Macrocyclic Polymers

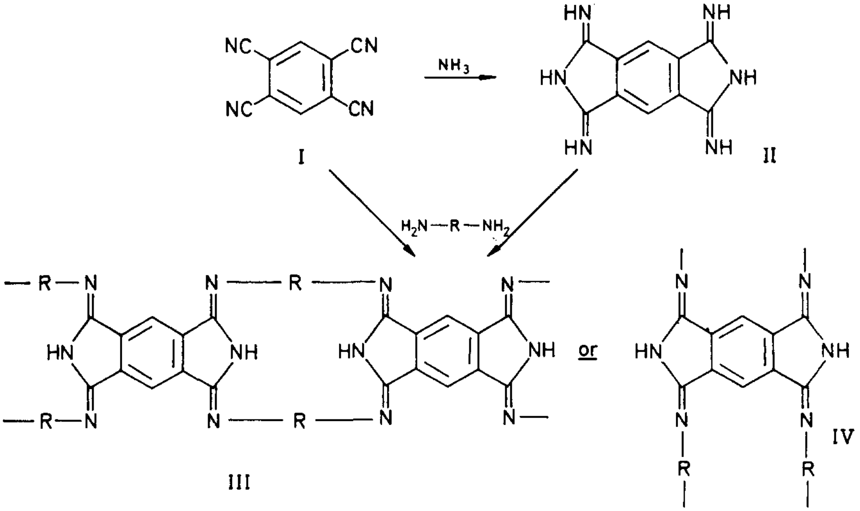
D. I. PACKHAM and F. A. RACKLEY

A new class of thermally stable polymers is described. Condensation of suitable tetraimines or tetranitriles with aromatic diamines under the appropriate conditions has afforded polymers that are composed essentially of repeating macrocyclic units. The conditions necessary to obtain a high concentration of macrocyclic units within the polymer have been investigated. Alternative structures and competing reactions have been considered. The polymers obtained by the condensation of pyromellitonitrile (1,2,4,5-tetracyanobenzene, PMTN) with aromatic diamines show a ten per cent loss in weight in air at 500° ±25°C at a constant rate of heating of 4 deg. C/minute. Enhanced stabilities have been observed in inert atmospheres. In particular the polymer prepared from PMTN and 4,4′-diaminodiphenyl ether has been studied in detail. The material can be moulded at 380° ±20°C at 10 000 to 20 000 lb/in² to give specimens of good tensile strength and high modulus.

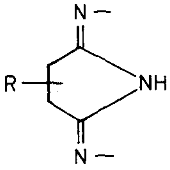
IN RECENT years considerable advances have been achieved in the synthesis of thermally stable polymers. Frequently thermal and oxidative stability in such materials has been realized by the combination of aromatic and heterocyclic units, for example: the polybenzimadazoles[1], polybenzoxazoles[2], polybenzthiazoles[3] and the polyimides[4]. The polybenzimidazolones or 'ladder polymers' described by Dawans and Marvel[5] represent an attempt to improve the stability of polymers by incorporating double strands in the chain. This paper describes the preparation and some properties of a new class of polymers, the macrocyclic polymers[6], in which macrocyclic units are linked together to form thermally stable polymers.

These polymers are conveniently prepared by the reaction of suitable tetranitriles or the corresponding tetraimines with diamines.

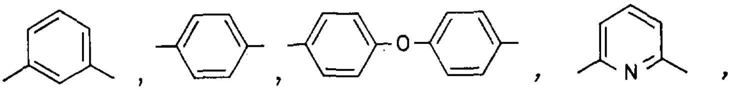
In order to form such macrocyclic structures the nitrile groups of the



tetranitrile must be in pairs capable of forming the ring structure



e.g. pyromellitonitrile (1,2,4,5-tetracyanobenzene), tetracyanodithiin, tetracyanothiophen, etc. The most suitable diamines for the formation of structure (III) were shown to be either *meta* or *para* substituted aromatic or heterocyclic diamines, e.g. R =



where steric factors favour the formation of the macrocyclic ring[7,8].

