidazole (VI, *Figure 1*). Subsequent reaction could then lead to: 1,2-*bis*-2′[5′(3″,4″-diaminophenyl)benzimidazolyl]benzene (VII), *bis*-5,5′[2(2′-cyanophenyl)benzimidazole] (VIII), *bis*(benziminobenzimidazole) (IX), the macrocyclic benzimidazole (X), and higher homologues.

Examination of the infra-red spectra, mass spectra and elemental analysis of the reaction products confirmed the presence of the compounds III ($n = 2$), VII, VIII and X. Although the formation of homologous cyclic structures with larger rings are probably more favoured by steric factors their presence was not established. However such structures must be considered together with the other chain termination products.

CONDENSATION OF TETRANITRILES WITH AMINES

Model reactions—1,2,4,5-Tetracyanobenzene readily condensed with

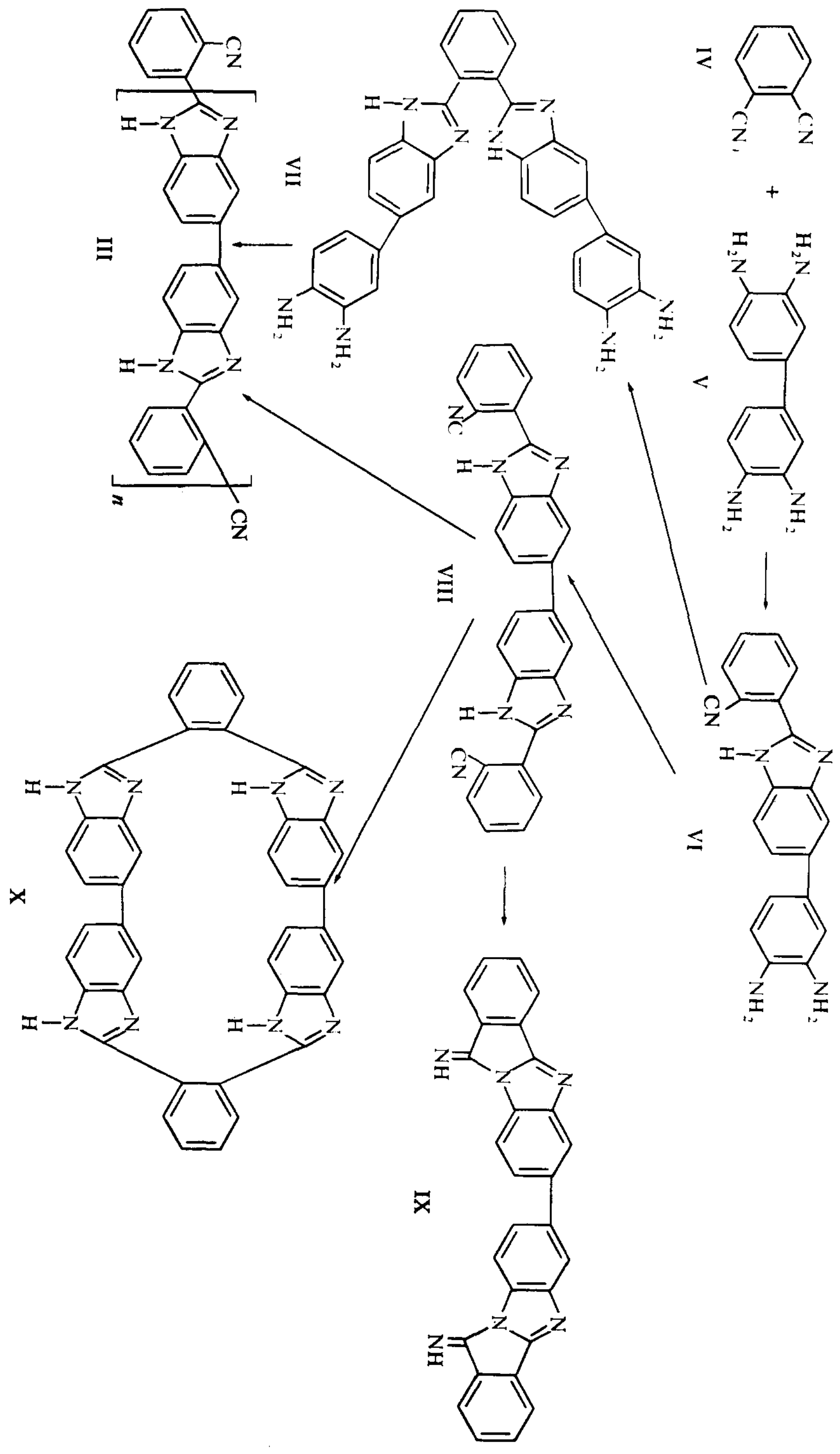


Figure 1

o-phenylenediamine in refluxing 2-methoxyethanol containing sodium 2-methoxyethanolate catalyst. The nature and yields of the products were dependent on the molar ratio of the reactants as well as the reaction conditions. Condensation of *o*-phenylene diamine with 1,2,4,5-tetracyanobenzene in a 2:1 molar ratio afforded the *bis*benzimidazolyl*bis*cyanobenzene (XII, *Figure 2*) as the major product. In contrast to the phenyl *o*-cyanobenzimidazole (I) the *bis*benzimidazolyl*bis*cyanobenzene (XII) readily cyclized to give the *bis*imino(benzo*bis*benzimidazole) (XIII). Hydrolysis