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# Synthesis of Polymers by Polycyclotrimerisation

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Research on the synthesis and properties of cross-linked polymers obtained by a promising new method—polycyclotrimerisation of monomers containing acetylenic and multiple carbon-nitrogen bonds—is surveyed with attention concentrated mainly on recent studies of the laws governing the reaction, elucidation of the influence of the heterounit character of cross-linked systems on their properties, and the development of methods for effecting highly selective polycyclotrimerisation with the aim of diminishing the "defectiveness" of the polymers and obtaining molecularly regular networks. Characteristics of polycyclotrimerisation of monomers having various functional groups (C:CH, C:N, N:C:O, O.C:N, NH.C:N, NR.C:N) are identified, and the influence of the structure of the initial monomers on the properties of the resulting cross-linked polymers is examined. A list of 159 references is included.

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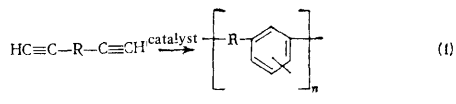
## I. INTRODUCTION

Progress in the chemistry of macromolecular compounds results not only from the introduction of increasing numbers of novel monomers into known polymerisation reactions but also from the application and development of new synthetic methods. Investigations devoted to the latter occupy an important place in the work of Korshak and his pupils: for example, Korshak and Kolesnikov[1] discovered transarylation, and Korshak and Sosin[2] polyrecombination. Recently Korshak and his coworkers have been actively studying polycyclotrimerisation, a new reaction in polymer chemistry[3-7]. This process permits the synthesis of cross-linked polymers of regular chemical structure containing segments of definite size between cross-links, and six-membered carbocyclic and heterocyclic rings at the branch points: i.e. cross-linked polymers can be obtained of a qualitatively new standard in comparison with hitherto known synthetic methods for such systems.

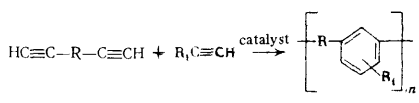
The present Review surveys the polycyclotrimerisation of monomers containing triple carbon-carbon and multiple carbon-nitrogen bonds— the two main types used for such synethses of cross-linked polymers.

## II. POLYCYCLOTRIMERISATION OF ACETYLENIC COMPOUNDS

The new synthetic method is based on the cyclotrimerisation of various acetylenic compounds, a reaction known in organic chemistry[3]. When diacetylenic compounds or mixtures of diacetylenic with monoacetylenic compounds are used, the formation of polymers can be represented by the general schemes[8]




(1)



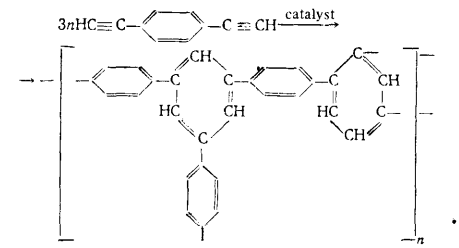

(2)

Polymer formation can thus be regarded as polycyclotrimerisation (1) or copolycyclotrimerisation (2). Such reactions had not previously been studied systematically with the aim of obtaining polymers. However, a considerable body of results have already been published on various cases of the polycyclotrimerisation of acetylenic compounds, which we can summarise in the light of the formation of polymeric products as a whole.

Conversion of acetylene into benzene, naphthalene, and other aromatic compounds at high temperatures (above 600°C) was first achieved by Berthelot[9] as early as 1866. Zelinskii[10] obtained high yields of aromatic hydrocarbons by passing acetylene over activated charcoal at 600–650°C. Studies were made[11-15] of the influence on the aromatisation of acetylenes of diverse catalysts–activated charcoal, kaolin, coke, alumina, quartz, china, pumice, brick, and also metals such as aluminium, iron, nickel, cobalt, etc.

