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"LADDER" AND "PARQUET" POLYMERS

Yu. E. Doroshenko

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INTRODUCTION

The accompanying diagram illustrates schematically the molecular structures of all polymers known at the present time.

Polymers of types *1*, *3*, and *6* have been studied for many years. Research workers have recently been paying increasing attention to polymers whose molecules correspond to the remaining three types (*2*, *4*, *5*). This is not accidental, since regularly arranged cyclic units confer on the polymer exceptionally high resistance to the action of temperature, radiation, and corrosive media. This applies especially to aromatic systems.

Structures of types *4* and *5* are distinguished from the others by the presence of regularly fused cyclic systems. The structure of these cyclic systems resembles either a rope ladder, whence the name "ladder polymers", or a parquet, when an ideal network structure is formed ("parquet polymers"). These two types of macromolecular structures will be briefly discussed in the present review.

I. LADDER POLYMERS

The rings in ladder polymers comprise either carbon atoms alone (carbocyclic ladder polymers), carbon together with various heteroatoms, such as oxygen, nitrogen, phosphorus, etc. (heterocyclic ladder polymers), or no carbon at all. The last type include inorganic and organoelementary polymers, the rings of which contain oxygen atoms alternating with silicon, titanium, etc. atoms to which are attached organic or inorganic substituents.

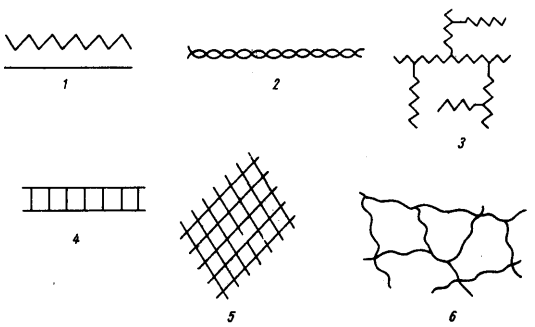


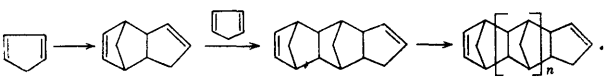
Diagram of structure of various polymers:
1) linear polymers; 2) spiran polymer; 3) branched polymer; 4) ladder polymer; 5) parquet polymer; 6) three-dimensional network polymer.

A. CARBOCYCLIC LADDER POLYMERS

This fairly considerable group of ladder polymers may contain rings of two types—(1) alicyclic or hydroaromatic and (2) aromatic—which show fundamental differences in modes of preparation and in properties, so that the two groups will be considered separately.

1. Alicyclic Ladder Polymers

A representative of ladder polymers having five-membered carbon rings, which has been known for a long time, is polycyclopentadiene. At room temperature cyclopentadiene readily forms a dimer, and by prolonged heating Staudinger[1] was able to obtain tri-, tetra-, and pentacyclopentadienes and products of higher molecular weight. Polymerisation proceeds by the Diels–Alder reaction[2–4] as follows:



The melting point increases sharply with increase in molecular weight. Thus the di-, tri-, tetra-, and pentamers have melting points of 32°, 60°, 190°, and 270°C respectively, while polymers of higher molecular weight soften with decomposition at 373°C. Tetracyclopentadiene is readily soluble in benzene, whereas pentacyclopentadiene is very sparingly soluble, and the products of higher molecular weight are completely insoluble in benzene[1].

Cyclic polymers of butadiene, isoprene, and their derivatives are of great theoretical and practical interest. A good review of cyclised rubber has been given by van Veersen[5,6] who has made a valuable contribution to the study of the structure, properties, and methods of preparation of this polymer.

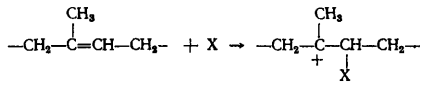
Harries[7] first reported that he had obtained an insoluble cyclisation product of natural rubber by treating a benzene solution of the latter with sulphuric acid. Later Kirchhof[8] and Staudinger[9] observed that the physical and chemical properties of rubber were greatly changed by the action of sulphuric acid. Staudinger[9] obtained a brittle solid having the same empirical formula as the original rubber. Fisher[10] developed the technical production of cyclised rubber: a mixture of rubber, sulphuric acid, and kieselguhr (or titanium oxide) was heated and stirred at 130°C. Besides sulphuric acid, aromatic sulphonic acids could be used successfully.

Bruson et al.[11] cyclised rubber in solution, using such Friedel–Crafts catalysts as $SnCl_4$, $TiCl_4$, and $FeCl_3$ for this purpose.

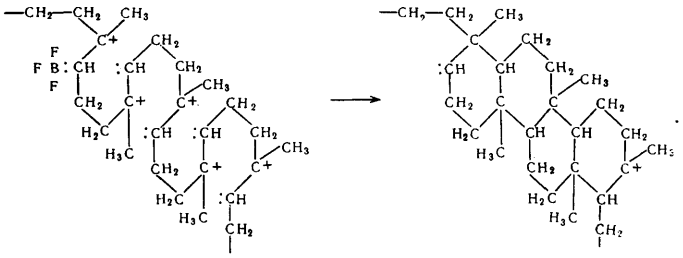
Cyclisation was found to take place under the influence of electrophilic reagents[12] or on heating[13]. Staudinger showed[14] that cyclised rubber can be obtained from hydrochlorinated rubber by the prolonged heating of a solution of

the latter in toluene in the presence of zinc chloride. Hydrobrominated or hydriodinated rubber can also be used for this purpose.

A mechanism of chain initiation and growth in the cyclisation of rubber was suggested by van Veersen[5], according to which a double bond first interacts with an electron acceptor X;



where X = H^+, $AlCl_3$, BF_3. The resulting carbonium ion, in its turn, reacts as an acceptor for the next double bond:



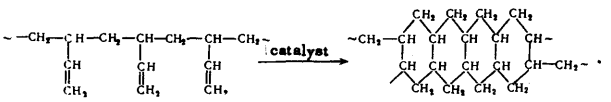
In this way macromolecules containing fused six-membered rings are formed. In van Veersen's view[5] the probability of interaction between different macromolecules is very small, and cyclised rubber represents an aggregate of fused six-membered rings separated by shorter or longer polyisoprene sections.

With increasing degree of cyclisation the material becomes harder and harder, and when the content of cyclic groups is sufficiently large, brittleness ensues. Polymers in which 60–80% of the double bonds have disappeared by cyclisation have softening points of 50–80°C.[6] The cyclised polymer is stable to the action of 10% H_2SO_4 and 50% NaOH at room temperature, but it is rapidly oxidised by oxygen owing to the presence of a tertiary hydrogen atom.

Considerable progress has been made during recent years in the synthesis of polymers using catalysts of ionic type. Attention has been paid also to diene monomers. It was found that the chemical nature, composition, and quantity of the ionic catalyst has a fundamental effect on the structure, properties, and yield of polymers obtained from conjugated dienes. It was established that insoluble products can be formed by the polymerisation of dienes in the presence of titanium tetrachloride and organometallic compounds[15–19].

When isoprene is polymerised in the presence of triethylaluminium and titanium tetrachloride with the molar ratio of the components of the catalyst below 0.8 (especially at 0.3), a large amount of gel is formed[17]. A similar effect has been observed in the case of the triisobutylaluminium–titanium tetrachloride catalytic system[17,18]. When the molar ratio of these components is 1.25 or less, the polymerisation of butadiene in a solvent also results in products which are insoluble in hot xylene[19].

Kropacheva et al.[16] obtained two types of polymers—an elastomer soluble in petroleum ether and an insoluble amorphous powder—in an investigation of the polymerisation of isoprene in petroleum ether solution at room temperature in the presence of equimolecular proportions of isopentylsodium and titanium tetrachloride. Analogous products are formed in the polymerisation of butadiene. The yield of the insoluble solid polymer increases with increase in the quantity of titanium tetrachloride, and it is the sole product when the ratio of isopentylsodium to titanium tetrachloride is 1 : 3. Solid polybutadiene softens and begins to decompose at about 400°C. Such a high softening point is due to the cyclic structure of the polymer, which is formed according to the scheme



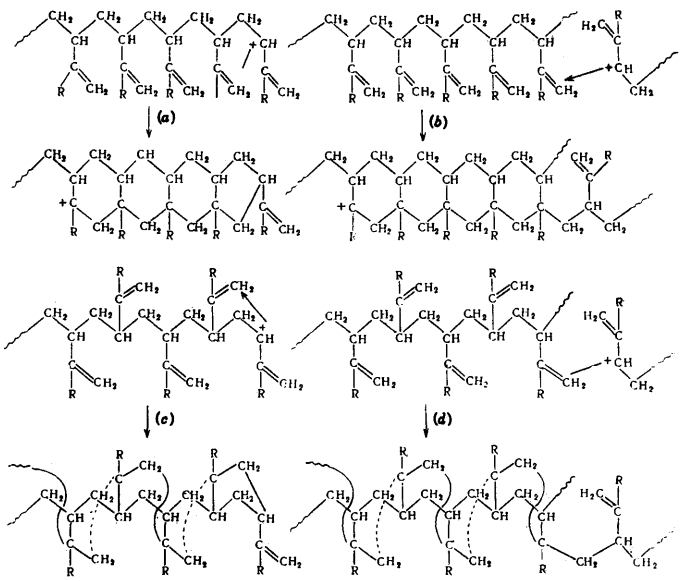
In an investigation of the isomerisation of natural rubber, Dolgoplosk and his collaborators have shown[15,16,20–22] that diethylaluminium chloride, triethylaluminium, ethylbis-2-phenylbutylaluminium, tri-isobutylaluminium, ethylaluminium dichloride, and also titanium tetrachloride and hydrogen chloride cause chemical changes in the polymers accompanied by a diminution in the unsaturation as a result of intramolecular cyclisation. A similar phenomenon is observed in the action of alkylmagnesium halides on a solution of 1,4-polybutadiene[21].