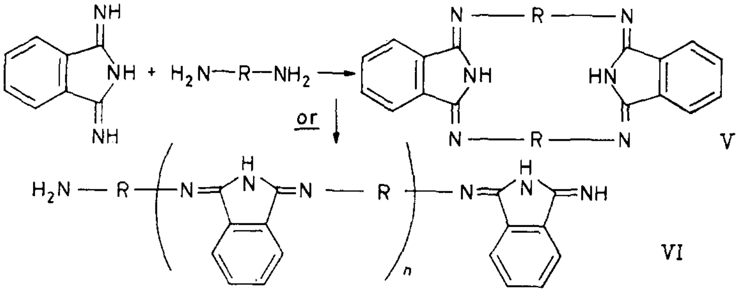
RESULTS AND DISCUSSION

Model compounds

Since a number of reactions other than those leading to the macrocyclic structures are possible, not least of which is the homopolymerization of the tetranitrile to give polymeric phthalocyanines[9], it was essential to determine the optimum conditions for the formation of the repeating macrocyclic units. A study was therefore made of (*i*) the reaction of diamines with diimino*iso*indoline and with phthalonitrile to give the optimum yield of the simple macrocyclic compounds (V) and (*ii*) the reaction of benzo*bis*-(diiminopyrrolidine) (II) and pyromellitonitrile (I) with aniline in order to establish the conditions for the formation of the benzo*bis*(diphenylimino-pyrrolidine) (IX) in good yield.

Formation of the basic macrocyclic units

In their study of the synthesis of macrocyclic compounds Linstead, Elvidge *et al.*[7] examined the reaction of diiminoisoindoline with *meta* substituted aromatic or heterocyclic diamines. The diamines were chosen as sterically favourable for ring closure since they postulated that other diamines might give rise to linear polymers:



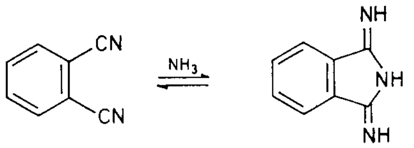
V

VI

We have examined in detail the condensation of aromatic imines and nitriles with amines leading to the formation of macrocyclic compounds and polymers. Since this is a very complex system the majority of our findings will be reported elsewhere[8]. We restrict our present discussion to the formation of the basic macrocyclic units of the type (V).

First considerations suggested that whilst *meta* substituted diamines would give the macrocyclic compounds, *para* substituted diamines might favour the formation of linear polymers (VI). However, our experiments on the condensation of diimino*iso*indoline or phthalonitrile with *p*-phenylene diamine and 4,4′-diaminodiphenyl ether invariably led to the formation of macrocyclic compounds. There appeared to be little difference in the products of the reaction whether diimino*iso*indoline or phthalonitrile was used as the starting material. Examination of the properties of diimino*iso*indoline in alcoholic solutions demonstrated that the reaction 1 is reversible. We also showed that under the conditions of our experiments diimino*iso*indoline is more susceptible to pigment formation than is phthalonitrile. As condensation of phthalonitrile with diamines in refluxing alcoholic solution contain-

Reaction 1



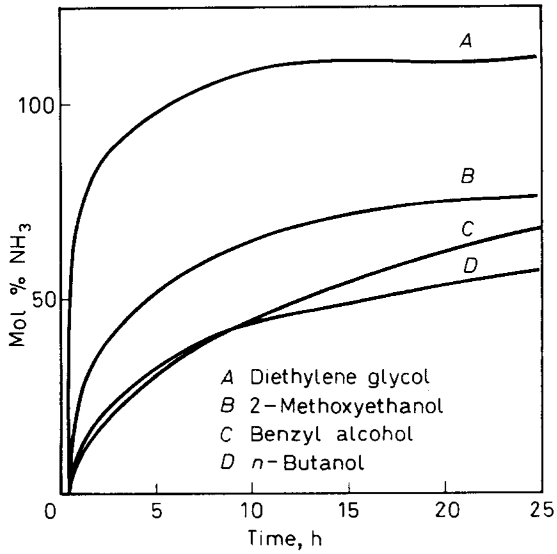
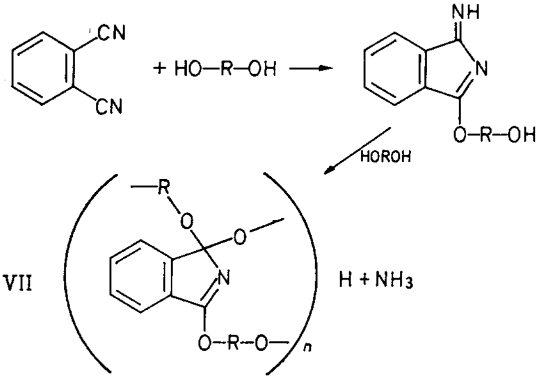