of the exocyclic imino groups gave the known *bis*benzoylenebenzimidazole. Condensation of *o*-phenylene diamine with 1,2,4,5-tetracyanobenzene in a 4:1 molar ratio afforded 1,2,4,5-*tetrakis*(2′-benzimidazolyl)benzene (XIV) as the principal product. In all cases the structures were established or confirmed by elemental analysis, infra-red and mass spectra.

Polymerization reactions—The condensation of equimolar quantities of 1,2,4,5-tetracyanobenzene and 3,3′,4,4′-tetra-aminodiphenyl in refluxing 2-methoxyethanol containing sodium 2-methoxyethanolate catalyst proceeded smoothly with the evolution of ammonia. The product was a dark brown to black insoluble polymer that could be moulded to give specimens of good tensile strength. Programmed thermal gravimetric analysis in air at 15°C/min. showed a 10% loss in weight at 500°C. The polymer showed considerably greater stability in an inert atmosphere; a 10% weight loss at 700°C was recorded with the same rate of heating. A polymer with essentially similar properties was obtained by the reaction of 1,2,4,5-tetracyanobenzene and 3,3′,4,4′-tetra-aminodiphenyl ether in equimolar proportions under the same conditions. The condensation of this tetra-amine with tetracyanothiophene or tetracyanodithiin also gave black polymers. As expected the polymers containing sulphur were thermally less stable.

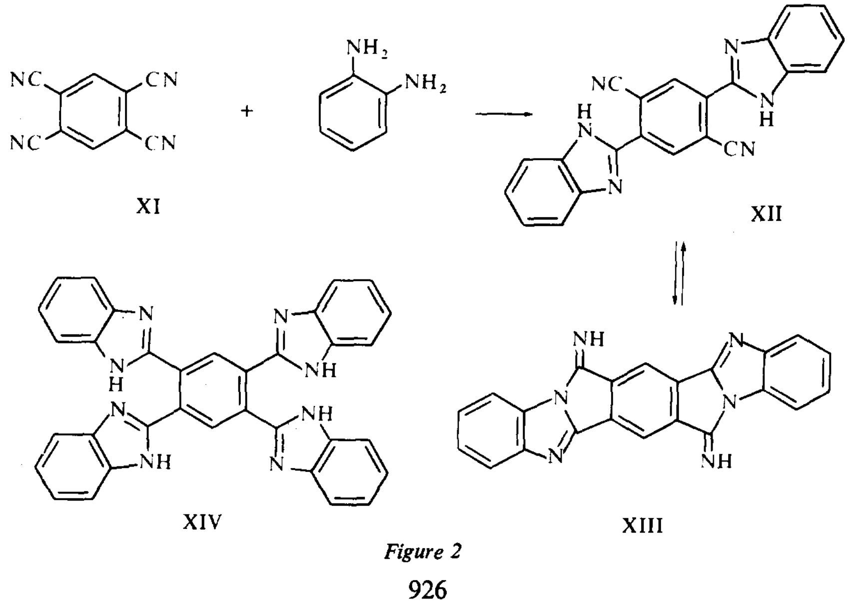
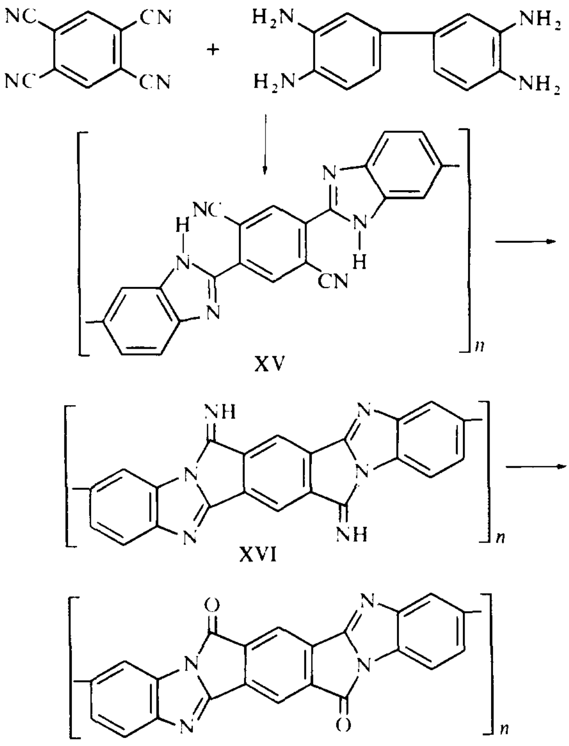