Cyclic polymers of butadiene and isoprene, obtained by direct polymerisation of the monomers in the presence of an alkylaluminium dichloride or titanium tetrachloride[21], have softening points of 420° and 370°C respectively. The cyclopolymerisation of isoprene in the presence of ethylaluminium dichloride has been subjected to a detailed investigation by Kössler et al.[23]

Gaylord and a number of Czechoslovak investigators have published interesting work on the polycyclisation of diene monomers with conjugated double bonds, and also on the cyclisation of stereoregular polymers of dienes[24–27]. Thus by the polymerisation of butadienes, isoprene, and chloroprene with the aid of a Grignard reagent and titanium tetrachloride at molar ratios of Mg/Ti < 2 (especially with Mg/Ti = 0.5–1), and also by the polymerisation of butadiene and chloroprene with triethylaluminium and titanium tetrachloride at molar ratios of Al/Ti ≤ 0.5, Gaylord, Kössler, et al.[24,25] obtained insoluble polymeric powders, whose spectra resembled the infrared spectra of cyclised *trans*-1,4-, *cis*-1,4-, and 3,4-polyisoprenes. These investigators suppose that cyclic structures are formed in the course of polymerisation from 1,2-polymers, not as a result of action by the catalyst on initially formed linear chains. The products obtained, still containing a definite proportion of linear structures, were completely cyclised by the action of sulphuric acid on a suspension of the polymers in toluene.

The following mechanism has been suggested for the cyclopolymerisation of conjugated dienes. Since the metal halide is present in considerable quantity, the polymerisation can be regarded as cationic. The first stage involves 1,2-isotactic or 1,2-syndiotactic polymerisation (3,4-isotactic or 3,4-syndiotactic in the case of isoprene or chloroprene). Initiation of polycyclisation can take place in two ways: (1) the end of a growing chain may interact with a double bond in the penultimate monomeric

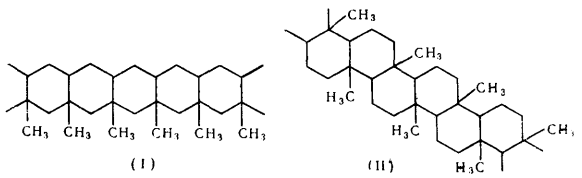
unit (*a*, *c*); or (2) the growing chain may interact with a double bond in another chain (*b*, *d*):



Thus an isotactic polymer yields a planar ladder structure, whereas a syndiotactic polymer gives a spiral structure, one chain being curled around another and joined to the latter at every third carbon atom.

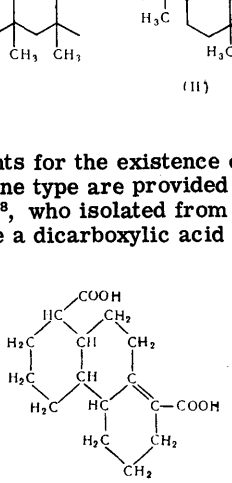
A characteristic feature of cyclopolymers is their high thermal stability. The decomposition temperatures of cyclopolyisoprene, cyclopolybutadiene, and cyclopolychloroprene are respectively[24,25] 370°, 405°, and 422°C.

Kössler et al. concluded[27] from their investigations, which involved mainly a study of the infrared spectra of cyclopolymers of isoprene and cyclised steroregular polymers of isoprene, that polycyclic ladder systems may be of two types—perhydroanthracene (I) and perhydrophenanthrene (II).

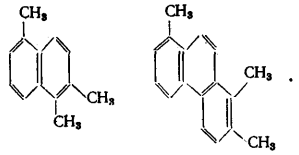


(I) (II)

Definite arguments for the existence of polymers of perhydrophenanthrene type are provided by results obtained by Shelton and Lee[28], who isolated from the oxidation of cyclic polybutadiene a dicarboxylic acid having the structure



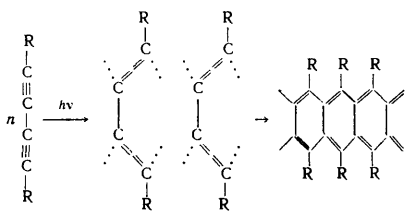
and also by Wallenberger[29], who by the aromatisation of the polymer of isoprene obtained 1,2,5-trimethylnaphthalene and probably 1,2,8-trimethylphenanthrene.



The technical application of cyclised rubber is extremely promising. It can be successfully used as a filler for natural and synthetic rubbers[6,30-32], the properties of the resulting products being improved and the processing technology facilitated. Cyclised rubber is employed for the production of paints[6,32], coatings for paper[6,32] and textiles[32], etc.

2. Aromatic Ladder Polymers

The aromatic ladder polymers obtained by Bohlmann[33,34] by the photopolymerisation of polyacetylenes are of great interest. Thus irradiation of deca-4,6-diyne-1,10-diol $HO[CH_2]_3[C{:}C]_2[CH_2]_3OH$ and also of its diurethane yields insoluble red polymers. If the diurethane is heated below the melting point, a red polymeric product is formed, but on rapid heating above the melting point the compound melts without change in colour and does not polymerise at 250°C. In Bohlmann's opinion this indicates that, for polymerisation to occur, the molecular chains of the polyyne should be arranged in parallel. The polymerisation of a conjugated diyne can then be represented by the scheme



Under the influence of light energy the π-electron pairs of the triple bonds break down, and polymerisation takes place by a Diels–Alder type of synthesis. Reaction takes place only in the crystalline monomer, but not in solution or in the melt.

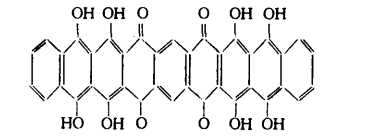
The infrared spectrum of the polymers shows broad peaks in the region of absorption by aromatic hydrocarbons, but neither triple nor isolated double bonds have been detected in the spectrum. X-Ray examination of the polymers indicates that they are amorphous substances[33].

In an attempt to prepare 1,6-dicyanohexa-2,4-diyne, Lee[35] obtained chemically inert polymeric products of high melting point (above 600°C), resembling "brick dust". His starting materials were a dihalogeno-, ditoluene-*p*-sulphonyl-, or dihydroxy-hexadiyne and sodium or copper(I) cyanide. Polymerisation proceeds as follows

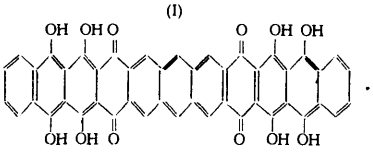
$$X{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}X \xrightarrow[\text{salt}]{\text{cyanide}} [X{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}CN]^{\cdot} \rightarrow \text{polymer.}$$

Although Lee does not attribute a definite structure to this polymer, nevertheless in his view it may contain fused aromatic rings, recalling in this respect the structures of heat-treated polyacrylonitrile or of graphite.

By the interaction of the dianhydrides of aromatic tetracarboxylic acids (pyromellitic and anthracenetetracarboxylic acids) with 1,4-dihydroxyanthraquinol in the presence of aluminium chloride, Marschalk obtained[36] fused polycyclic aromatic systems, to which he ascribed the structures



(I)

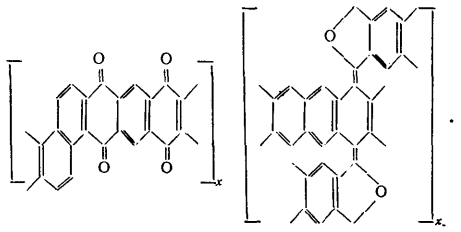


(II)

These compounds were synthesised by heating 1 mole of the dianhydride with 2 moles of the anthraquinol in the presence of a Friedel–Crafts catalyst to 310–320°C. The product (I) is a brown-violet substance, insoluble in alkalis and organic solvents, which can be crystallised from slightly fuming sulphuric acid on gradual dilution. The product (II) likewise does not dissolve in alkalis or organic solvents, and is crystallised in a similar manner to (I).