Figure 1—Condensation of pyromellitonitrile with diaminodiphenyl ether in various solvents

ing the sodium alkoxide as catalyst afforded the macrocyclic compounds in good yield most of our subsequent experiments were made with the nitriles.

The condensation of phthalonitrile with *m*- or *p*-phenylene diamine or 4,4′-diaminodiphenyl ether in refluxing ethyl alcohol containing sodium ethoxide catalyst afforded the simple macrocyclic compounds in good yields (> 80 per cent). The reaction, however, was extremely slow. An examination of the effect of various hydroxylic solvents on the rate of reaction showed that, as expected, an increase in reaction temperature resulted in an increased rate of reaction as assessed by the evolution of ammonia. However, with the higher boiling solvents, in particular the cresols and diethylene glycol, polymeric products were obtained. Subsequent experiments showed that at these elevated temperatures (> 170°C) dihydric alcohols or difunctional phenols (i.e. with active sites in the *ortho* or *para* positions) react with phthalonitrile in the absence of diamines to yield polymeric products possibly of the type:

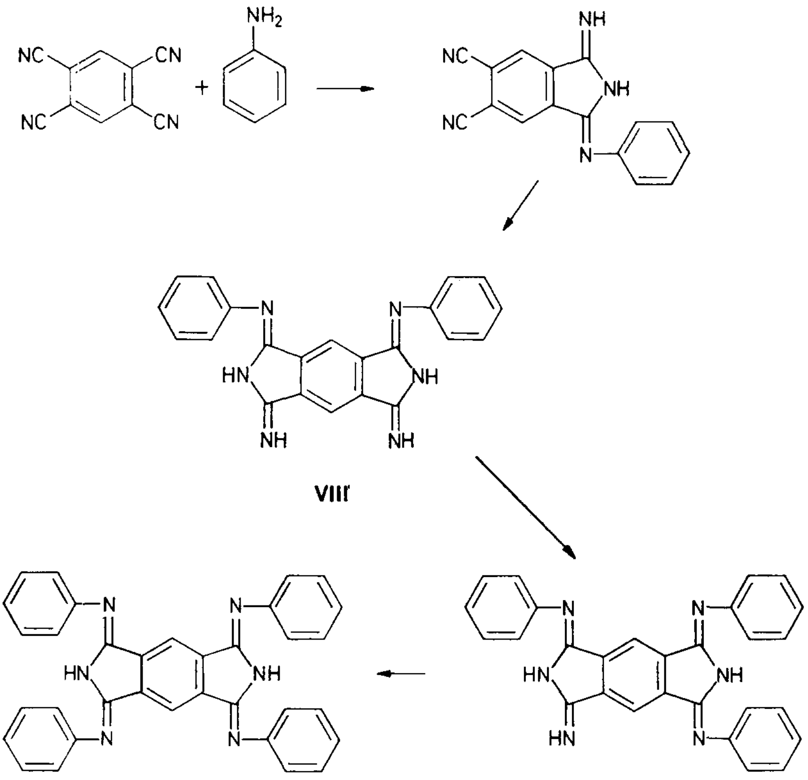


VII

The choice of solvent was therefore restricted to monohydric alcohols. Of these 2-methoxyethanol (b.pt 125°C) and *n*-butanol (b.pt 118°C) were most successful. In these solvents the macrocyclic compounds were prepared at a reasonable rate and in high yield (> 90 per cent) from phthalonitrile and the diamine. The higher boiling point solvent *n*-butoxy ethanol (b.pt 170°C) showed no advantage over 2-methoxyethanol. Benzyl alcohol was shown to be an unsuitable solvent by the formation of black tarry products of indefinite structure.

