

# THERMALLY STABLE POLYMERS

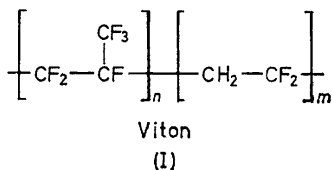
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Most organic polymeric materials melt below 200°C and most of them begin to degrade rapidly at temperatures only slightly above 200°C. Thermally stable polymers are generally considered to be those which will withstand much higher temperatures without loss of strength or change of structure. In general we expect these materials to withstand at least 300°C in air and up to 500°C or higher in inert atmospheres. Polymers which show these properties are usually highly aromatic in structure, often with heterocyclic units, high melting, sometimes infusible and usually with low solubility in all solvents. This makes their fabrication very difficult and as a consequence limits their usefulness.

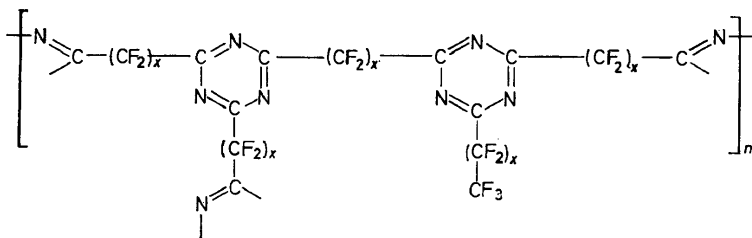
There are a relatively few polymers which are available commercially as plastics, films, wire-coating polymers, etc. which are stable in the temperature ranges indicated. There are other polymers which have been synthesized and tested in pilot-plant scale which show promise but are still very expensive and not generally used. Finally there are other classes which have been studied in the laboratory and have not yet reached the development stage. In this report I shall mention examples of these various classes of polymers.

There is a need for thermally stable rubbers but at the present time I know of none that will stand up to 500°C for any appreciable length of time. The best of the commercially available materials are the fluoro-rubbers but even these decompose rather rapidly in a thermogravimetric test at 400°C and are useful only at considerably lower temperatures. Viton (I) which is a perfluoropropylene-vinylidene fluoride copolymer can be used continuously at temperatures of 200°C in air for months without complete loss of properties. At that elevated temperature its tensile strength is much less than at room temperature. It is recommended for continuous service at 260°C for up to 1000 hours. For fleeting use it can give temporary protection at temperatures up to about 500°C.



I know of no rubber under development which is more promising than Viton. Although the work of Brown<sup>1</sup> has shown that the triazine unit joined by perfluoroalkylene units (II) has some promise, information on the current state of development is not available in the literature.

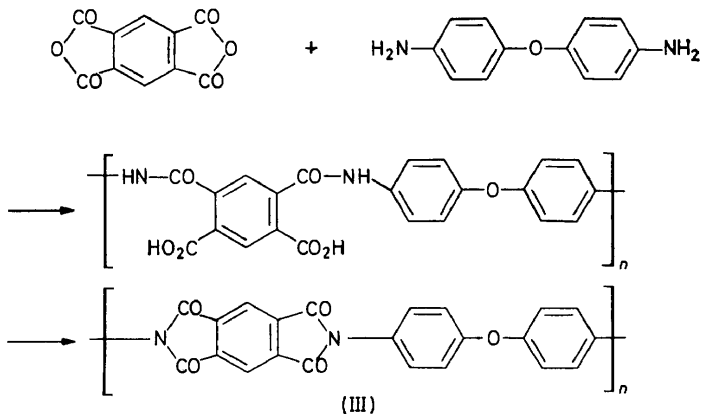
The polyimides are the most thermally stable of the polymers available for use as plastics and films. They have also been spun into fibres in experimental tests but are not generally available as fibres. A variety of polyimides have been synthesized and described in various papers but two commercial names, Vespel and Kapton, have been designated names for the plastic and films which are marketed. These are believed to be the polyimide (III) of pyromellitic anhydride and *p,p'*-diaminodiphenyl ether<sup>2</sup>.



(II)

At 400°C in air, it loses less than 10% of its weight in 100 hours. It can be cooled to liquid nitrogen temperature without loss of strength. As a film it has been used successfully in air over the range of -269°C to 400°C. It begins to char at 800°C but it does not melt up to 900°C. It can be used in air at 300°C for a month and at 400°C for a day. It retains a tensile strength of 4000 psi at 500°C. At 500°C in helium its weight loss in 1000 minutes is about 7½%.

The polyimides must be fabricated at the amic acid stage before the final cyclization to the imide is performed. In the amic acid stage, the polymers are soluble in aprotic solvents and can be cast or spun. Then the imide ring is closed to give an insoluble infusible polymer. The polyimides are somewhat



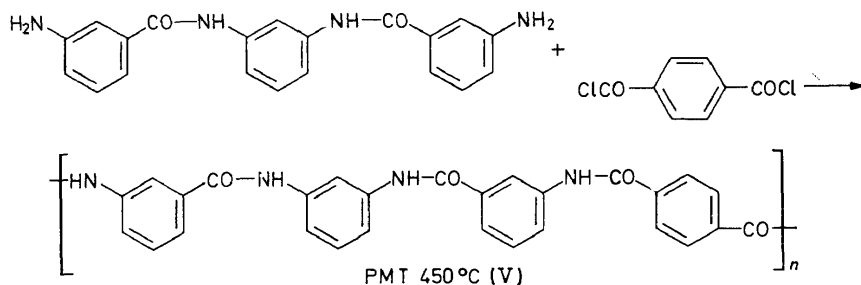
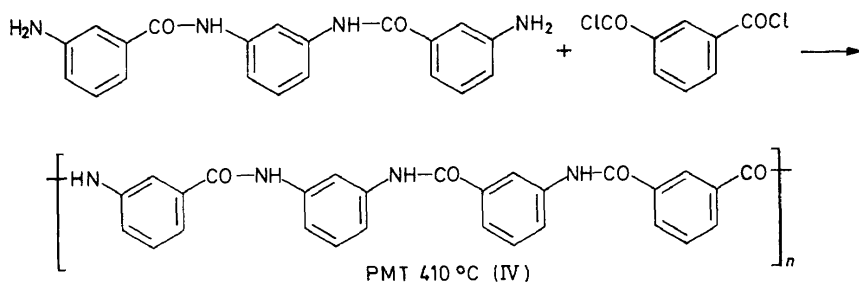
(III)

sensitive to base-catalysed hydrolysis, but this has not limited their utility.