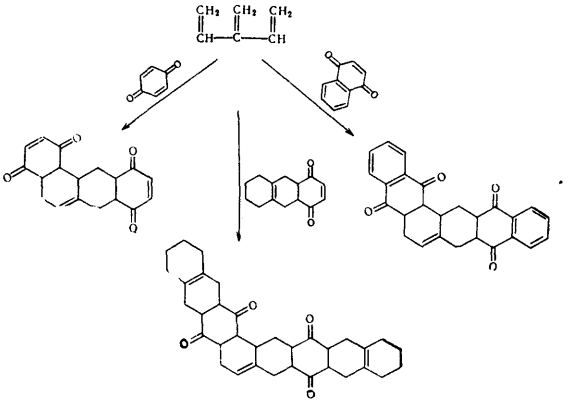
In order to study the mechanism of conduction in semiconductor materials, Pohl and Engelhardt[37] synthesised polymers from various acenes (naphthalene, anthracene, phenanthrene, pyrene, chrysene, perylene, dibenzopyrene, and picene) and aromatic acid anhydrides (phthalic and pyromellitic) in the presence of zinc chloride or aluminium chloride. (Polyacenes were also prepared by the Wurtz–Fittig method from 1,2,4,5-tetrabromobenzene by its interaction with a sodium–potassium alloy.) Pyromellitic dianhydride or phthalic anhydride was carefully mixed with zinc chloride and the various acenes, and heated at 256° or 306°C for 24 h. The resulting polymers were insoluble, infusible black products. Yields were 5–50% based on the mixture of dianhydride and acene. Elementary analysis indicated that the polymers contained approximately 2 molecules of acene for each molecule of pyromellitic dianhydride after allowing for a loss of 2 molecules of water. Polymers containing up to 14 aromatic nuclei could be prepared. It was found that the resistance diminished with increase in the proportion of the initial acene.

In the opinion of Pohl and Engelhardt[37], two reaction mechanisms are possible, one resulting in the formation of keto-groups or quinone groups, whereas the second yields lactone structures—

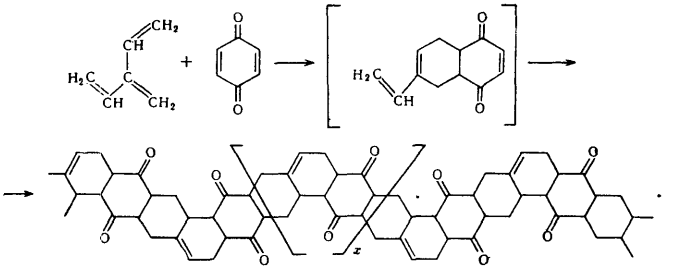


By analogy with the work of many other investigators, however, they consider that the former types of structures are mainly produced, rather than lactone structures, although secondary reactions of the quinone groups are not excluded.

An extremely interesting method for obtaining quinones of hydrogenated acenes has been worked out by Bailey and Economy[38], using 3-methylenepenta-1,4-diene and mono-, di-, and tri-cyclic quinones. Toluene solutions of the hydrocarbon and the quinone are mixed, left at room temperature for 24 h, and then boiled for 24 or 48 h. On cooling, crystalline products separate. The reactions underlying the synthesis of these compounds are



This original variety of diene synthesis has been used somewhat later for the preparation of ladder polymers[39] from 3-methylenepenta-1,4-diene and benzoquinone in equimolecular proportions: a chloroform solution of the mixture was kept at room temperature for 4 days, and then boiled for 24 h, after which most of the solvent was distilled off and boiling continued in the presence of tetrachloroethane for 48 h, until a brown deposit was formed. Two products—a polymer softening at 340–400°C, practically insoluble in all solvents in the cold, but soluble in hot solvents, and probably having a molecular weight of ~ 2000; and a soluble polymer, softening at 170–200°C, and of molecular weight 440—were obtained, the first of these polymers being assigned the following ladder structure[39]



B. HETEROCYCLIC LADDER POLYMERS

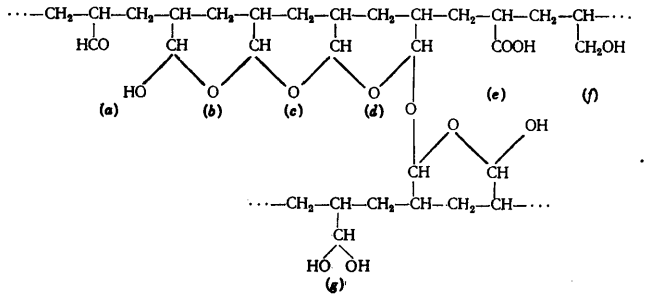
Heterocyclic ladder polymers constitute a group of numerous compounds of high molecular weight. Their macromolecules contain heterocycles comprising carbon atoms together with one, two, or more atoms of other elements, e.g. oxygen and nitrogen. Many organoelementary and inorganic polymers, either containing no carbon at all or containing it only in side-chains, are of the same type.

1. Ladder Polymers Consisting of Oxygen Heterocycles

Polyacrylaldehyde, obtained by the spontaneous polymerisation of acrylaldehyde, was first described by

Redtenbacher[40] in 1843. The polymer was termed "disacryl". The "disacryls" are colourless substances, either flocculent or powdery, having no definite melting point and decomposing at temperatures above 220°C.[42]

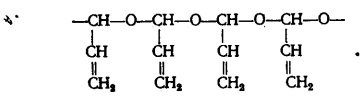
A systematic investigation of the polymers formed by acrylaldehyde was made by Schulz[41]. The polyacrylaldehydes which he obtained by a radical mechanism, as well as those formed by spontaneous polymerisation (also proceeding by a radical mechanism), were polymers of vinyl type, with a "head-to-tail" structure. However, the formyl groups in the polymers can interact to form rings. From the chemical properties and the infrared spectra Schulz attributes to such polymers the structure[41]



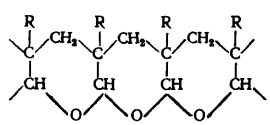
The formyl groups may be present either in the free state (*a*), hydrated (*g*), in ethereal form (*c*), or in an intermediate form (*b*). The hydroxyls of the hydrated formyl groups are able to form cross-links (*d*). Under certain conditions they break down, the polymers acquiring solubility and reacting as polyals.

In the presence of metallic sodium, the polymerisation of acrylaldehyde in boiling benzene takes place in the 1,4-positions, as Andreeva and Koton[43] have shown.

According to Schulz[44] the polymerisation of acrylaldehyde in the presence of various anionic catalysts and the boron trifluoride–ether complex results in a polymer having the structure

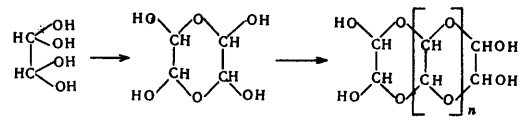


Andreeva et al.[45] polymerised acrylaldehyde and methacrylaldehyde in the presence of respectively ~ 1.5 and 2.5–3 mole % of boron trifluoride at temperatures from −20° to −40°C. The vitreous polyacrylaldehyde obtained under these conditions contained no detectable free formyl groups. It was insoluble in organic solvents, it dissolved in sulphurous acid, and it decomposed at about 270°C. The polymethacrylaldehyde had rather greater thermal stability than the acrylaldehyde polymer, and differed from the latter in being insoluble in most organic solvents and only swelling in sulphurous acid. In view of their properties, these polymers were assigned[45] the polycyclic structure



where R = H or CH_3.

The polymerisation of glyoxal yields a white solid, aqueous solutions of which comprise a mixture of hydrated forms capable of changing from one into another[46,47]:



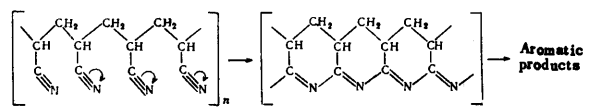
where n = 3 or 4. Okamura et al.[48] investigated the polymerisation of glyoxal under the influence of γ-rays at −196°, −78°, and 0°C, obtaining degrees of conversion of 23.9%, 42.2%, and 60.6% respectively after irradiation for 65 h. The infrared spectra of the polymer showed absorption corresponding to C–O–C and C–H bonds, but no absorption due to the carbonyl group. The polymers were distinguished by infusibility and insolubility. At 222°C some 45% of the polymer had decomposed after 10 min.

2. Ladder Polymers Consisting of Nitrogen Heterocycles

Most investigators consider that a ladder type of polymer is formed by the heat-treatment of polyacrylonitrile. A fair number of papers have been published on the thermal transformation of polyacrylonitrile and the properties of the products, and only a proportion of these will be briefly discussed in the present review.

Houtz[49] heat-treated polyacrylonitrile fibre, and obtained a thermostable material which withstood brief heating in the burner flame. He was the first to ascribe a polycyclic structure to it.

Burlant and Parsons[50] heated samples of polyacrylonitrile in an atmosphere of nitrogen over a range of temperatures from 200° to 320°C, and investigated their infrared spectra. The process of polycyclisation was represented as follows:

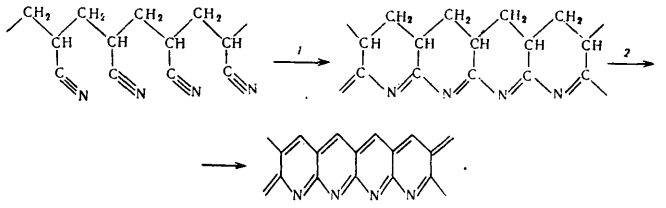


This scheme explains the high nitrogen content of the heated polymer and the gradual, almost complete disappearance of nitrile groups, with the simultaneous appearance of conjugated C=N bonds. Aromatisation occurs slowly below 300°C, whereas at higher temperatures aromatic products are readily formed.