Figure 2

Condensation of the tetranitriles with the tetra-amines under the same reaction conditions with a molar ratio of 1:2 afforded dark coloured polymers with somewhat similar properties, but more difficult to mould.

By analogy with the reactions on model compounds it is proposed that the polymers contain repeating benzimidazole units (XV, *Figure 3*). The absence of any absorption in the 2 240 cm^{-1} region of the infra-red spectra of the polymers, suggests that under the conditions employed in the preparation of the 1:1 polymers cyclization occurred. The resultant polymers therefore probably have the benziminobenzimidazole structure (XVI). Hydrolysis of the exocyclic imino group would then give rise to the known[4] benzoylenebenzimidazoles (XVII). The properties of the polymers, including the infra-red spectra, were in accordance with the proposed structures.



XV

XVI

XVII

Figure 3

Dawans and Marvel[4] reported the reaction of pyromellitic di-anhydride with tetra-amines to obtain the benzolyenebenzimidazole ‘ladder’ polymers. Where the reaction was carried out with rapid heating or at high temperature the crosslinked structures were formed. In order to obtain the benzoylenebenzimidazoles as soluble polymers it was necessary to form the aminoimide initially and then effect cyclization by heating to 140–150°C. In some cases it was found to be necessary to heat to 250°C under vacuum to complete the cyclization. Intermolecular cyclization as well as intramolecular reaction was encountered. Under our reaction conditions the cyclization of the cyanobenzimidazole polymers readily occurred. However as our products are virtually insoluble in the normal solvents some crosslinking must also have taken place.

The polymers prepared by reacting the tetranitrile with the tetra-amine in a 1:2 molar ratio exhibited no carbonyl absorption in the infra-red spectra. As the products are insoluble and in many examples very difficult to mould they are most probably highly crosslinked polybenzimidazoles.

In the literature idealized structures are frequently proposed. Clearly where multifunctional components are condensed together, complex structures will result. On the basis of our experiments on model compounds, we propose that the principal structural units of the polymers we describe are the benzimidazole, the benziminobenzimidazole and the benzoylenebenzimidazole groups. However the formation of large ring structures must also be considered.

EXPERIMENTAL

Monomers

o-Phenylene diamine, phthalonitrile, 3,3′,4,4′-tetra-aminodiphenyl and 3,3′,4,4′-tetra-aminodiphenyl ether were obtained from commercial sources and recrystallized before use.

1,2,4,5-Tetracyanobenzene (pyromellitonitrile) was prepared from pyromellitic dianhydride by the method described by Lawton and McRitchie[11] with the modification suggested by Thurman[12].

Tetracyano-1,4-dithiin and tetracyanothiophene were prepared from carbondisulphide and sodium cyanide by the method described by Simmons *et al*[13].