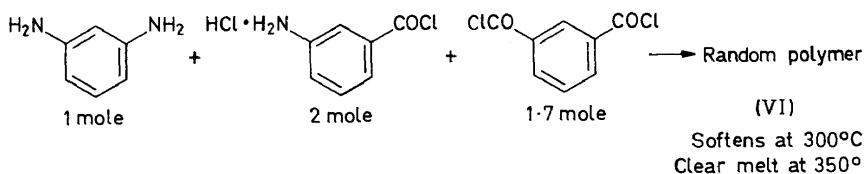
There is an aromatic polyamide called Nomex which is used as a fibre and a paper at elevated temperatures. It does not melt but degrades rapidly above 370°C. Preston and his coworkers<sup>3</sup> have become interested in wholly-ordered aromatic copolyamides which show excellent high-temperature

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properties and better flexibility than do random polyamides. For example, the amine *N,N'*-*m*-phenylene-bis-(*m*-aminobenzamide) and isophthaloyl chloride in interfacial polymerization give a polymer (IV) with a melt temperature of 410°C which loses about 10% of its weight in thermogravimetric analysis at 450°C. The same amine with terephthaloyl chloride



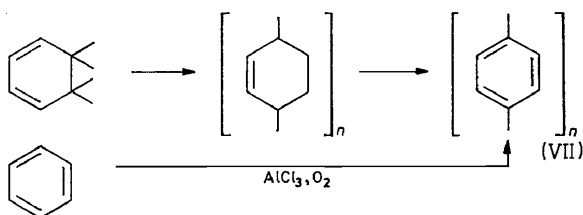
gives an ordered copolyamide (V) with a melt temperature of 450°C which loses only 10% of its weight at 500°C. A random *meta*-copolymer (VI) of the same units softened at 300°C and melted to a clear melt at 350°C. The above ordered-copolyamides gave tough films and strong fibres.



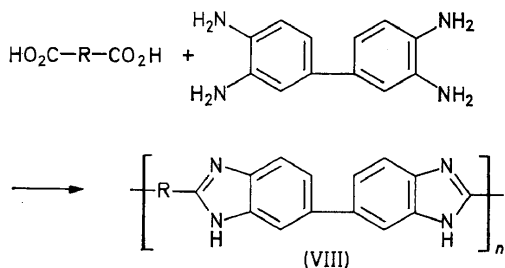
These ordered copolyamides have excellent radiation resistance. They have also been made with a variety of fused and multiple ring systems. Also heterocyclic units have been successfully introduced into experimental polymers to give materials which produce excellent fibres which are heat and radiation resistant. These ordered copolyamides are now available industrially on a selective evaluation basis.

Another group of experimental thermally stable polymers are the polyphenyls (VII). Some of these have reached the stage of experimental testing but as far as I am aware, none are commercially produced. Polyphenyls have been made by dehydrogenation of poly-1,3-cyclohexadiene<sup>4</sup> and by the Friedel and Crafts condensation of benzene<sup>5</sup>. The polyphenyls are deep brown to black, insoluble, infusible polymers which are extremely difficult

to fabricate. Some success has been achieved by use of powdered metallurgy techniques to attain compacted materials for use as ablative materials in aerospace applications<sup>6</sup>. When *o*-, *m*- or *p*-terphenyls were used in the Friedel and Crafts condensation, a less regular structure resulted and the polymers were fusible and more tractable than the more simple polymers<sup>7</sup>.



In the last few years a large amount of work on the study of polyaromatic heterocycles has been carried out. In 1961 Vogel and Marvel<sup>8</sup> described the aromatic polybenzimidazoles (VIII and IX) which were obtained by the condensation of aromatic tetraamines with diphenyl esters of dibasic aromatic acids. The condensation reaction which produced the heterocyclic rings is the reaction which produces the polymer and this general type of condensation has been extended to produce a wide variety of polyaromatic heterocycles, all of which have excellent thermal stability. Brinker and Robinson<sup>9</sup> had previously made polybenzimidazoles with aliphatic recurring units, but had not reported any unusual properties in these materials which were prepared by condensing aliphatic dibasic acids with aromatic tetraamines. This reaction was not useful for making all aromatic polybenzimidazoles since the aromatic acids seem to decarboxylate to some extent at the temperature required for the condensation. After investigating a variety of

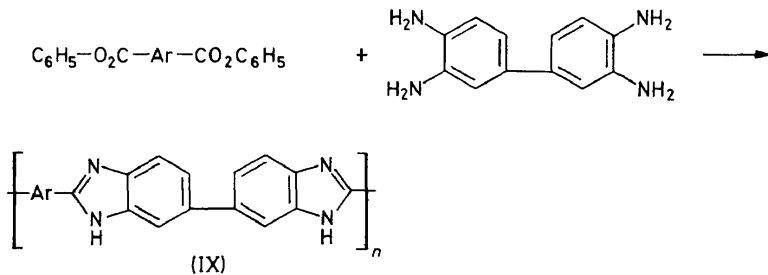


conditions it was found that the condensation of aromatic tetraamines with the diphenyl esters of aromatic dibasic acids gave good yields of high-molecular-weight polymers. Many such polymers have been made by this general type of condensation<sup>10</sup> in my laboratory. Korshak and his co-workers<sup>11</sup> have also made a number of polymers of this same general type.