Topchiev et al.[51] showed that heat-treatment of polyacrylonitrile fibre or powder may yield materials possessing semiconductor properties and electronic conduction. The number of electrons having unpaired spins in the substance is 10^{18}–10^{19} g^{-1}. After heat-treatment the semiconductor material can be used at far higher temperatures than, for example, germanium, since the polymer does not decompose even at 300°C. Preliminary exposure of polyacrylonitrile to γ-rays followed by heat-treatment leads to a sharp increase in the concentration of electrons with unpaired spins in comparison with the unirradiated polymer.

From a study of the infrared absorption spectra Topchiev and his collaborators[52] consider that the thermal

transformation of polyacrylonitrile takes place in two stages:



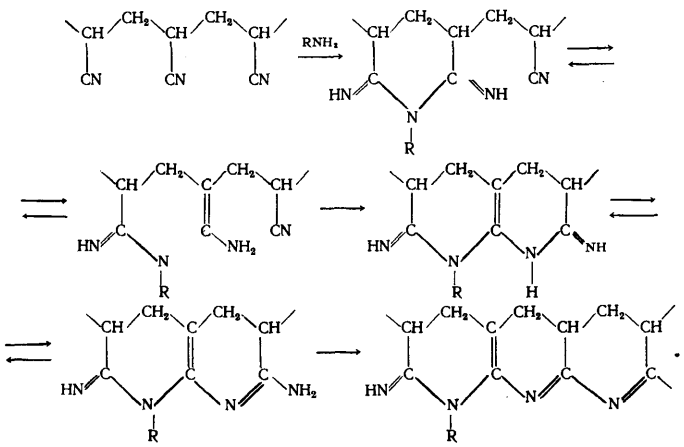
Intramolecular cyclisation, resulting from conversion of a C≡N into a C=N bond, is mainly completed by 270°C. At higher temperatures dehydrogenation takes place, with the formation of C=C bonds. The conditions of heat-treatment have a great effect on the electrical properties of the semiconductors. Thus heat-treatment of polyacrylonitrile in ammonia under pressure increases its conductance by factors of the order of 10^2 in comparison with specimens which have been subject to the same heat-treatment but in an atmosphere of an inert gas.

Vosburgh[58] made a detailed study of the conditions required for the production of non-flammable cyclised polyacrylonitrile fibres and fabrics. He heated the polymer in air above 160°C, and established that the logarithm of the reaction time is inversely proportional to the temperature. The most important parameters in this process are the duration of heating, the temperature, the fabric construction, and the atmosphere in which reaction occurs. The optimum concentration of oxygen is 15–20%. The cloth obtained in this way considerably surpasses all others in thermal stability. At 900°C the material is completely destroyed in 3 h.

Drabkin et al.[54] investigated the processes occurring in polyacrylonitrile on heating. They studied the absorption spectra after heating in a vacuum of 10^{-5}–10^{-6} mmHg.

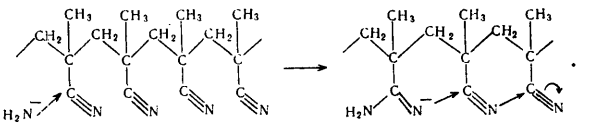
Airapetyants et al.[55] investigated the temperature dependence of the electrical properties of polyacrylonitrile (in a vacuum of 5×10^{-6} mmHg) for specimens of the polymer which had been heat-treated from 520° to 730°C.

Many authors[56-61] consider that the coloration of polyacrylonitrile and polymethacrylonitrile is caused by the formation of fused polycyclic systems. This process is accelerated by the presence of bases or organic acids. Thus La Combe[56] found that heating polyacrylonitrile in the presence of a small quantity of a base at 100°C for 1 h results in the appearance of a yellow colour in the polymer. He explains this phenomenon by means of the suggested scheme



Dilute mineral acids hydrolyse the fused rings, with almost complete disappearance of the colour[56].

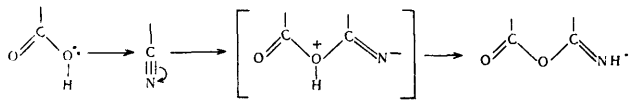
Overberger et al.[57] investigated the polymerisation of methacrylonitrile in the presence of lithium and ammonia at −75°C. The appearance of a colour in the polymer was, in their view, due to the reactions



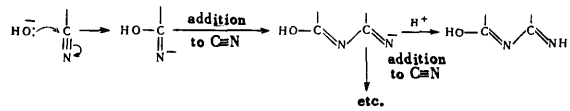
Chain growth occurs by interaction of an imino-anion with a nitrile group.

Lipatnikov[58] also explains the coloration of polymethacrylonitrile, when the monomer is polymerised in the presence of benzoyl peroxide under pressure (6000 kgf cm^{-2}) at or above 100°C, by the formation of fused pyridine rings.

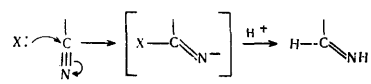
From an investigation of the appearance of a colour in polymethacrylonitrile[59-62] and polyacrylonitrile[62], Grassie concluded that this process is in considerable measure bound up with the presence of carboxy-groups, which initiate polymerisation:



Carboxyls are usually present in the polymer, since the monomer contains methacrylic acid as impurity. However, other compounds, not necessarily located in the polymer chain, can also initiate cyclisation[60]. The efficiency of initiation by acids of the type RCOOH is then strongly dependent on the nature of R: the more strongly developed the electron-acceptor properties of R, the more difficult is initiation[61]. An analogous relationship is observed with phenols. Initiation by alkalis occurs as follows:



In summarising the results of observations on the change in colour in polymethacrylonitrile and polyacrylonitrile, Grassie[61] gives the general mechanism



for the initiation of polycyclisation. Thus the start of the reaction is reduced to attack on a nitrile group by a nucleophilic reagent. Here OH, NH_2, etc. are stronger nucleophilic reagents, and carboxylic acids and phenols less strong. All these compounds are in essence Lewis bases.

While noting much in common in the behaviour of polyacrylonitrile and polymethacrylonitrile on heat-treatment, Grassie[62] nevertheless points out two fundamental differences. Firstly, in the absence of nucleophilic reagents polymethacrylonitrile does not change colour below 200°C,

whereas pure polyacrylonitrile becomes coloured at a definite rate, which does not decrease after careful purification of the monomer. This fact is explained by the presence in the polyacrylonitrile molecules of hydrogen atoms attached to tertiary carbon atoms, which are capable of initiating polycyclisation. Polymethacrylonitrile molecules, however, do not contain the $\geq$C–H group. Secondly, even intensely coloured polymethacrylonitrile does not lose its solubility, whereas polyacrylonitrile rapidly becomes insoluble. The explanation given for this is that in the latter polymer the process of chain growth takes place by the cross-linking of the latter (propagation cross-linking) owing to the denser packing of the macromolecules [62].

Kennedy [63] considers that, besides the ionic reactions which accompany the heat-treatment of polyacrylonitrile, radical processes must also be considered.

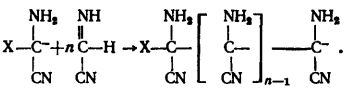
Nizova et al. [64] have synthesised a polyacetylenenitrile whose structure does not essentially differ from that attributed to heat-treated polyacrylonitrile. The polymer obtained is a dark coloured powder, insoluble in the usual organic solvents and readily soluble in concentrated acids. It neither melts nor decomposes up to 450°C, and is distinguished by a narrow electron spin resonance (e.s.r.) signal, which is characteristic of polyconjugated systems. The number of unpaired electrons is 10^{18}–10^{19} g^{-1}. The infrared spectra support the structure proposed for the polymer, and contain an absorption band characteristic of polyconjugated C=N bonds. They indicate that prolonged heating in a vacuum up to 300°C has practically no effect on the chemical structure of the polymer.

The literature on the polymer of hydrocyanic acid was reviewed by Völker [65], who synthesised this polymer by anionic polymerisation in aqueous solution. Polymeric hydrocyanic acid consists of dark brown amorphous flakes, which do not dissolve in any solvent without chemical change. Ammonia is eliminated by the action of aqueous alkali, and gaseous compounds of nitrogen are formed by concentrated nitric acid. The polymer possesses limited solubility in other dilute mineral acids. It is thermally stable up to 200°C, but at higher temperatures hydrogen cyanide, ammonia, carbon dioxide, and an amine are split off.