Model reactions

Phthalonitrile and o*-phenylene diamine*—A solution of phthalonitrile (5·12 g, 0·04 mole) and *o*-phenylene diamine (4·32 g, 0·04 mole) in *n*-butyl alcohol (85 ml) containing sodium butoxide catalyst (0·1 g) was refluxed under a stream of nitrogen for 22 h. The ammonia liberated was titrated against standard acid (35 mequiv, 87·5%). The hot suspension was filtered to give 1,2-*bis*(2′-benzimidazolyl)benzene (1·4 g) m.p. 418–420°C (Lit. 445–450°C). The mass spectrum showed an intense peak at *m/e* 310 calculated for $C_{20}H_{14}N_4$ *m/e* 310·122.

As the solution cooled a white crystalline product precipitated (2·5 g, m.p. 244–9°C). Addition of light petroleum (40/60) afforded a further quantity (0·9 g) of the product. Recrystallization of the combined product from ethanol/water gave white needle crystals (m.p. 244–252°C) (analysis: C, 76·7; H, 4·8; N, 18·7%: $C_{14}H_9N_3$ requires C, 76·7; H, 4·1; N, 19·2%. The infra-red spectrum showed a strong band at 2 240 cm^{-1} ($C \equiv N$). The mass spectrum showed an intense peak at *m/e* 219·080 calculated for 2(2′-benzimidazoyl)-cyanobenzene *m/e* 219·080.

Under the same reaction conditions condensation of phthalonitrile (1 mole) with *o*-phenylenediamine (2 mole) gave *bis*benzimidazoylbenzene as the major product in 60% yield.

1,2,4,5-Tetracyanobenzene and o*-phenylene diamine*—A solution of 1,2,4,5-tetracyanobenzene (1·78 g, 0·01 mole) and *o*-phenylene diamine (4·32 g, 0·04 mole) in 2-methoxyethanol (75 ml) containing sodium 2-methoxyethanolate (0·05 g) was refluxed in an atmosphere of nitrogen for 60 h. During this period ammonia (29 mequiv, 73% theory) was liberated. The hot suspension was filtered to give an olive green product (4·5 g, 83%, m.p. > 360°C). The infra-red spectrum was the same as that previously reported for 1,2,4,5-*tetrakis*(2′-benzimidazoyl)benzene[14]. Sublimation at 400°C and 10^{-6} mmHg afforded a yellow-green solid. (Analysis: C, 74·5; H, 3·9; N, 20·2%; $C_{34}H_{22}N_8$ requires C, 75·3; H, 4·1; N, 20·8%).

Reaction of 1,2,4,5-tetracyanobenzene (3·56 g, 0·02 mole) and *o*-phenylene diamine (4·32 g, 0·04 mole) under essentially the same conditions afforded a yellow-green product (5·75 g, 80%, m.p. 290°C). Recrystallization from ethanol–water gave a yellow solid (m.p. 320°C). The infra-red spectrum contained a strong band at 2 240 cm^{-1} ($C \equiv N$) and was consistent with *bis*-benzimidazoyl*bis*cyanobenzene (XII). Mass spectral analysis gave *m*/*e* 360·113 (calculated for $C_{22}H_{12}N_6$ = 360·112). A small peak at *m*/*e* 451·146 corresponded to the *tris*benzimidazocyanobenzene (calculated for $C_{28}H_{17}N_7$; *m*/*e* 451·154).

Hydrolysis of the product with dilute acid, followed by sublimation, afforded a yellow solid (m.p. > 360°C). The mass spectrum showed an intense parent ion at *m*/*e* 362·081, *bis*benzoylenebenzimidazole ($C_{22}H_{10}N_4O_2$ requires *m*/*e* 362·080). A minor peak was observed at *m*/*e* 452·137 ($C_{28}H_{16}N_6O$ requires *m*/*e* 452·139).