Iwakura and his co-workers have found that this type of polymer can be made by condensing aromatic dibasic acids, their methyl esters, their amides or the corresponding nitriles with aromatic tetraamines in polyphosphoric acid<sup>12</sup>. This method avoids the use of the highly-oxidatively-sensitive free aromatic tetraamines.

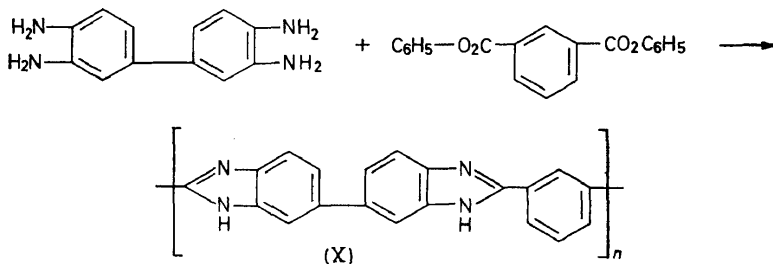
The polybenzimidazoles are all coloured polymers varying from deep golden yellow to black, usually without a melting point below 400°C. They

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vary in crystallinity and solubility. All have been found to be soluble in sulphuric acid, a few in formic acid and a few in trifluoroacetic acid. Those polymers which are not crystalline as shown by x-ray patterns, are soluble in such aprotic solvents as dimethylsulphoxide, dimethylformamide, dimethylacetamide, *N*-methylpyrrolidone and hexamethylphosphoramide. All of the materials are nonconductors of electricity. When heated to about 400°C for a short time, they become insoluble in all solvents, even sulphuric acid. In a nitrogen atmosphere they do not lose weight up to 500°C. In air they begin to oxidize rather rapidly at about 300°C. They are extremely stable to hydrolysis and are not attacked by hot strong sulphuric acid solutions or hot 25% potassium hydroxide solutions.

The polybenzimidazole (X) which has been most completely evaluated is the one derived from the condensation of 3,3'-diaminobenzidine and



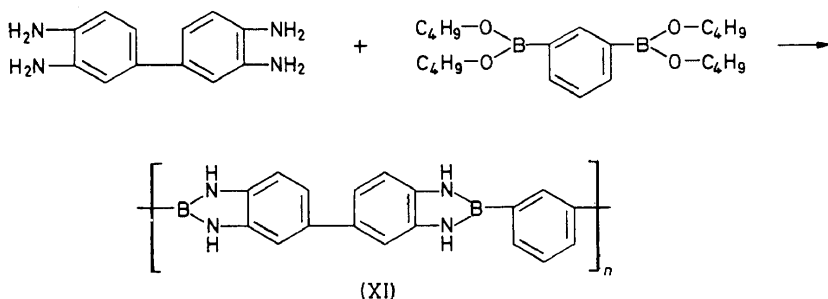
diphenyl isophthalate. The polymerization is carried out by mixing the two solid monomers and heating for an hour or two in an inert atmosphere at about 250°C until a solid foamy mass is produced. This mass is cooled to room temperature and broken up to give fine granules so that heat transfer to the interior of the mass is better and then the solid is again heated out of contact with air for several hours at 350–400°C to complete the polymerization which proceeds in the solid state. The polymer that is produced is a golden yellow solid, soluble in such solvents as dimethylsulphoxide and dimethylacetamide. It has an inherent viscosity in dimethylacetamide solution of 0.5 to 1+ depending on the time of polymerization and the exact balance of reagents. A sample which had an inherent viscosity of 0.8 in dimethylsulphoxide had an inherent viscosity of about 3.3 in sulphuric acid solution and by the light-scattering technique had a molecular weight of 54 000<sup>13</sup>.

This polymer has been converted into films and fibres by casting or

spinning from dimethylacetamide solution. These films and fibres show good mechanical properties up to a temperature of 300°C. In air, films lose their strength rather rapidly at temperatures above 300°C. Fibres from this polymer with tensile strength of about 7 g/denier are undergoing extensive industrial tests for high temperature use<sup>14</sup>.

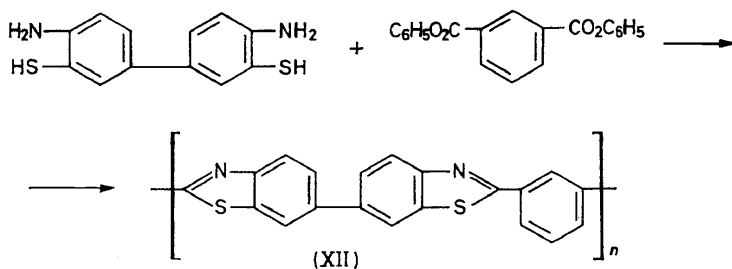
This polybenzimidazole has been shown to have merit as a glass laminating resin and as a metal adhesive when properly used. It must be applied as a low-molecular-weight polymer which can melt and wet the surfaces involved. Then polymerization must be completed *in situ* to obtain good adhesive strength<sup>15</sup>.

Some structurally related polymers (XI) have been prepared by substituting esters of diboronic acids for the aromatic dibasic acids<sup>16</sup> in the polybenzimidazole synthesis. In this case it was necessary to use butyl rather



than phenyl esters since in the latter case the liberated phenol was a sufficiently strong acid to cause cleavage of the carbon-boron linkages. These polymers possess good molecular weight, solubility and heat stability. Their sensitivity to hydrolysis was so great that they were not extensively studied.