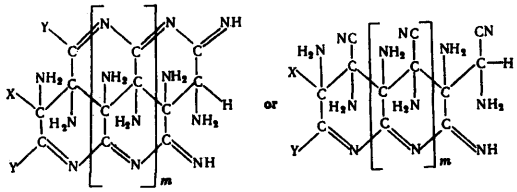
Polymerisation is initiated by interaction of an anion with the dimer of hydrocyanic acid:

$$X^- + HN{=}CH{-}CN \rightarrow H_2N{-}\overline{C}(X){-}CN.$$

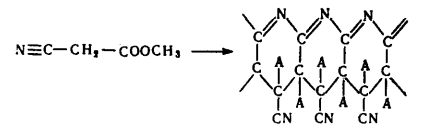
Chain growth proceeds by interaction of the dimeric acid with the resulting anion:



Chain termination results from addition of a cation (usually a proton) to the polymeric molecule. Völker [65] considers that, owing to steric hindrance, the nitrile groups occupy *trans*-positions in the course of polymerisation, which leads to formation of the polycyclic structures

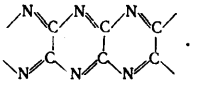


Korshak and Sosin [66] prepared a polymer from methyl cyanoacetate by polyrecombination:



where A = $COOCH_3$. Polyrecombination is accompanied by polymerisation of the nitrile groups with formation of a system of conjugated C=N bonds in fused six-membered rings. The infrared spectra of the polymer exhibit absorption characteristic of C=N bonds, and also of nitrile and ester groups. The molecular weight of the polymer is 7200, and its softening point 500°C. The product possesses semiconductor properties. A signal is observed in the e.s.r. spectra (7 oersteds), and the number of electrons having unpaired spins is 10^{18} g^{-1}. An analogous structure (with fused nitrogen heterocycles) is possessed also by polymers based on malononitrile [67], adiponitrile [67,68], and benzyl cyanide [67], as well as copolymers of methyl cyanoacetate and benzyl cyanide [69].

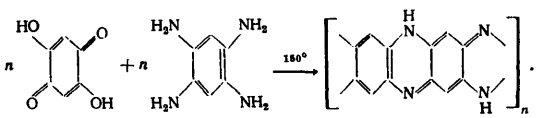
Bircumshaw [70] published a survey of work on polymers of cyanogen $(CN)_2$ obtained in various ways, and reported the synthesis and a study of the properties of a polymer, paracyanogen, formed by the polycondensation of oxamide in the solid phase under pressure at 250–300°C. Paracyanogen contains conjugated double bonds and no free nitrile groups. The polymer molecules consist of fused pyrazine rings



Paracyanogen is insoluble in water and most organic solvents, but soluble in inorganic acids. The polymer withstands being heated in a vacuum at 450°C. Strong heating in air leads to decomposition with the formation of carbon dioxide. Davydov et al. [71] investigated the temperature dependence of the semiconductor properties of paracyanogen.

Several polymers containing a conjugated system of C=N groups have been obtained by Paushkin et al. [72] from amides and ammonium salts of mono- and di-carboxylic acids heated in the presence of zinc chloride in an autoclave (at 400°C). The polymers were insoluble, infusible powders, from dark brown to black in colour. They possessed very high thermal stability: the losses in weight on heating to 800°C were only 7–12%. The infrared spectra of these products are identical with those of polymers obtained by polymerisation of the corresponding nitriles. The electrical properties of the polymers were examined over the range 20–300°C.

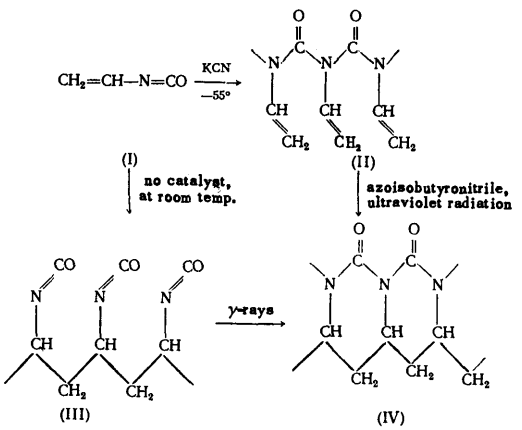
By heating equivalent amounts of 2,5-dihydroxy-*p*-benzoquinone and benzene-1,2,4,5-tetra-amine in dimethylacetamide, hexamethylphosphoramide, or polyphosphoric acid at 150°C, Stille and Mainen [73] have quite recently obtained ladderlike polyquinoxalines:



With dimethylacetamide the polymers form extremely stable compounds, which decompose only on prolonged

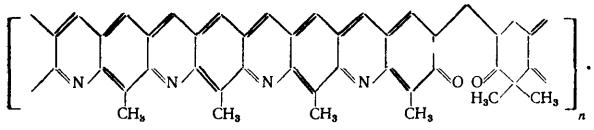
heating in a vacuum. Removal of solvent from the association complex results in an insoluble polymer. Thermogravimetric tests showed that the structure of the polymer is evidently not completely ladderlike.

Overberger et al.[74] obtained a ladder polymer of vinyl isocyanate by the series of reactions

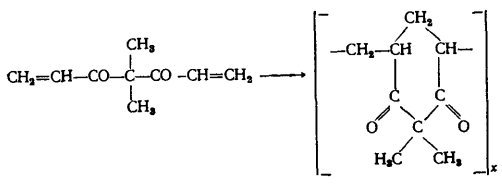


The polymer (IV) is soluble in solvents of high dielectric constant. The intrinsic viscosity of its solution in pyridine is 0.45. The polymer decomposes at 385–390°C. The structures of the intermediate products (II) and (III) and of the polymer (IV) have been demonstrated by means of the infrared spectra.

De Winter and Marvel[75] synthesised a ladder polymer whose molecules were made up of fused alternating aromatic pyridine and toluene rings:

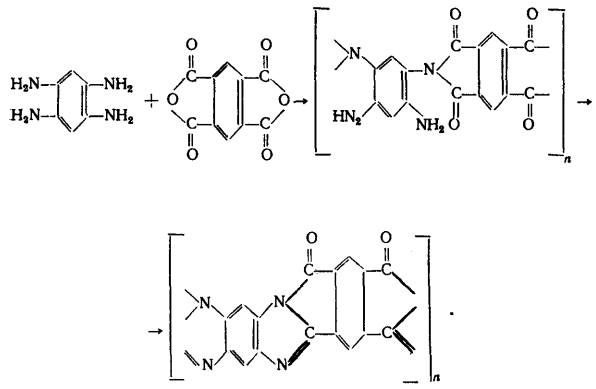


Polymerisation in a solution of 4,4-dimethylhepta-1,6-diene-3,5-dione in the presence of azoisobutyronitrile at 65°C first yielded a polymer containing six-membered rings in the chain:

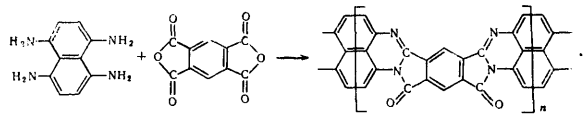


Then hydroxyimino-groups (approximately one group for each ring) were introduced into it in strongly alkaline medium. Careful dehydration of the polyoxime yielded a ladder polymer (whose structure has been given above), soluble in hot quinoline, dimethyl sulphoxide, and dimethylacetamide. Thermogravimetric tests showed that the loss in weight of the polymer on being heated from 300° to 500°C was ~ 20%, after which only a slight change in weight was observed right up to 900°C.

Novel thermostable ladder polymers have recently been obtained based on aromatic tetra-amines and aromatic tetracarboxylic acids or their dianhydrides[76–80]. Dawans and Marvel[76] have synthesised such polymers from benzene-1,2,4,5-tetra-amine and pyromellitic dianhydride:



They also replaced the benzenetetra-amine by naphthalene-1,4,5,8-tetra-amine for the polycondensation:



These workers observed with model compounds that the nature of the intermediate products depends on the conditions of the condensation, and concluded that, in order to obtain the above ladder structures, the process must be carried out with a slow rise in temperature (2 deg min^{-1}). The polycondensation was conducted in a melt or a solution in a stream of nitrogen[76]. Reactions begins in the melt at 105–110°C, but intramolecular cyclisation takes place only at 140–150°C. Polymers of maximum molecular weight are obtained with the starting materials in equimolecular proportions: when the molar ratio of anhydride to amine exceeded unity, the yield of the polymer was higher, but its molecular weight lower.

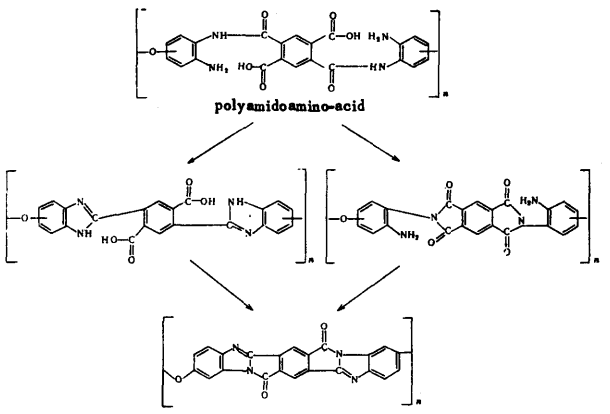
The polymer based on benzene-1,2,4,5-tetra-amine was prepared by gradually heating a mixture of the amine with the dianhydride to 220°C, and then heating in a vacuum at 300°C for 3 h. The yield was 86%. The reduced viscosity of a 0.25% solution in concentrated sulphuric acid was 0.3. Use of polyphosphoric acid as solvent for the synthesis of this polymer[76] makes it possible to employ the stable tetra-amine tetrahydrochloride instead of the readily oxidisable amine, and also gives the same yield (86%) of polymers of high molecular weight. The intrinsic viscosity of the polymer based on benzene-1,2,4,5-tetra-amine, measured in concentrated sulphuric acid, was 1.10.