Polymerization reactions

Phthalonitrile and 3,3′,4,4′-tetra-aminodiphenyl—A solution of pthalonitrile (6·4 g) and 3,3′,4,4′-tetra-aminodiphenyl (5·35 g) in 2-methoxyethanol (175 ml) containing sodium 2-methoxyethanolate (0·2 g) was boiled under reflux for 22 h in a stream of nitrogen. The ammonia liberated was titrated against standard acid (51·3 mequiv, 102%). A small quantity of phthalocyanine (0·6 g) was filtered off and the solution concentrated (to 75 ml). The viscous solution was poured into methanol (700 ml), to precipitate a white solid (3·5 g). The product contained N, 18·3% (calculated N, 18·2%). Evaporation of the solvents afforded a further yield of polymer (6·0 g). The polymer softened at 250°C and melted at 275°C. Thermal gravimetric analysis in air at 5°C/min (Stanton thermobalance) showed an initial loss at 320°C and a 10% loss at 540°C. Attempts to fractionate the polymer by selective precipitation afforded samples with molecular weights in the range $\bar{M}_n$ 1 300–5 900 (v.p.o.).

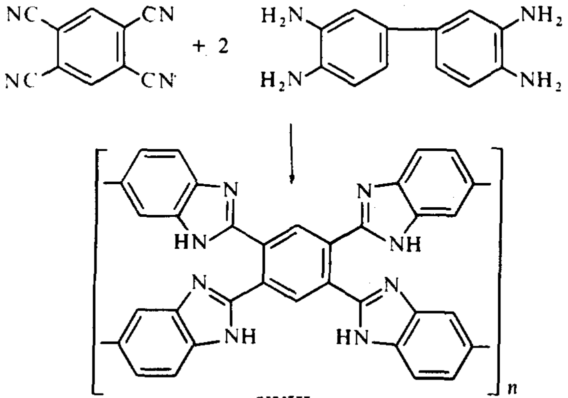
The mass spectra of the products from similar reactions showed strong peaks at:

(1) *m*/*e* 436·141: *bis*-5,5′[2(2′-cyanophenyl)benzimidazole] (VIII, *Figure 1*) requires *m*/*e* 436·144.

(2) *m*/*e* 616·213: the macrocyclic compound (X) requires *m*/*e* 616·212.

(3) *m*/*e* 744·248: the five unit structure (III) $n = 2$ requires *m*/*e* 744·249.

Bis-5,5′[2(2′-cyanophenyl)benzimidazole] (VIII) was isolated from the mixture by extraction with methanol followed by sublimation. The pale yellow solid (m.p. 335°C) had the following analysis: C, 77·1; H, 3·6; N, 19·5%; $C_{28}H_{16}N_6$ requires C, 77·0; H, 3·7; N, 19·3%. Infra-red analysis showed the following bands 3 280 (s), 2 240 (s), 1 600 (w), 1 390 (s), 1 440 (s), 800 (s), 770 (s), cm^{-1}. Attempts to isolate the other components in a pure state were not successful. Similar results were obtained from the reaction of phthalonitrile with 3,3′,4,4′-tetra-aminodiphenyl ether.



XVIII

Figure 4

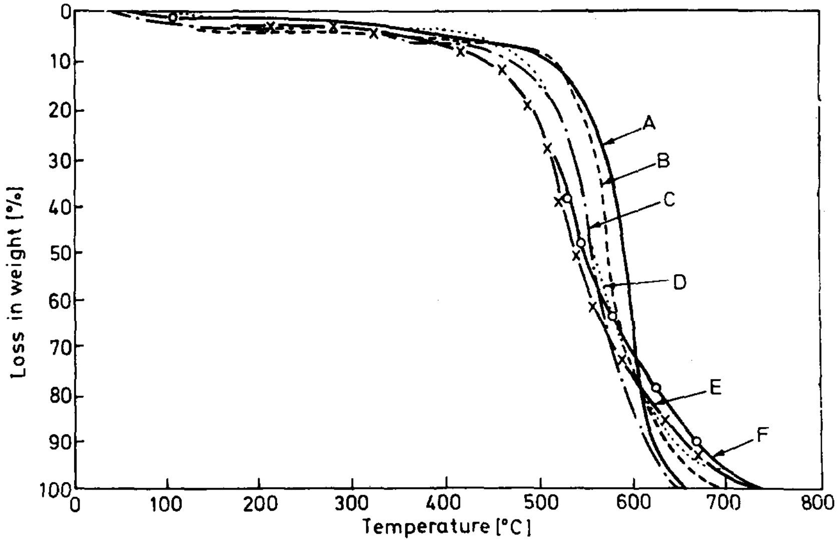


Figure 5—Thermal gravimetric analysis in air (ΔT = 15°C/min)