*Benzo*bis(*diphenyliminopyrrolidine*)

In order to extrapolate the results of the formation of the simple macrocyclic compounds from phthalonitrile, to the formation of macrocyclic polymers from pyromellitonitrile, it was necessary to determine the optimum reaction conditions for the formation of benzo*bis*(diphenyliminopyrrolidine) (IX) from pyromellitonitrile and aniline.



VIII

IX

In alcoholic solvents and with the alkoxide as catalyst, it was found that the rate of reaction and the nature of the products were dependent on the temperature as well as the duration of the reaction.

In refluxing ethyl alcohol containing sodium ethoxide catalyst only the diphenyl derivatives (VIII) were obtained despite a molar ratio of aniline to pyromellitonitrile of 4:1 and prolonged periods of reflux. In refluxing 2-methoxyethanol containing alkoxide catalyst a mixture of di-, tri- and tetra-phenyl derivatives was obtained after 24 hours, whilst after five days at reflux the tetraphenyl derivative was obtained in high yield (> 80 per cent). Once again attempts to increase the rate of reaction by using higher boiling solvents, e.g. diethylene glycol etc., resulted in black polymeric products of ill-defined structure.

Similar results were obtained using benzo*bis*(diiminopyrrolidine) in place of pyromellitonitrile. The tetraimine, however, was less soluble than pyromellitonitrile in these solvents and exhibited a greater tendency to pigment formation.

Polymerization

In view of the similarity of the conditions for the formation of the macrocyclic compounds and the benzo*bis*(diphenyliminopyrrolidines) in good yield, it might reasonably be assumed that similar conditions would be optimal for the formation of the macrocyclic polymer. In order further to avoid the formation of the polymeric phthalocyanine attention was also given to the order in which the reactants were mixed. Addition of the tetranitrile to a solution of the diamine afforded a wine-red solution of the charge transfer complex. Subsequent addition of a solution of the catalyst caused a change in the colour of the solution from red to brown which, after an induction period of 10 to 20 minutes at reflux, was followed by the evolution of ammonia. Estimation of the ammonia evolved in the reaction afforded a convenient means of following the condensation.

As the molecular weight of the polymer increased precipitation of insoluble material occurred. Filtration of the mixture afforded the polymer, generally as a swollen, coloured solid. After extraction of this solid with suitable solvents and drying, it was invariably found to consist of a mixture of finely divided particles with a small quantity of pieces of polymeric film that had formed on the sides of the reaction vessel and the stirrer.

In refluxing 2-methoxyethanol containing sodium methoxyethanolate as catalyst the reaction between pyromellitonitrile (1 mol.) and 4,4′diaminodiphenyl ether (2 mol.) proceeded smoothly to yield a brown-red insoluble polymer in high yield (85 per cent). Whilst the reaction appeared to be 75 per cent complete in one day, as judged by the evolution of ammonia, it was generally continued for five days in order to effect as near complete cyclization as possible. Attempts to increase the rate of reaction by increasing the temperature of the reaction, i.e. using diethylene glycol (*Figure* 1), once again resulted in materials of indefinite structure. Almost certainly such materials were mixtures of polymeric phthalocyanines, macrocyclic polymers and polymers formed by combination of the alcohol with the tetranitrile. We therefore elected to carry out most of our experiments using 2-methoxyethanol as solvent.

Variation of the diamine

Condensation of pyromellitonitrile with *m*- or *p*-phenylene diamine or 2,6-diaminopyridine in place of 4,4′-diaminodiphenyl ether also afforded polymeric products. The colour of the resultant polymers, however, showed some variations not only between the different diamines but from different experiments with the same amine. The colour of the polymers from 4,4′-diaminodiphenyl ether generally ranged from light brown to red. Polymers from *m*-phenylene diamine were either brown-red or blue-black in colour. The 2,6-diaminopyridine and *p*-phenylene diamine products were blue-black in colour. With such highly conjugated structures these colours are not too surprising. Some variation may be expected since the colour must be dependent not only on the degree of conjugation within the molecule but also on molecular weight and particle size.