The polymer based on naphthalene-1,4,5,8-tetra-amine was obtained in 60% yield in 2,5,8-trioxanonane solution. The reduced viscosity of a 0.25% solution in concentrated sulphuric acid was 0.41.

It was established that in a solvent the reaction between tetra-amine and dianhydride occurs essentially at room

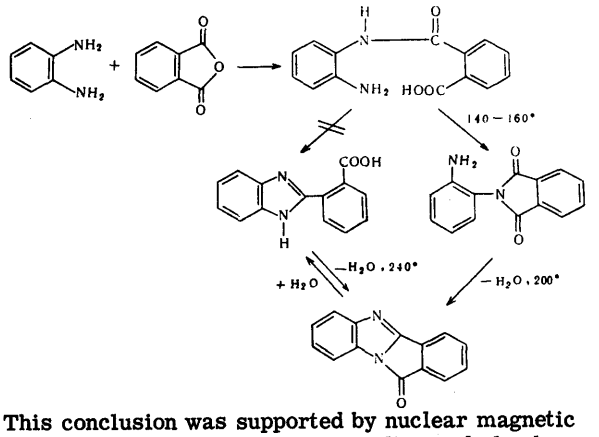
temperature and is weakly exothermic. A polyamido-amino-acid is formed as intermediate product [77,78].

Scheme 1



On the basis of infrared spectroscopic data Bell [78] suggests Scheme 1 for ring formation in the interaction of pyromellitic dianhydride with bis-3,4-diaminophenyl ether. According to this both imide and benzimidazole rings are formed in the cyclisation of the polymeric amido-amino-acid. In a study of the condensation of *o*-phenylenediamine with phthalic anhydride when they were heated at 160°C for 30 min, Colson et al.[79] found that only a phthalimide ring is formed, and no benzimidazole ring formation is observed (see Scheme 2).

Scheme 2

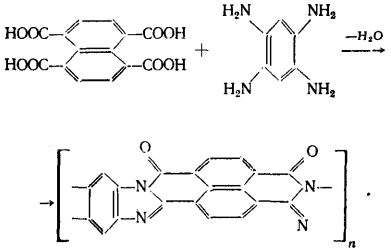


This conclusion was supported by nuclear magnetic resonance and infrared spectral results, and also by a comparison of the melting point of *N*-*o*-aminophenylphthalimide with published values. The imide obtained is converted, when heated to 200–210°C, into benzoylbenzimidazole (see Scheme 2). This last product cannot be formed from *o*-benzimidazol-2-ylbenzoic acid below 240–250°C, which provides additional evidence for the scheme of cyclisation given by Colson et al.[79]

Ladder polymers of this type, termed "pyrrones" [77], are coloured substances, which do not melt below 400°C. They are not soluble in the usual organic solvents, but dissolve in concentrated sulphuric acid [76]. Thermogravimetric tests have shown that in an inert atmosphere (nitrogen) pyrrones are thermostable up to 450–500°C. In air they oxidise fairly rapidly at 350–400°C, [76] but they are non-flammable. Pyrrones are extremely resistant to the action of radiation [78].

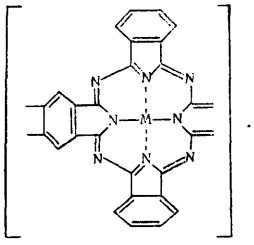
The possibility of obtaining soluble intermediate products in the synthesis of pyrrones facilitates the technical production of thermostable films, coatings, adhesives, filaments, and plastics based on them [77,78].

By the polycondensation of naphthalene-1,4,5,8-tetracarboxylic acid with benzene-1,2,4,5-tetra-amine in polyphosphoric acid, the system being heated in an atmosphere of nitrogen at 220°C, van Deusen [80] obtained novel thermostable polymers, closely resembling pyrrones in structure:



In contrast to pyrrones, however, the imide ring of these polymers is six-membered. They are dark coloured products, partly soluble in sulphuric, polyphosphoric, and sulphonic acids, and also in aqueous alkalis. The polymer obtained at ~ 100°C has a reduced viscosity of 0.3. Polymers obtained at higher temperatures are very sparingly soluble, but have analogous infrared spectra. These products are distinguished by very great thermal stability: on heating in air, loss in weight does not begin below 400°C, and in nitrogen at about 600°C.

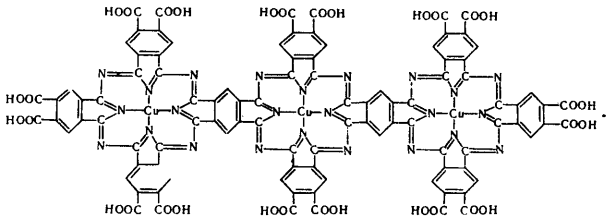
Phthalocyanine polymers have now been synthesised which are characterised by the presence of complicated polycyclic structures containing nitrogen. Individual members of this group are able to form ladder systems. Thus Marvel [81] heated pyromellitic acid, phthalic anhydride, urea, and copper(II) chloride to 200°C, and obtained polymers which may have the structure



The polymers vary in colour from bluish green to greenish black. They are soluble in dimethylformamide, they are stable when heated in air to 350°C, and they burn with great difficulty.

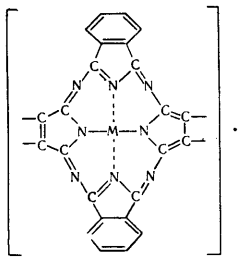
Soluble phthalocyanine polymers were prepared by Felmayer and Wolf [82] and also by Berlin et al.[83] by the polycondensation of pyromellitic acid with urea and copper(I) chloride. Felmayer investigated the electrical properties of these black products, and found that the activation energy for conduction diminished with increase in the number of fused rings in the polymers. Berlin's polymers were blue-green powders, with molecular weights of 3000–4000, and were insoluble in dimethylformamide but soluble in concentrated sulphuric acid. The magnetic and electrical properties of these polymers were examined, as well as their thermal stability. The number of paramagnetic particles was 5×10^{21} g^{-1}. The polymers were stable in air up to 350°C.

Drinkard and Baylar[84] prepared phthalocyanine polymers from pyromellitic dianhydride, urea, copper(II) chloride, and a catalyst (ammonium molybdate or $ZrOCl_2 \cdot 8H_2O$) at 180°C, and attributed to them the structure



The maximum molecular weight of the polymers obtained was 4000, corresponding to six phthalocyanine units.

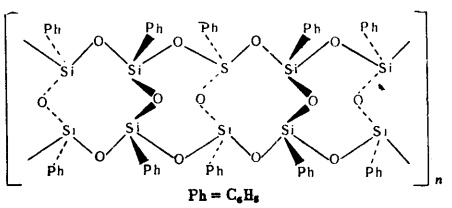
Berlin et al.[85] showed that the interaction of an equimolecular mixture of copper acetylacetonate, tetracyano ethylene, and phthalonitrile yields a chelate copolymer, which probably has the structure



3. Organoelementary Ladder Polymers

In 1939 Koton[86] reported the preparation of organosilicon polymers by the polycondensation of phenyl-, benzyl-, and also 1-naphthyl-silanetriol. These polymers were recommended for use as heat-resistant materials for electrical insulation.

By the equilibrium alkaline polycondensation of phenylsilanetriol, in toluene, xylene, or 2,5,8-trioxanonane, Brown et al.[87] have fairly recently obtained ladder polymers, to which they assign the structure



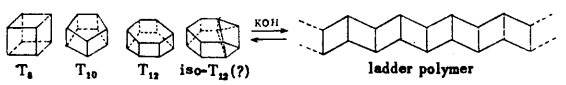
Ph = C_6H_5

The polymer obtained by the hydrolysis of phenyltrichlorosilane followed by polycondensation in toluene had $\overline{M}_n = 14\,000$ and $\overline{M}_w = 26\,000$, with a "most probable" molecular-weight distribution. A steep linear relationship ($a = 0.92$) exists between values of $\lg[\eta]$ and $\lg\overline{M}_w$ for fractions of this polymer, this being characteristic of a rigid elongated polymer. By using small amounts (e.g. 5–30%) of solvent, a polymer can be obtained having a molecular weight of the order of several millions. With $\overline{M}_w > 2 \times 10^5$, however, chain branching is observed[87]. Analogous products were synthesised by Sprung and Guenther[88] by the hydrolysis of phenyltriethoxysilane. These products had a somewhat higher molecular weight and a narrower molecular-weight distribution than the polymer synthesised by Brown.

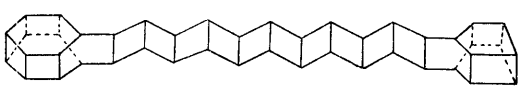
Brown considers[89] that the trifunctional product forms initially a syndiotactic Si–O–Si chain having phenyl side-groups attached to each silicon atom. This chain then reacts with another chain, to form the "unidimensional" ladder structure shown above.

From a detailed study of the influence exerted by the equilibrium conditions on the nature of the products, Brown[90] showed for the polycondensation of phenylsilanetriol that in dilute (5%) solutions oligomers of cagelike structure are formed, in 5–70% solutions a linear ladder polymer of low molecular weight, at 85–95% a ladder polymer of high molecular weight, and at 100% a ladder gel. All these products are interconvertible by varying the concentration in the solution.