A,	1:1	tetracyanobenzene/3,3′,4,4′-tetra-aminodiphenyl
B,	1:2	
C,	1:1	tetracyanobenzene/3,3′,4,4′-tetra-aminodiphenyl ether
D,	1:2	
E,	1:1	tetracyanothiophene/3,3′,4,4′-tetra-aminodiphenyl ether
F,	1:1	tetracyano-1,4-dithiin/3,3′,4,4′-tetra-aminodiphenyl ether

1,2,4,5-Tetracyanobenzene and 3,3′,4,4′-tetra-aminodiphenyl (1:1 molar ratio) A solution of 1,2,4,5-tetracyanobenzene (3·56 g) and tetra-aminodiphenyl (4·28 g) in 2-methoxyethanol (150 ml) containing sodium 2-methoxy ethanolate (0·1 g) was heated under reflux with stirring for 7 days. During this period ammonia (38·5 mequiv, 96% theory) was liberated. The black solid was filtered off, extracted with methanol and dried (yield 6·6 g, 92%). The polymer contained 19·3% nitrogen. It was moulded at 400–420°C to give compact specimens (density 1·3 g ml^{-3}). Tensile strengths at room temperature up to 8 500 p.s.i. ($\sim$60 N mm^{-2}) were obtained on moulded specimens. Thermal gravimetric analysis (15°C/min.) showed a 10% weight loss at 500°C in air and 700°C in nitrogen (*Figure 5*).

1,2,4,5-Tetracyanobenzene and 3,3′,4,4′-tetra-aminodiphenyl (1:2 molar ratio). A solution of 1,2,4,5-tetracyanobenzene (3·56 g, 0·02 mole) and 3,3′,4,4′-tetra-aminodiphenyl (8·56 g, 0·04 mole) in 2-methoxyethanol (130 ml) containing sodium methoxyethanolate (0·2 g) was heated under reflux for 48 h. During this period ammonia (52·2 mequiv) was evolved. The hot suspension was filtered and the black insoluble polymer extracted with 2-methoxyethanol. The product (8·5 g) contained 20·0% nitrogen (calculated 20·8%).

Similar polymeric products were obtained from the condensation of 1,2,4,5-tetracyanobenzene with tetra-aminodiphenyl ether and the condensation of tetracyanodithiin or tetracyanothiophene with the tetra-amines.

This work forms part of the research programme of the National Physical Laboratory.

Division of Molecular Science (D.I.P. and J.D.D.)
and Division of Chemical Standards (H.M.P.)
National Physical Laboratory,
Teddington, Middlesex.

(*Received July 1969*)

REFERENCES

[1] Packham, D. I. and Rackley, F. A. *Chem. and Ind.* 1967, p 1254
[2] Packham, D. I. and Rackley, F. A. *Chem. and Ind.* 1967, p 1566
[3] Vogel, H. and Marvel, C. S. *J. Polym. Sci.* 1961, **50**, 511
Plummer, L. and Marvel, C. S. *J. Polym. Sci.* (*A*) 1964, **2**, 2559
Foster, R. T. and Marvel, C. S. *J. Polym. Sci.* (*A*) 1965, **3**, 417
[4] Dawans, F. and Marvel, C. S. *J. Polym. Sci.* (*A*) 1965, **3**, 3549
[5] Elvidge, J. A. and Golden, J. H. *J. Chem. Soc.* 1957, p 700
[6] Packham, D. I. and Davies, J. D. Unpublished work
[7] Phillips, M. A. *J. Chem. Soc.* 1930, p 1415
[8] Holljes, E. L. and Wagner, E. C. *J. Org. Chem.* 1944, p 31
[9] Brinker, K. C. and Robinson, J. M. *U.S. Patent* 2 895 948 1959
[10] Iwakura, Y., Uno, K. and Imai, Y. *J. Polym. Sci.* (*A*) 1964, **2**, 2605
[11] Lawton, E. A. and McRitchie, D. D. *J. Org. Chem.* 1959, **24**, 26
[12] Thurman, J. C. *Chem. and Ind.* 1964, p 752
[13] Simmons, H., Vest, R. D., Blomstrom, D. C., Roland, J. R. and Cairns, T. L. *J. Amer. Chem. Soc.* 1962, **84**, 4746
[14] Manukian, B. K. *Helv. Chim. Acta.* 1964, **47**, 2215