The catalytic cyclotrimerisation of acetylenes was discovered by Reppe et al.[16,17] in 1940; it enabled high yields of products of diverse structure to be obtained under comparatively mild conditions. At the present time it is a process of great practical interest. The broad groups of catalytic systems used for the cyclotrimerisation of acetylenes comprise various complex organometallic catalysts, based e.g. on hydrides[18,19], salts[20-22], and π-complexes of metals[23,24], complexes of zerovalent metals[25], metal-oxide catalysts[26], and others[27].

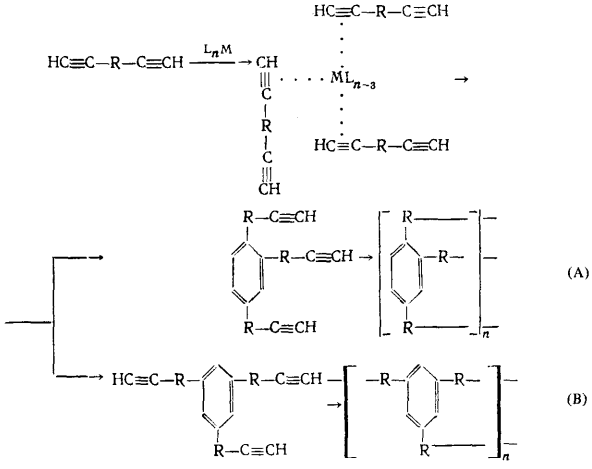
Korshak et al.[28] were the first to develop the new method for obtaining polymers of polyphenylene type from *p*-diethynylbenzene, whose polycyclotrimerisation can be represented by the scheme




The new aromatic rings formed are substituted at positions 1,2, 4 and 1,3, 5.[29,30] The proportions of the trisubstituted aromatic isomers depend on the nature of the catalytic system (mainly a metal) and on the reaction conditions.

Kinetic investigation of the polycyclotrimerisation of *p*-diethynylbenzene in the presence of trialkyl-phosphite cobalt complexes of general formula $[(AlkO)_3P]_nCoHal$ (where $n = 3$ or 4) has established[31] that the degree of conversion of the initial monomer depends not only on its initial concentration and that of the catalyst but also on the nature of the organic solvent and the duration of heating. Almost complete (97%) conversion of *p*-diethynylbenzene into a polymer can be achieved by selecting appropriate conditions by trial and error. The kinetic order with respect to *p*-diethynylbenzene is approximately first, with a rate constant of 0.01183 $s^{-1}$. Polycyclotrimerisation on the above catalytic complex forms strongly branched polymers containing mainly unsymmetrically trisubstituted benzene rings. This was demonstrated by nuclear magnetic resonance data for soluble specimens obtained in the initial stages at low degrees of conversion[31].

The reactions involved in the catalytic polycyclotrimerisation of diacetylenes can be represented by the general scheme[20,31]

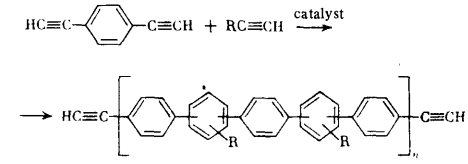



where $L_nM$ is a catalytic complex of a metal M and a ligand L. The reaction mechanism may involve other intermediate stages, but the slowest stage is probably interaction of the intermediate complex with the third acetylenic group[20,31].

Polymers of polyphenylene type based on *p*-diethynylbenzene are yellow-brown powders. The maximum molecular weight of the soluble polyphenylenes reaches 2600. However, the reaction mixture may also contain a large quantity of alcohol-soluble oligophenylenes of molecular weight $\geqslant 350$ together with insoluble and infusible polyphenylenes, which are amorphous to X-rays, in contrast to the crystalline poly-*p*-phenylenes obtained by the oxidative dehydropolycondensation of benzene[32]. The infusible amorphous polyphenylenes from *p*-diethynylbenzene do not dissolve when heated in chlorosulphuric and concentrated sulphuric acids, an indication of their cross-linked structure. The comparatively high yield of lower oligomers at 86% conversion is attributed to relatively low reactivity of the macromolecular products (in comparison with the monomer), which may be due to steric inhibition of cyclotrimerisation in the highly branched polymer[33].