The equilibrium between the oligomers and the polymer can be represented in general as follows:



where $T = RSiO_{1.5}$. The phenyl derivatives T_8, T_{10}, and T_{12} have been isolated as pure crystals. Since the product of low molecular weight contains no unchanged silanolic groups, while the spectra confirm the presence of rings similar to T_{10} or T_{12} at the ends of the chains, the polymer was given the structure



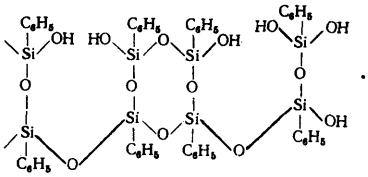
Raising the equilibrium temperature results in an increase in the proportion of cagelike compounds. At 250°C and a polymer concentration exceeding 80%, branchings appear in the macromolecules, accompanied by a decrease in the concentration of cagelike compounds.

From a study of the properties of the solutions, X-ray examination of oriented specimens, determination of the infrared and ultraviolet spectra, and calculations of bond angles, Brown[87,90] concluded that the product of the polycondensation of phenylsilanetriol is a ladder polymer having a *cis*-syndiotactic structure of the double bond.

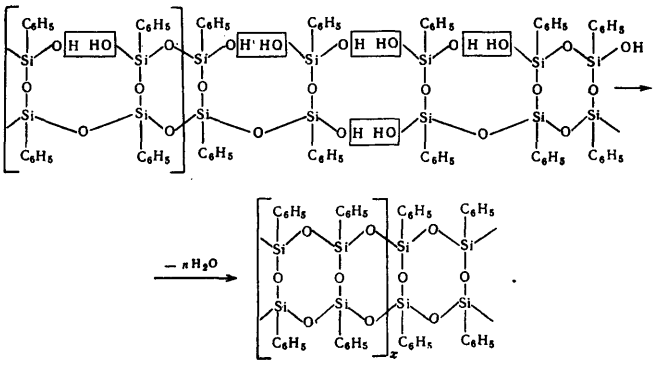
The above organosilicon ladder polymers have been investigated also by Pavlova et al.,[91,92] who used benzene, toluene, xylene, and succinonitrile as solvents for the synthesis. All the polymers obtained, having high glass points (~ 300°C), were divided into 6–10 fractions. The closely similar glass points for all four polyphenylsiloxanes indicate that the conditions of preparation have no fundamental effect on their structure. These conditions likewise have little influence on the degree of polydispersity of the polyphenylsiloxanes: thus in the series—benzene, toluene, xylene, and succinonitrile—the ratio M_w/M_n has the values 1.82, 2.15, 2.50, and 2.70 respectively.

The suggested mechanism[91] for the formation of ladder polyphenylsiloxanes involves the initial production, by the

hydrolysis of phenyltrichlorosilane, of polymers of low molecular weight, containing free hydroxyls:



followed by further intramolecular and intermolecular condensation:



Polyphenylsilsesquioxanes have been obtained also by Andrianov et al.[93] by polymerising the crystalline octamer $(C_6H_5SiO_{1.5})_8$ in a solvent (diphenyl oxide, nitrobenzene, etc.) in the presence of 0.05% of an alkali, and then removing the solvent and heating at 250–270°C. The polymers have glass points above 300°C.

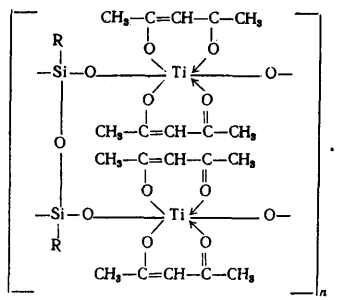
Study of the properties of dilute benzene solutions of polyphenylsilsesquioxanes has shown[92] that at molecular weights of 10 000–50 000 the polymers are present in the form of short rods, whereas over the range 50 000–2 700 000 they exist as tangles of thread. The relation between the intrinsic viscosity and the molecular weight of the polymers is given by

$$[\eta] = 1.305\times10^{-7}M^{1.29} \quad (M = 10\,000 - 50\,000);$$
$$[\eta] = 1.93\times10^{-4}M^{0.634} \quad (M = 50\,000 - 2\,700\,000).$$

The mean square distances between the ends of the macromolecular chains and the flexibility of the chains have also been calculated.

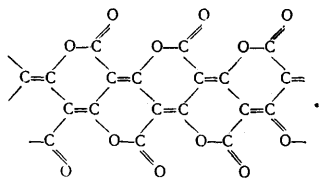
Ladder polyphenylsiloxanes are infusible products, which can dissolve, however, in benzene, tetrahydrofuran, chloroform, and dichloromethane[87,89]. Films can be obtained from the solutions, and these can be oriented in the swollen state. The polymers are more stable towards hydrolysis than are ordinary silicones, and they have a higher tensile strength than have silicones of iregular structure (281–422 kgf cm^{-2}). They possess very good dielectric properties and high thermal stability. Losses in weight are observed at temperatures above 525°C. The polymer withstands brief (1–2 min) heating at 650°C, and several months at 300°C.[90]

Hydrolysis of compounds of type $RSiCl_3$ together with bisacetylacetonatotitanium dichloride yields[94] ladder polymers containing cyclic titanium atoms.

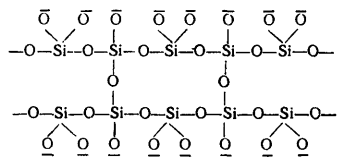


4. Inorganic Ladder Polymers

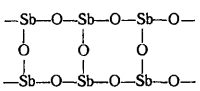
Smith et al.[95] obtained variously coloured—from yellow to violet—polymers of carbon suboxide C_3O_2. The polymers of low molecular weight dissolved in water and aqueous alkali to give red solutions; those of high molecular weight were insoluble. The polymers decomposed above 300°C, and at 500°C were converted into carbon. In Smith's opinion, these products have the structure



Inorganic polymers having molecules or ladderlike structure are quite often encountered in Nature. For example, the mineral tremolite, of which asbestos is a variety, contains amphibole chains[96]:



One form of antimony oxide, valentinite, also has a ladder structure[97]:

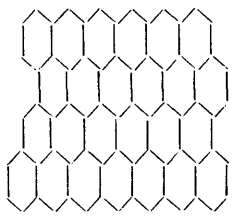


Arsenic sesquioxide[98] and bismuth sesquioxide[99] have similar structures.

II. PARQUET POLYMERS

A typical representative of polymers having a parquet type of structure is graphite. It consists of fused six-membered carbon rings, the distance between the carbon

atoms in them being 1.42 Å, close to the corresponding length in the benzene molecule[100,101]:



The planar networks of carbon atoms form parallel layers, 3.38 Å apart. Graphite is formed in Nature by reducing processes at high temperatures[102]. The graphite layers readily separate from one another, so that this polymer is used in the manufacture of pencils and antifriction materials. The refractoriness and ability to conduct an electric current make it possible to employ graphite for the manufacture of crucibles and electrodes and in foundry work[103].

Graphite can be prepared artificially. Thus flexible fibres and fabrics containing up to 99.9% of graphite have been obtained[104,105] by heating viscose rayon fibre in conformity with the following scheme:

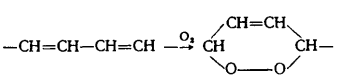
$$\underset{\text{viscose rayon fibre}}{(C_6H_{10}O_5)_x} \xrightarrow{800^\circ} \underset{\text{carbon fibre}}{(C_{36}H_5O)_x} \xrightarrow{3000^\circ} \underset{\text{graphite fibre}}{(C_{28}H)_x}$$

A carbonised fibre containing 90–91% of carbon is first formed, then on further heating a carbon fibre (91–98% of carbon), and at ~ 3000°C the graphite fibre (> 98% of carbon). Carbonisation and graphitisation are complicated processes, which occur when various carbonaceous materials are gradually heated without access of air (up to 3000°C). Practically any textile material can be converted into graphite.

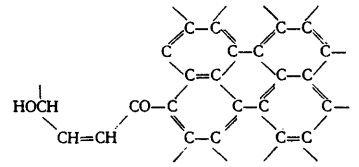
Graphitised fibres are used for reinforcing thermostable plastics, and for manufacturing corrosion-resistant equipment and thermal insulation. Phenolic plastics reinforced with graphite fabric and silicon dioxide fabric can be used for the manufacture of rocket nozzles[104,106].

Winslow et al.[107] investigated the pyrolysis of a 48% divinylbenzene–ethylvinylbenzene copolymer. On heating to 960°C the yield of carbon product was only 6% on the weight of the initial copolymer. Preliminary oxidation (to a content of 18% of oxygen in the polymer), however, leads to a sharp increase in the yield of carbonaceous product (47% calculated on the oxidised copolymer). The pyrolysis of the chlorinated polymer (45% of chlorine) up to 1000°C gives a 55% yield of carbonaceous residue. In Winslow's opinion graphitelike structures are ultimately formed as a result of the thermal changes undergone by the copolymer.