By applying the phenyl-ester condensation reaction with aromatic amines, two new groups of polymers, the polybenzothiazoles and polybenzoxazoles, have been prepared. Hergenrother, Wrasidlo and Levine<sup>17</sup> condensed 3,3'-dithiobenzidine and diphenyl isophthalate to obtain a polybenzothiazole (XII) which is remarkably stable in air up to 600°C. Under these conditions the polymers lose only 1% of their weight. The polymers are soluble only in sulphuric acid and have had little application as yet.

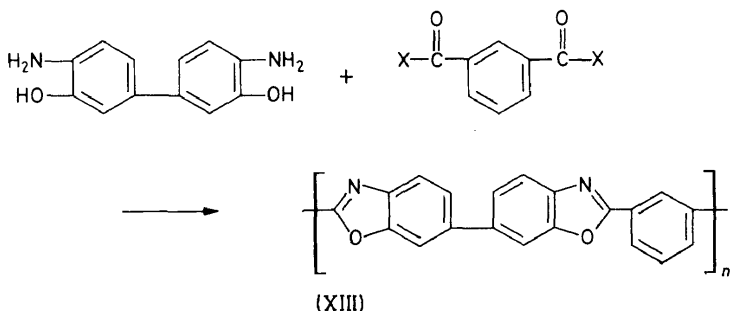


Polybenzoxazoles (XIII) have been prepared from 3,3'-dihydroxybenzidine by its reaction with isophthaloyl chloride<sup>18</sup> and by condensation with

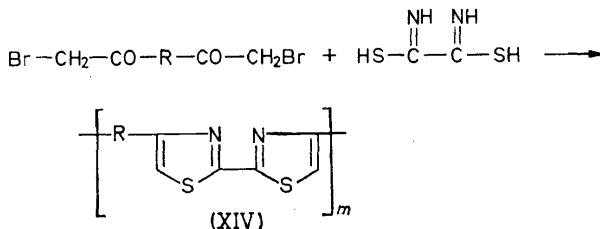
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diphenyl isophthalate<sup>19</sup>. These polymers are stable to 500°C in nitrogen but are soluble only in sulphuric acid and are generally quite intractable.

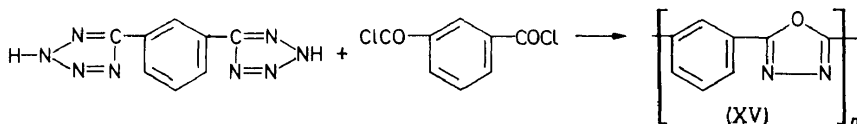
Longone and Un<sup>20</sup> have synthesized a number of polybisthiazoles (XIV) from bisbromomethyl ketones and dithioxamide. These polymers had unusual thermal stability with weight losses of only 20% up to 500°C and



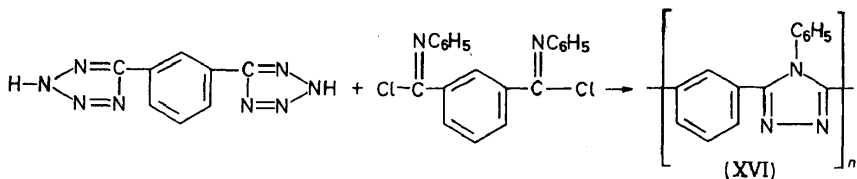
only 50% up to 900°C. They were yellow-brown and turned pink on long exposure to light. There was some evidence of photo-oxidation. The polymers did not melt and were generally insoluble.



Another group of heat stable polymers has been developed which contain oxadiazole and triazole recurring units. By using bifunctional reagents, Abshire<sup>21</sup> in my laboratory was able to adapt Huisgen's<sup>22</sup> dipolar addition reaction for the preparation of oxadiazoles so that polymers with alternate aryl and oxadiazole recurring units (XV) could be obtained. These polymers

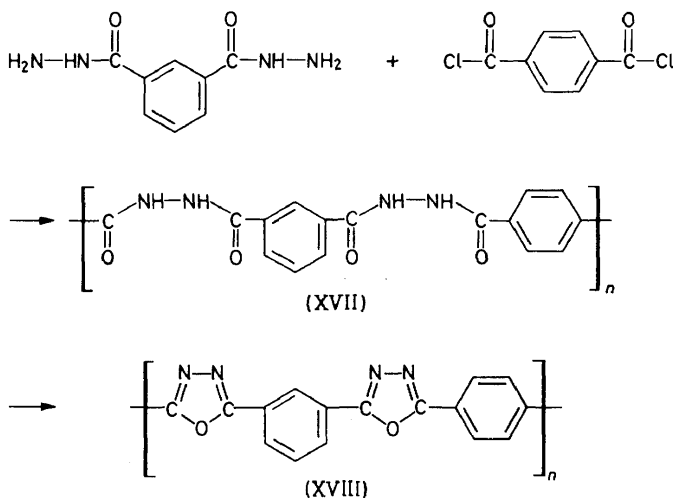


were obtained in the 6000 molecular weight range. They were coloured, did not melt below 350°C and were soluble only in sulphuric acid. Hence, they were not useful for processing. They were, however, very thermally stable and only lost weight when heated above 520°C in nitrogen.



Abshire<sup>21</sup> used an analogous reaction of Huisgen<sup>23</sup> to prepare polymers with alternate aryl and triazole recurring units. These polymers (XVI) were slightly higher in molecular weight, slightly more soluble and slightly less heat stable than the corresponding oxadiazole polymers.

New procedures have been devised for synthesizing the polymers with



oxadiazole<sup>24</sup> and triazole<sup>25</sup> recurring units. The corresponding polyhydrazides (XVII) were prepared and then converted to either the oxadiazole (XVIII) or triazole structure. This has permitted the synthesis of high-molecular-weight products which can be fabricated into fibres at the polyhydrazide stage and then converted to the fully aromatic structure. Both classes of polymers have yielded potentially useful fibres which are stable at high temperatures and which have particularly good resistance to oxidation. The fibres which have been prepared from the polyoxadiazoles have good tensile strength (3 g/denier) and good knot strength<sup>26</sup>. They maintain at least half of their strength after 30 hours of ageing at 400°C in air. At 300°C in air they maintain half strength for 700 hours. When tested at 300°C their strength is at least 2 g/denier.