Soluble polyphenylenes are formed from *p*-diethynylbenzene in the presence of titanium tetrachloride and diethylaluminium chloride or of a nickel(II) catalyst up to 88.5% conversion of the monomer[33]. The number-average molecular weights of the polymers measured osmometrically increase slowly with conversion of the monomer, but remain fairly low (up to 1460). Complete transformation of the reaction product into a high polymer occurs at ~90% conversion, close to the point of gel formation, which corresponds to a content of 8 mass % of ethynyl groups in the polymer. The properties of the soluble oligophenylenes based on *p*-diethynylbenzene depend largely on their content of unchanged ethynyl groups, whose presence is due to the incompleteness of polycyclotrimerisation. When such oligophenylenes are heated, the ethynyl groups are involved in polymerisation and the formation of three-dimensional structures.

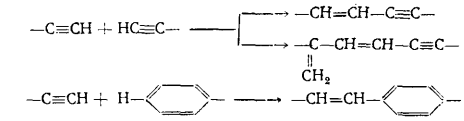
Thus the polycyclotrimerisation of *p*-diethynylbenzene yields either strongly cross-linked polyphenylenes or branched oligophenylenes of relatively low molecular weight. In order to obtain soluble oligophenylenes of higher molecular weight one active position in the newly formed benzene ring was blocked during chain growth. This was achieved by using as initial monomers various mixtures of aromatic and aliphatic mono- and di-ethynyl derivatives, whose copolycyclotrimerisation can be represented by the general scheme




where R = Ar, Alk, $CH_2:CH$, etc.

The copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene has been studied[34] in the presence of $[(C_2H_5O)_3P]_4CoBr$ as catalyst. However, when the process was conducted under conditions similar to those for the polycyclotrimerisation of the diyne, even when the initial mixture contained three moles of phenylacetylene per mole of the diyne, insoluble polyphenylenes were formed in yields up to 16%. Kinetic investigation established[34] that the rate of conversion of *p*-diethynylbenzene exceeded considerably that of phenylacetylene under the same conditions.

The polyphenylenes obtained by the polycyclotrimerisation of a mixture of *p*-diethynylbenzene and phenylacetylene were oily or solid products, whose properties were directly dependent on the reaction conditions, primarily on the molecular proportion of phenylacetylene and the initial concentrations of the acetylenes. Soluble and insoluble polyphenylenes were obtained; the infrared spectra indicated that those of greater molecular mass had lower contents of ethynyl groups relative to the aromatic portion of the polymer molecule. The maximum molecular weight of the soluble polyphenylenes was 4800. When soluble polyphenylenes containing terminal ethynyl groups were heated, they set with the formation of infusible and insoluble products, in which the process of structure formation could be represented[35]

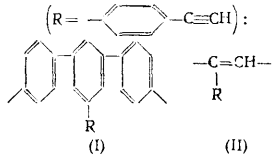



A catalytic system of the Ziegler–Natta type, comprising a trialkylaluminium and titanium(IV) chloride, is most often used for the copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene. Such a system in which the alkyl was isobutyl was employed[36] because the trimerisation of phenylacetylene in the presence of such a catalyst gave 1,3,5-triphenylbenzene in almost theoretical yield. In order to obtain soluble polyphenylenes of more regular

structure by the preferential formation of 1,3,5-substituted benzene rings, therefore, the copolycyclotrimerisation of *p*-diethynylbenzene with various quantities of phenylacetylene was conducted in solution (in heptane) at room temperature. Polymers that were completely soluble in benzene, toluene, and other organic solvents were obtained only when the molecular ratio of phenylacetylene exceeded unity[36]. Yet copolycyclotrimerisation of the components in benzene solution in the presence of the above catalyst at 60°C gave soluble and insoluble products, with the yield of insoluble polymers and the molecular weights of the soluble oligophenylenes (1170–5300) almost independent of the initial proportions of the monomers (within the range 1 : 2, 1 : 1, and 2 : 1).[37]