By oxidising conjugated polyenes Berlin and his collaborators[108,109] obtained polymeric peroxides:

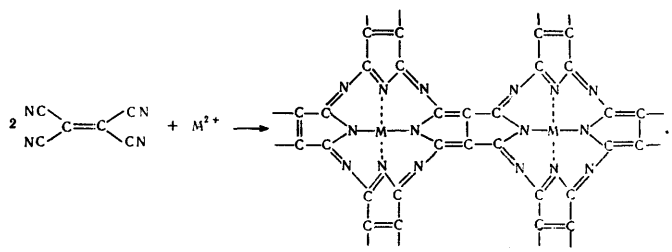


which on being heated over the range 200–300°C underwent complicated chemical reactions resulting in the elimination of water, carbon dioxide, alcohols, ketones, unsaturated hydrocarbons, and benzene with the formation of fused aromatic systems containing up to 15% of oxygen



This polymeric product possessed paramagnetic and semiconductor properties.

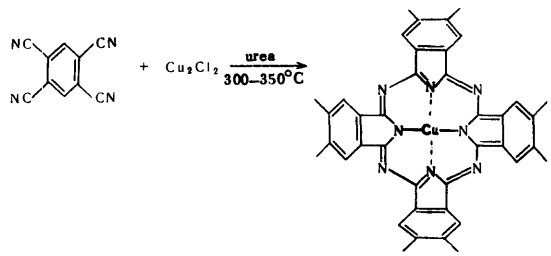
A parquet polymer was obtained by Berlin et al.[85] in the reaction of copper acetylacetonate with two molecules of tetracyanoethylene under vacuum at temperatures from 160° to 300°C:



The polymer was an infusible black product, insoluble in organic solvents, alkalis, and dilute acids. The polymeric chelate complexes of tetracyanoethylene are crystalline and chemically stable; they do not burn, and withstand prolonged heating at 500°C without degradation[110,111]. These products possess semiconductor properties. Analogous polymeric compounds have been obtained using iron and magnesium[112].

Berlin and Matveeva[113] synthesised polymers of tetracyanoethylene also in the absence of metals or their salts. These polymers were regarded as close to the polymeric metal complexes in structure (azaporphyrin rings). When heated in a vacuum (1–2 mm) at 200°C for 200 h, the polymer is probably stabilised, and losses in weight produced by raising the temperature to 350°C reach only 9.6%. Further rise in temperature causes appreciable degradation. The electrical properties of polytetracyanoethylenes and of polychelates of tetracyanoethylene are analogous.

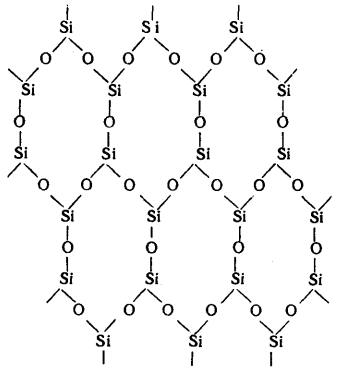
Epstein and Wildi[114] examined the electrical properties of the polymer of copper phthalocyanine obtained by heating the tetranitrile of pyromellitic acid with copper(I) chloride and urea:



The polymer is a purple-black powder. When it is heated in a vacuum (0.25 mm) at 410°C for 18 h, the loss in weight is 10.8%.

A considerable number of parquet polymers are found among the silicates. All silicates are based on the tetrahedral silicon atom combined with four oxygen atoms

located at the vertices of the tetrahedron. Coupling such tetrahedra together may yield the layer structure



in which each silicon atom is attached to an oxygen atom (not shown in the diagram) located either above or below the silicon atom on the normal to the plane of the diagram.

An example of the layer silicates of magnesium is talc, whose composition corresponds to the formula $Si_8O_{20}Mg_6(OH)_4$ or $Mg_3(Si_4O_{10})(OH)_2$. The structure of this mineral can be represented schematically as

$$\begin{matrix} 6\,O \\ 4\,Si \\ 4\,O+2\,(OH) \\ 6\,Mg \\ 4\,O+2\,(OH) \\ 4\,Si \\ 6\,O \end{matrix}.$$

In this polymer two layers of silicon–oxygen tetrahedra are linked together by a "brucite" layer, which consists of $Mg(OH)_2$ and is located between them. The vertices of the tetrahedra in the two silicon–oxygen layers point towards one another[115]. These three layers are firmly bound into packs, between which very weak attactive forces operate, which explains the low hardness, easy cleavage, and absence of elasticity in talc.

Talc is a poor conductor of heat and electricity. It does not melt below 1300–1400°C, and does not dissolve in acids even on heating[116]. Talc is widely used in the manufacture of rubber (as a filler), in perfumery, in the paint and ceramic industries (insulators, etc.), and in other fields[117].

A layer structure is possessed also by crystals of chrysotile asbestos, which forms fine fibres[118] sometimes reaching 160 mm in length. It is stable to the action of fire and alkali, but is broken down by hydrochloric acid. This material is of great practical value as a consequence of its stability at high temperatures.

The chief component of most clays is the mineral kaolinite $Al_4(Si_4O_{10})(OH)_8$, which is a variety of aluminium hydrosilicate. The crystals of kaolinite form two-layer packs, comprising a layer of silicon–oxygen tetrahedra and a "hydrargillite" layer. The structure of kaolinite crystals can be written

$$\begin{matrix} 6\,O \\ 4\,Si \\ 4\,O+2\,(OH) \\ 4\,Al \\ 6\,(OH) \end{matrix}.$$

They are easily cleaved into thin plates. The mineral is stable towards hydrochloric and nitric acids, but is readily decomposed by sulphuric acid, especially on heating. Kaolin is used in the ceramic industry (for the manufacture of china and pottery, firebricks, etc.), in building, and in other fields[119].

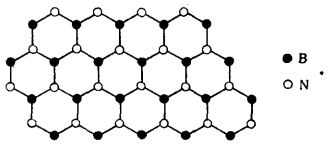
A layer structure is possessed also by montmorillonite. In contrast to kaolinite, it forms a three-layer structure comprising two layers of silicon–oxygen tetrahedra, between which is located a "hydrargillite" layer[120].

Micas are aluminosilicates which occur quite widely in Nature. Their composition can be expressed by the formulae[121] $M^+M_3^{2+}(AlSi_3O_{10})(OH)_2$ or $M^+M_2^{3+}(AlSi_3O_{10})(OH)_2$, where M^+, M^{2+}, and M^{3+} are uni-, bi-, and ter-valent cations. The hydroxyls may be replaced by fluorine. Micas are minerals having a crystal lattice of typical layered structure, in which 25% of the silicon–oxygen tetrahedra have been replaced by aluminium–oxygen tetrahedra.

A typical representative of the micas is muscovite $KAl_2(AlSiO_{10})(OH)_2$. As with many micas, the crystalline leaflets of this mineral are elastic on flexure[122]. It is stable towards acids. Muscovite possesses excellent electrically insulating properties, and is widely used for the manufacture of electrically insulating materials.

The manufacture of synthetic mica has now been organised[123–127]. It is produced in electric furnaces, by fusing together at 1370°C a stoichiometric mixture of magnesium oxide, aluminium oxide, silicon dioxide, potassium fluorosilicate, and orthoclase, and then slowly cooling the molten mass. The resulting mica has the same structure as the natural variety, but contains fluoride instead of hydroxyl groups, which confers on it a higher thermal stability (800°C) than natural mica (500–600°C).

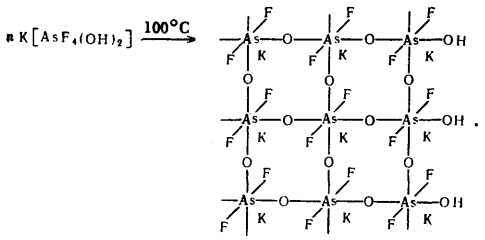
A layer structure resembling graphite is exhibited also by a variety of boron nitride BN:[128–130]



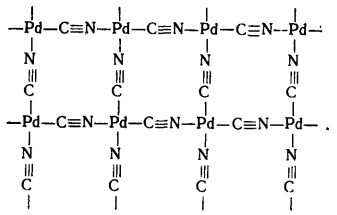
The distance between nitrogen and boron atoms is 1.45 Å, while that between the layers is 3.35 Å, as in graphite. Boron nitride can be prepared by heating boron and nitrogen above 1200°C or by heating boron or boron sesquioxide in an atmosphere of ammonia[131]. Boron nitride is a powder similar to talc, melting at ~ 3000°C (under pressure). It is stable towards acids and alkalis.

Crystals of the mineral molybdenite MoS_2 have a hexagonal structure of layer type[132,133], in which the molybdenum atom is surrounded by six sulphur atoms forming a trigonal prism. The unit cell of the crystal contains three lattices of molbdenum atoms, two layers of sulphur atoms being arranged between two of these lattices. Like graphite, molybdenum disulphide is easily cleaved, and is therefore used as a lubricant[134]. When rapidly heated in an inert atmosphere, it melts with decomposition at 1700–1800°C. At atmospheric pressure thermal dissociation of the polymer begins above 1300°C. In air molybdenum disulphide is stable up to 300–350°C; it is practically insoluble in water and dilute sulphuric and hydrochloric acids, but it dissolves in aqua regia and hot concentrated nitric and sulphuric acids[133].

Polymers of parquet type can be obtained by heating fluoroarsenates[135]:



According to Pauling[136] complex palladium cyanides have the structure



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