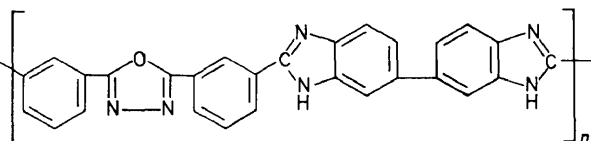
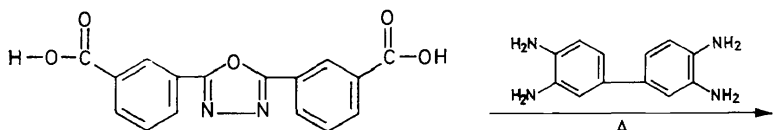
Frazer and Fitzgerald<sup>27</sup> have prepared the corresponding thiadiazoles from the thiahydrazides. In this case the cyclization reaction is much simpler to carry out. These fibres have good tensile properties which are retained to the extent of 92% after 114 hours heating in air at 300°C. At 400°C, 60% of their tensile strength is retained after 32 hours in air which is even better than shown by the oxadiazole fibres.

Preston and Black<sup>28</sup> have used their ordered copolymer idea to develop a series of thermally stable ordered heterocyclic polymers (XIX-XXIV). The thermal properties of the series are listed in *Table 1*. The decomposition temperatures noted are the temperatures at which the weight loss in nitrogen is approximately 10%. For comparison, the figure for polybenzimidazole is 600°C, for polyimides 570°C, for oxadiazoles 500°C and for triazole 490°C, in the same test.

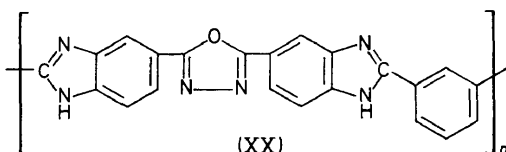
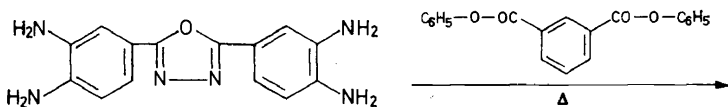
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Table 1. Thermal properties of ordered heterocyclic copolymers

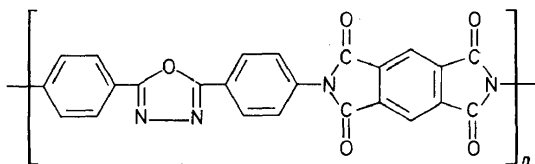
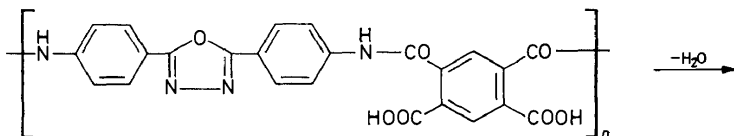
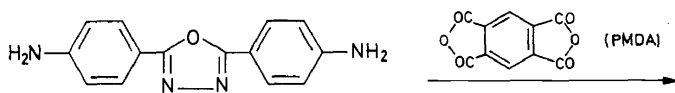
Polymer No.	Melt transition temp. (°C)	Decomposition temp. (°C)
XIX	530	—
XX	525	520
XXI	525	550
XXII	530	510
XXIII	565	550
XXIV	450	510



(XIX)



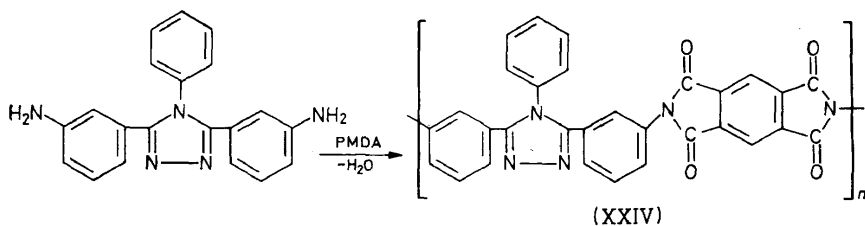
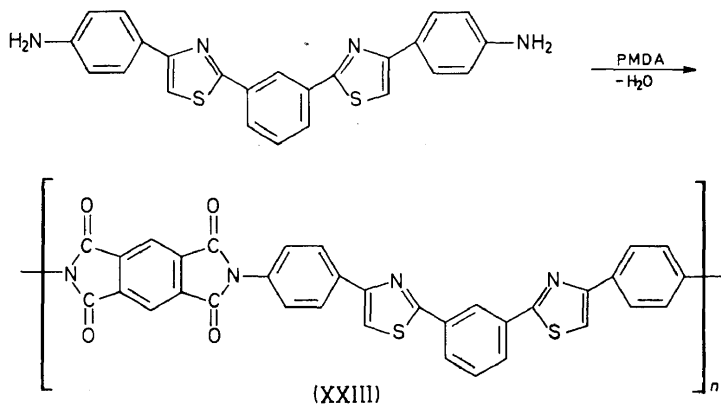
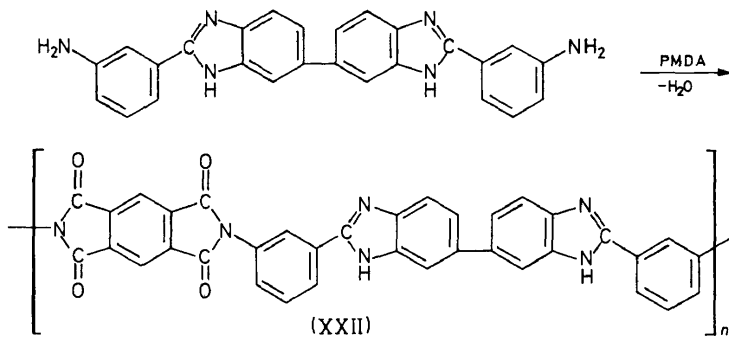
(XX)