Differences in the rate of reaction of the various diamines with pyromellitonitrile were observed (*Figure* 2). The rate of reaction seemingly is dependent on the basicity of the primary amino groups. Hexamethylene

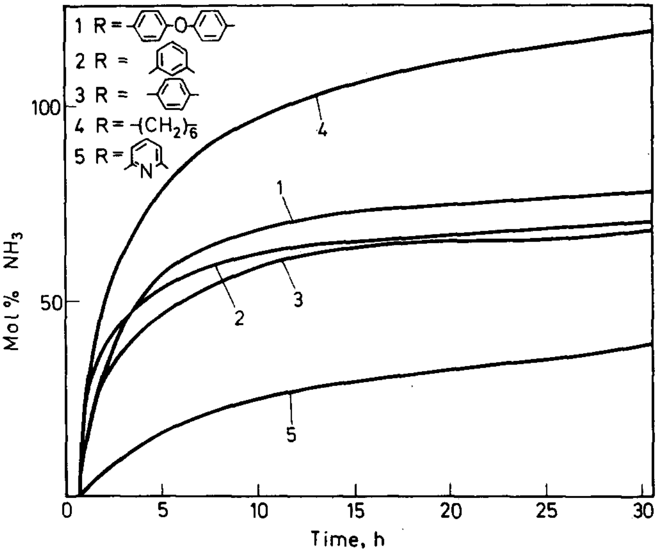


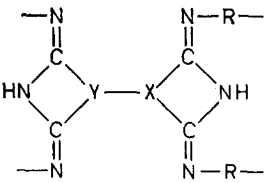
Figure 2—Condensation of pyromellitonitrile with various diamines in 2-methoxyethanol

diamine reacted rapidly with pyromellitonitrile to give an excess of the calculated stoichiometric amount of ammonia. In view of the flexibility of the aliphatic chains it is considered that macrocycle formation is less probable in this case than with the more rigid aromatic diamines. Consideration of the factors involved and the results of our experiments, particularly with the monomeric macrocyclic compounds, would suggest that structure (III) is most likely when *m* or *p* substituted aromatic diamines are used. A small percentage of other structures, e.g. type (IV), or of crosslinks cannot be disregarded.

With either *meta* or *para* phenylene diamine or 2,6-diaminopyridine a very rigid structure would result. 4,4′-Diaminodiphenyl ether affords an intermediate example of restricted flexibility of the molecule. The ether link should soften the rigidity of the structure composed of repeating macrocyclic units. This was reflected in the easier moulding of this polymer. Most of our subsequent work was therefore carried out using 4,4′-diaminodiphenyl ether as the preferred diamine.

Variation of the tetranitrile

The basic requirement of a suitable tetranitrile for the formation of this type of macrocyclic polymer is that the nitrile groups should be in *ortho* pairs in order to form the ring system:



As pyromellitonitrile is the simplest aromatic tetranitrile in this series and in order to minimize the complications that might occur, most of our work was carried out using that nitrile. However, other tetranitriles, in particular, tetracyanodithiin and tetracyanothiophen[10] were also studied. Condensation of these nitriles with 4,4′-diaminodiphenyl ether proceeded smoothly in refluxing 2-methoxyethanol containing alkoxide catalyst. Mouldable polymeric products were obtained. Since some sulphurous compounds were evolved during the reactions degradation of the thiophene or dithiin nucleus must have occurred and some complications in the structure of the polymers must be inferred.

Properties of the macrocyclic polymers

Thermal stability—The thermal stability of the polymers in air and in an inert atmosphere either argon or nitrogen were measured using a Stanton thermobalance. A programmed constant rate of heating of 4 deg. C per minute was employed throughout. Under these conditions it was difficult to determine accurately the temperature at which the polymers began to decompose. The decomposition temperature and the rate of decomposition were dependent on the rate of heating, particle size, surface area, gas flow-rate etc. In order to assess the relative merits of these polymers and to draw comparisons with other thermally stable polymers, we adopted the procedure of measuring the temperature at which a ten per cent loss in weight occurred under these standard conditions. The results obtained are given in *Table 1* and illustrated in *Figures 3* and *4*.