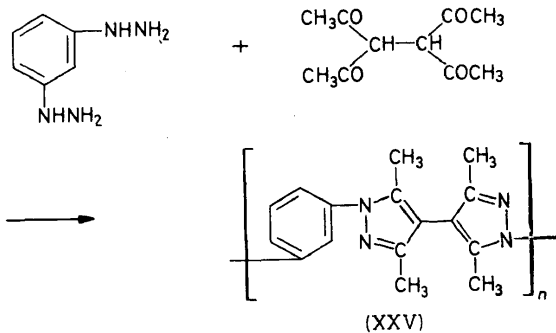
(XXI)

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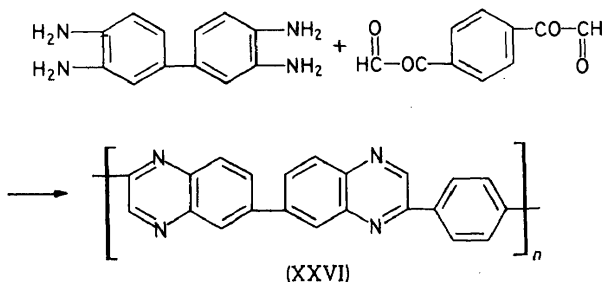
A number of other polyaromatic heterocycles have been briefly described. Schaefer and Bertram<sup>29</sup> have prepared some polymers (XXV) with alternate phenyl and pyrazole recurring units by the reaction of aromatic dihydrazines with tetraacetoethane. This polymer is remarkably stable up to 400°C in nitrogen but decomposes rapidly above that temperature. Similar products have been described by Korshak and coworkers<sup>30</sup>. Stille and Williamson<sup>31</sup> and de Gaudemaris and Sillion<sup>32</sup> have prepared polymers with quinoxaline



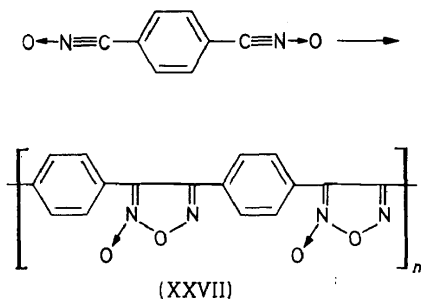
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recurring units (XXVI) by condensing 3,3'-diaminobenzidine with 1,4-diglyoxalylbenzene. These polymers are reported to be stable in air up to 500°C and to nearly 800°C in nitrogen. Thus far they have not been fabricated into useful objects.

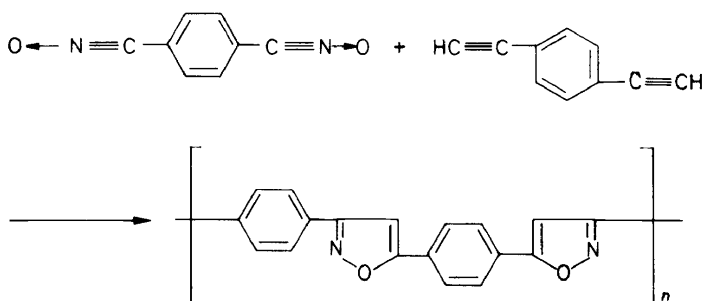


By introducing an oxygen atom between two quinoxaline units<sup>33</sup>, polymers soluble in hexamethylphosphoramide were obtained and then could be cast into films stable in air to 500°C. Polyquinoxalines with a sulphur atom and with a sulphone group between the quinoxaline segments<sup>34</sup> have been prepared. These are much more soluble than the others and still show great heat stability.

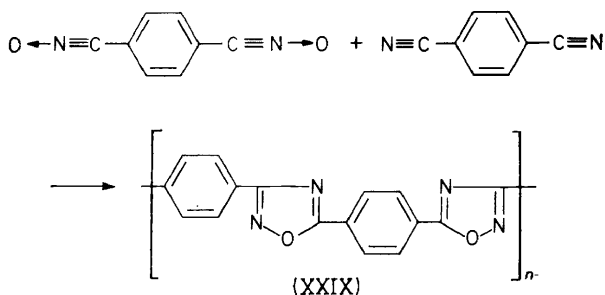


In the last few years a number of 1,3-dipolar addition reactions have been used to yield new heterocyclic polymers. Overberger and Fujimoto<sup>35</sup> have discovered that terephthalonitrile oxide in solution polymerizes to give a

product with alternate phenyl and furoxan units (XXVII). When terephthalonitrile oxide and 1,4-diethynylbenzene are allowed to react, a polymer with alternate phenyl and isooxazole units results (XXVIII). The bis-nitrile oxide reacts with terephthalonitrile to yield a polymer with oxadiazole units (XXIX).

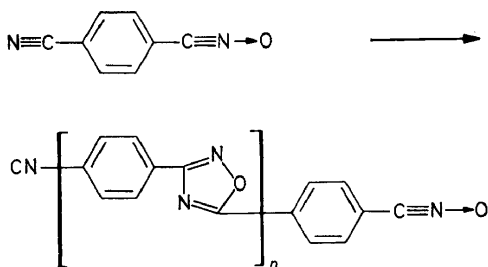


(XXVIII)



(XXIX)

Akiyama, Iwakura, Shiraishi and Iami<sup>36</sup> have been able to homopolymerize *p*-cyanobenzonitrile oxide to obtain a product with alternate phenyl and oxadiazole units (XXX) in a solid state reaction.



(XXX)

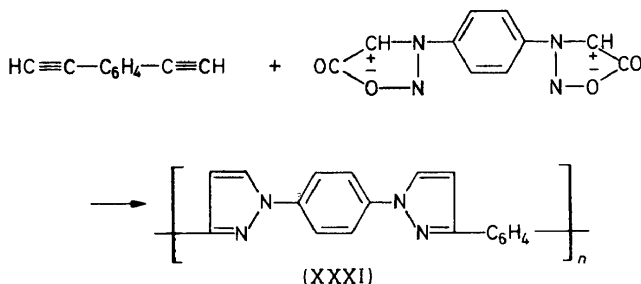
Stille and Bedford<sup>37</sup> have treated *m*- and *p*-diethynylbenzene with sydnone to obtain polymers with alternate phenyl and pyrazole rings (XXXI).

Stille and Harris<sup>38</sup> have condensed bis-nitrile imines with diacetylenes to obtain polymers with phenyl and pyrazole rings (XXXII) which are stable to about 420°C.

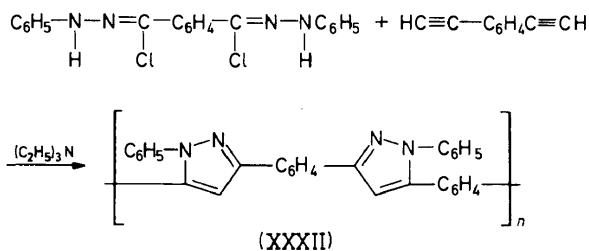
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All these new 1,3-dipolar addition reactions have yielded polymers which are still rather incompletely characterized.

An examination of the results obtained with these various aromatic heterocyclic polymers shows that when the recurring units are connected

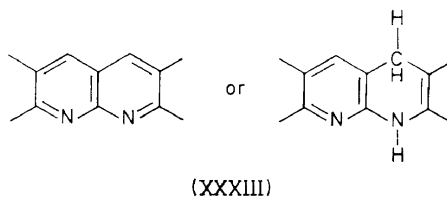


with single bonds between the aromatic segments, the polymers are stable in nitrogen to about 500–600°C. There is not much variation between the various heterocyclic recurring units. The stability of these polymers in air does vary somewhat and it seems that the ones with the least hydrogen content are least susceptible to oxidation. There is a marked variation in



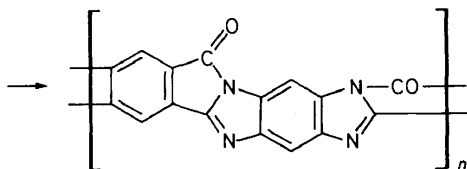
solubility behaviour and the polybenzimidazoles seem to be the most tractable polymers in the series.

The remarkable thermal stability of 'black orlon' which is obtained by a regulated pyrolysis of polyacrylonitrile has attracted much interest. This pyrolysed material seems to be a polyquinizarine or a partially hydrogenated polyquinizarine<sup>39</sup> (XXXIII).

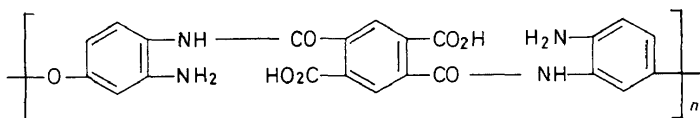
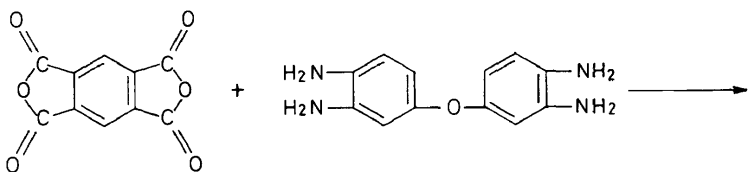


The stability of this two strand or ladder structure has led to many attempts to synthesize such structures with higher molecular weight. The first successful synthesis of such an aromatic heterocyclic structure came in 1965 in three laboratories at about the same time<sup>40</sup>. The reaction of pyromellitic anhydride with 1,2,4,5-tetraaminobenzene gave a ladder structure (XXXIV). The

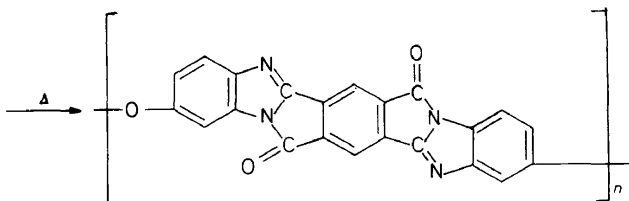
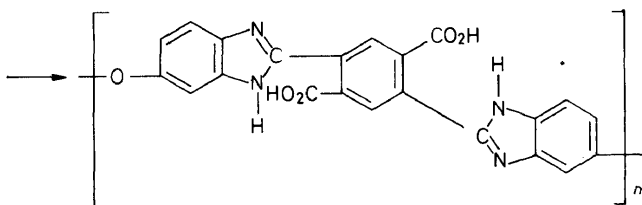
reaction is rather complex and there are several possible intermediate steps. There are also possibilities of isomerism which are not yet fully investigated. A considerable amount of work has been done with model structures of a non-polymeric nature and the reaction has also been applied to such tetraamines as 3,3'-diaminobenzidine and tetraaminodiphenyl ether to



(XXXIV)



(XXXV)



obtain non-ladder structures which are somewhat more tractable than the derivative from tetraaminobenzene.

The tetraaminobenzene derivative does not melt and is soluble only in sulphuric acid. Thermogravimetric analysis indicates it is stable in nitrogen to 600°C and the weight loss which occurs up to that stage seems to be caused by water loss due to the fact that the amide link had not been completely formed.