The macrocyclic polymers prepared from pyromellitonitrile and 4,4′-diaminodiphenyl ether, *m*- and *p*-phenylene diamines generally showed

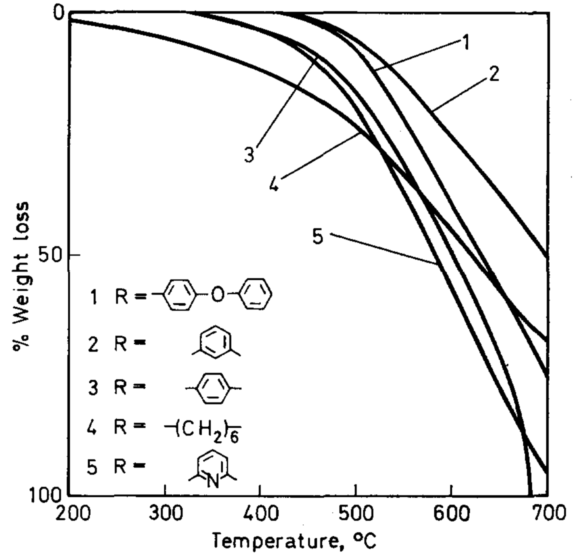
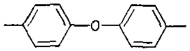
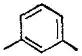
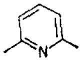


Figure 3—Thermal stability of macrocyclic polymers in air

Table 1. Macrocyclic polymers from pyromellitonitrile and diamines (R)

R	*Yield of polymer,* %	*Colour*	*Analysis*				*Thermal stability 10% loss in weight*	
				C	H	N	*in air*	*in nitrogen*
	92	Red-brown	Found	71·0	4·0	15·0	500	620
			Calcd	75·0	3·5	15·5		
	78	Blue-black	Found	67·8	4·4	22·6	490	570
			Calcd	73·4	3·3	23·3		
	67	Dark-red to black	Found	69·2	3·1	24·3	520	600
			Calcd	73·4	3·3	23·3		
	75	Black	Found	59·0	3·4	28·6	450	560
			Calcd	66·3	2·8	30·9		
$-(CH_2)_6-$	79	Black	Found	65·7	7·6	19·3	380	440
			Calcd	70·3	7·5	22·2		

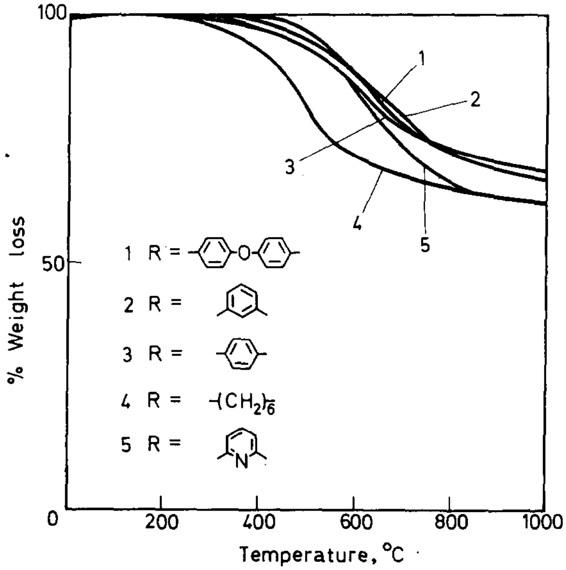


Figure 4—Thermal stability of macrocyclic polymers in nitrogen

similarities in their thermal stabilities; ten per cent weight loss was recorded in air at 500° ±25°C. The polymer prepared from 2,6-diaminopyridine was slightly less stable, ten per cent loss in weight in air was recorded at 450°, but this may have been due to incomplete reaction. As expected the polymer from the condensation of hexamethylene diamine with pyromellitonitrile was less stable (ten per cent loss in weight in air was recorded at 380°).

The polymers prepared by the condensation of tetracyanothiophen and tetracyanodithiin with diaminodiphenyl ether were slightly less stable than those obtained from pyromellitonitrile. As might be expected all of the polymers showed enhanced stability in an inert atmosphere. In nitrogen a gain of 60 to 100 deg. over the stability in air was generally observed. These results were confirmed by differential thermal analysis (DTA).