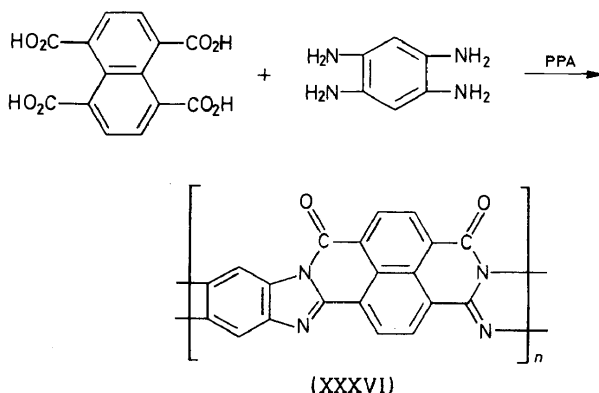
Bell and Pezdirtz have been able to control the reaction of pyromellitic anhydride and tetraaminodiphenyl ether to obtain a soluble intermediate amide-acid type of polymer (XXXV).

Before the last ring closure, the polymer can be dissolved in dimethylacetamide and cast into films. Then by further heating, the final ring closure can be achieved. The polymer thus obtained shows good thermal stability to 500°C. The films so prepared have exceptional stability toward radiation. Their tensile properties were essentially unchanged after exposure to 10 000 megarads.

Colson, Michel and Paufler made films in a similar manner from the polymer derived from 3,3'-diaminobenzidine. Their films were deep red in colour, quite flexible and had a modulus of 700 000 psi; a tenacity of 11 000 psi; and elongation of 2%. They showed no exotherm below 600°C and there was no significant loss in weight in dry air up to a temperature of 550–600°C.

Presumably the polymer from tetraaminobenzene which would have a full ladder structure can be made in a similar step-wise procedure. Hence, there is potentially a way to obtain films or fibres with the complete ladder structure.

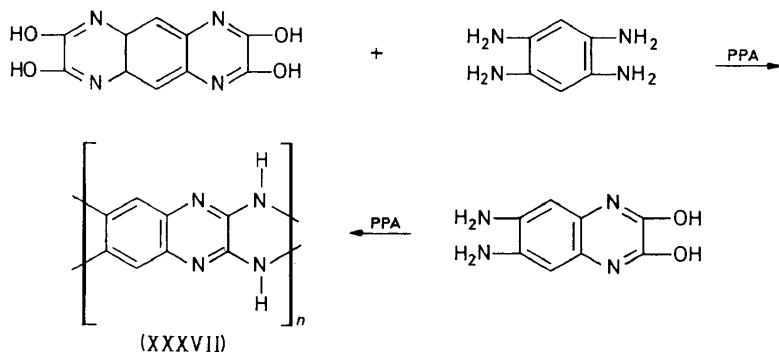
Van Deusen<sup>41</sup> has made a similar type of structure from 1,4,5,8-naphthalene tetracarboxylic acid and tetraaminobenzene in polyphosphoric acid (XXXVI). This polymer lost no weight in nitrogen below 600°C and in air there is very little break in the weight loss curve below 500°C. It can be spun



from sulphuric acid solution to give a fibre with a tensile strength of 3.4 g/denier.

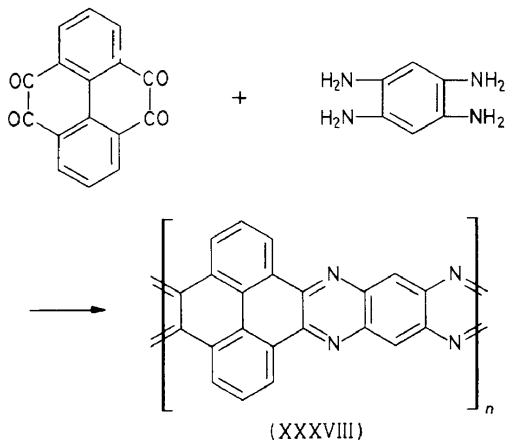
A third type of ladder polymer (XXXVII) has been obtained<sup>42</sup> by the condensation of 2,3,7,8-tetrahydroxy-1,4,6,9-tetraazaanthracene with 1,2,4,5-tetraaminobenzene in polyphosphoric acid and by the self condensa-

tion of 2,3-dihydroxy-6,7-diaminoquinoxaline in the same reagent. This is a highly coloured polymer which does not melt below 350°C. It is slightly soluble in sulphuric and methanesulphonic acids. In the latter solvent, it shows an inherent viscosity of 2.5. In the thermogravimetric test, it loses weight gradually from 200°C to 600°C and this loss of weight seems to be



due to loss of water showing that the ring closure to give a ladder structure has been incomplete. After 600°C there is a more rapid weight loss until 15% of the weight is lost at 900°C. In air the polymer lost weight rapidly above 400°C. As yet no way has been found to fabricate useful articles from this polymer.

Stille and Mainen<sup>43</sup> have prepared ladder polyquinoxalines from 1,2,4,5-tetraaminobenzene and 2,5-dihydroxy-*p*-benzoquinone and from the same amine and 1,2,6,7-tetraketopyrene (XXXVIII). The first type showed no



greater thermal stability than do ordinary linear poly-heterocycles and it was thought that ladder formation was incomplete. The second type of polymer showed good solubility in aprotic solvents and excellent thermal stability. In air the major break in the thermogravimetric curve came at 460°C and in nitrogen the break came at 683°C. In both cases the weight loss before the break was less than 4%.

These newer researches on ladder structures seem to show promise that products of this type can be fabricated into films and fibres which will show good thermal and oxidative stability at temperatures at least 100°C above those of non-ladder structures. All of the polymers which have been tested thus far, show evidence that complete ladder structures have not been obtained. Hence, the 600°–650°C limit may not be the final limit which can be obtained for such structures.

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