Mechanical properties—The polymers could be moulded by the combined effect of temperatures of 300° to 450°C and pressures of 10 000 to 20 000 lb/in^2. The best samples were obtained with the polymer from diaminodiphenyl ether and pyromellitonitrile (DDE–PMTN). Most of our evaluations were therefore undertaken on this polymer.

The optimum temperature for moulding small test pieces of the DDE–PMTN polymer was found to be 380° ±20° with an applied pressure of 10 000 lb/in^2. Excellent impressions could be moulded by this simple technique. Visual examination of the specimens showed that the polymer had flowed. This was confirmed by the high transmission of ultrasonic waves through the specimen, characteristic of a homogeneous single phase.

The ultimate tensile strength of the moulded specimens (2 in. × $\frac{1}{4}$ in. × $\frac{1}{8}$ in.) was determined using either the Houndsfield tensometer or an Instron TT–

BM. The Young's modulus was also determined using the Instron. The Young's, bulk and shear moduli of the specimen were determined at 5 Mc/s using an ultrasonic technique[11], the results obtained are given in *Table 2*.

Table 2. Properties of macrocyclic polymer from pyromellitonitrile and diaminodiphenyl ether at 25 °C

Ultimate tensile strength	12 000 ± 2 000 lb/in^2	Shear modulus (5 Mc/s)	292 000 lb/in^2
Young's modulus			
Instron	713 000 lb/in^2	Poisson's ratio	0·35
Ultrasonic (5 Mc/s)	795 000 lb/in^2	Hardness	Rockwell F 95
Bulk modulus (5 Mc/s)	910 000 lb/in^2	Electrical resistance	10^{17-18} ohm cm^{-1}

The tensile strength of the DDE–PMTN polymer was similar to those previously reported for other thermally stable polymers, e.g. Vespel polyimide[4]. As might be expected of a polymer with the double stranded macrocyclic structure the Young's modulus was considerably higher than that recorded for the essentially single stranded polyimides. Not only was the material stiffer than the corresponding polyimide but considerably harder (Rockwell F 95 as compared with 59 for polyimide).

Electrical properties—The electrical properties of these polymers were dependent on the structure, in particular the degree of conjugation within the polymer. The polymer from pyromellitonitrile and diaminodiphenyl ether was a good insulator with a room temperature resistivity of 10^{18} ohm/cm. Some abnormalities in the electrical properties of the other polymers were observed. Full details of the electrical properties of these polymers will be published elsewhere[12].

Chemical properties—Elemental analysis of the polymers for C, H, N presented some difficulties. Invariably the carbon contents were three or four per cent lower than calculated (*Table 1*). Similar difficulties were observed in the analysis of some of the simple macrocyclic compounds and have also been reported for other thermally stable polymers[13]. In view of the affinity of the macrocyclic compounds for solvents and the possibility of chemical reaction between the alcohol and the nitriles it may be that some alcohol may be retained as solvate or chemically combined. Drying the polymers at 200°C *in vacuo* did not affect the analytical results. Attempts to replace any hypothetical hydroxylic solvent with another solvent, e.g. benzene, nitrobenzene, dichlorobenzene, also had no effect on the analytical results.

Chemical resistance—The macrocyclic polymers were essentially insoluble in a wide range of organic solvents. A preliminary evaluation of the chemical resistance of moulded specimens of the DDE–PMTN polymer afforded the results given in *Table 3*.

In view of the basic nature of the polymers they might be expected to be more susceptible to attack by acids than by alkali. Degradation of the sample in dilute acid followed surface imperfections in the moulding. Apparently the acid penetrated the surface of the sample and formed the salt, causing differential swelling and flaking. Immersion of a moulded specimen in ten per cent sodium hydroxide solution for seven days had little effect on its tensile strength. Similarly the polymer appeared to be unaffected by hydrocarbon oil at 25°C for three months and at 200°C for one week.

EXPERIMENTAL

1,2,4,5-Tetracyanobenzene (pyromellitonitrile, PMTN) was prepared from pyromellitic dianhydride essentially by the method described by Lawton and McRitchie[14] with the modifications suggested by Thurman[15].

Table 3. Effect of reagents on the macrocyclic polymer from pyromellitonitrile and diaminodiphenyl ether

Reagent	*Time*	*Temperature, °C*	*Weight change, %*
Water	1 day	25	+1
	2 days	25	+2
	1 day	100	+3·5
10% sodium hydroxide solution	1 day	25	+1
	7 days	25	+3
	1 day	100	+2·5
10% sulphuric acid solution	1 day	25	+3
Hydrocarbon oil	1 day	25	+0·3
	3 months	25	+0·5
	1 day	200	−0·5
	1 week	200	−0·5

Tetracyano-1,4-dithiin and tetracyanothiophen were prepared from carbon disulphide and sodium cyanide by the method described by Simmons[10].

*Benzo*bis(*diiminopyrrolidine*) was obtained by the condensation of tetracyanobenzene with ammonia in methanolic solution at 25°C.

Diamines. The diamines were obtained from commercial sources and recrystallized or distilled before use.

Polymerization. The general procedure is illustrated by the following example:

4,4′-Diaminodiphenyl ether (200g, 1·0 mol.) was dissolved in 2-methoxyethanol (3·75 l.) at 50°C. Tetracyanobenzene (89g, 0·5 mol.) was added to the stirred solution. When the nitrile had completely dissolved a solution of sodium 2-methoxyethanolate (0·4g) in 2-methoxyethanol (20 ml) was added. The solution was refluxed with stirring under a stream of nitrogen for five days. The solid polymer was filtered off, washed with alcohol (2 ×) and extracted in a Soxhlet apparatus first with ethanol then with benzene. The polymer was finally dried at 200°C at 0·1 mm Hg pressure. The product (251·5g, 92 per cent) was a fibrous brown-red polymeric solid. Analysis: found C, 71·4; H, 4·0; N, 15·0 per cent. $(C_{34}H_{20}N_6O_2)_n$ requires C, 75·0; H, 3·5; N, 15·5 per cent. Other results are given in *Table 1.*

MODEL COMPOUNDS

Macrocyclic compounds—4,4′-Diaminodiphenyl ether (5g, 0·025 mol.) and phthalonitrile (3·2g, 0·025 mol.) were dissolved in 2-methoxyethanol (125 ml). Sodium 2-methoxyethanolate (0·05g) dissolved in 2-methoxyethanol (25 ml) was added and the clear solution refluxed for one day. The solution was concentrated by distillation of the solvent under reduced pressure to afford yellow-orange crystals. A further yield of the product was obtained by pouring the solution into water. Recrystallization of these solids from ethyl alcohol–dimethyl formamide gave yellow-orange crystals (6·8g, 93 per cent) m.pt > 360°C. DTA showed peaks at 171°, 385° and 424°C. Analysis: found C, 72·0; H, 5·0; N, 15·0 per cent. $C_{40}H_{26}N_6O_2$, 2DMF requires C, 71·9; H, 5·2; N, 14·6 per cent. After drying at 200°C, 0·01 mm Hg pressure: found C, 77·4; H, 4·2; N, 14·0 per cent. $C_{40}H_{26}N_6O_2$ requires C, 77·2; H, 4·2; N, 13·5 per cent. Mass spectral analysis (MSA) gave a mass number of 622·2121 (calculated 622·2117).

*Benzo*bis*(diphenyliminopyrrolidine)*—A solution of pyromellitonitrile (3·56g, 0·02 mol.) and aniline (7·44g, 0·08 mol.) in 2-methoxyethanol (150 ml) containing sodium 2-methoxyethanolate (0·4g) was refluxed for five days. The hot mixture was filtered. The yellow solution was poured into water to afford a yellow solid (8·1g, 77 per cent). Recrystallization from ethyl alcohol afforded yellow crystals of benzo*bis*(diphenyliminopyrrolidine) m.pt 288°–290°C. Analysis: found C, 79·1; H, 4·9; N, 15·5 per cent. $C_{34}H_{24}N_6$ requires C, 79·2; H, 4·7; N, 16·1 per cent. MSA gave a mass number of 516·2030 (calculated 516·2062).

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