Infrared spectral data and kinetic investigation by gas-liquid chromatography of copolycyclotrimerisation indicated that, with the catalyst ratio Al/Ti = 0.5 at 60°C, the rate of conversion of phenylacetylene and *p*-diethynylbenzene changed as the reaction progressed. The ratio of the numbers of diyne and monoyne molecules that have reacted after 8 h at the same total concentration but different molecular concentrations of the monomers, together with the composition of the soluble copolymers determined from the intensity of the 710-$cm^{-1}$ band characteristic of a monosubstituted benzene ring, shows that only at a molar ratio of diyne to monoyne of 2 : 1 is predominant formation of structural units of the above types (A) and (B) possible[37].

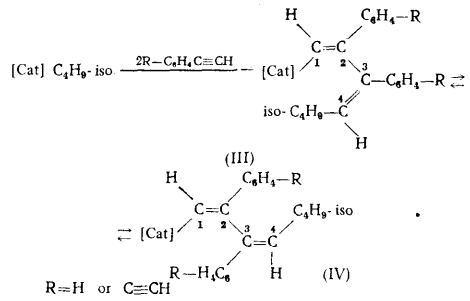
Investigation of the kinetics of the addition of ozone and the composition of the decomposition products from the ozonides indicated[37] structural non-uniformity of the soluble copolymers independently of the initial ratio of the monomers. The products of ozonolysis included benzoic and terephthalic acids. Thus the complicated mechanism of the copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene may result in copolymers containing not only phenylene segments but also anomalous units, including polyene segments. The study[38] of the influence of such anomalous units on certain properties of the copolymers formed from various ratios of the monomers in the presence of the tri-isobutylaluminium—titanium(IV) chloride catalytic system in benzene solution at 60°C revealed that increase in the proportion of the diyne in the initial mixture increased the content of triple bonds and polyene segments in the soluble oligomers. This may be due to the presence in the copolymer of the structures (I) and (II).




(I) (II)

since terephthalic acid was detected in the products of ozonolysis, whereas different acids were present in the degradation products from insoluble fractions of copolymers and homopolymers.

The formation of linear (polyene) and aromatic structures in the polymers involves cleavage of a triple bond[39], a cyclic trimer being formed by detachment of a linear trimer from a catalytic centre with ring closure[40]. This process depends not only on the nature of the acetylenic compounds and the catalytic system but also on the conditions of polycyclotrimerisation. With *trans*-cleavage of the triple bond, for example, linear polyenes are formed owing to the impossibility of *trans–cis* isomerisation with respect to the resulting double bond; with *cis*-cleavage of the triple bond, *cis-s*-cisoid (III) and *cis-s*-transoid (IV) conformations can be formed, responsible for the formation of cyclic and linear fragments respectively:




Cyclotrimerisation predominates in the case of phenylacetylene (R = H), which indicates *cis*-cleavage of the triple bond and free rotation about the $C_{(2)} - C_{(3)}$ single bond. In copolymers with *p*-diethynylbenzene (R = C≡CH) rotation about this single bond is hindered owing to the formation of branched and cross-linked structures, which increases the probability of polyenisation. These ideas find experimental support: increasing the diyne content in the mixture impedes polycyclotrimerisation and creates conditions for the formation of polyene structures, the quantity of which is determined from the quantity of ozone added per unit weight of the copolymer.

Investigations of the structural direction of copolymerisation of these monomers on the $AlR_3-(TiCl_4)_n$ catalytic system (R = $C_2H_5$ or iso-$C_4H_9$) have also revealed[41,42] that polycyclotrimerisation is not the only process of macromolecular chain growth.

In order to formulate optimum conditions for polycyclotrimerisation to high degrees of conversion of the initial acetylenic compounds into fusible and soluble polyphenylenes of practical interest the copolycyclotrimerisation of mono- and di-acetylenic compounds was studied[43,44] in the presence of the catalytic systems

$$[(C_2H_5O)_3P]_4CoBr;\quad NiCl_2\cdot 2P(C_6H_5)_3\cdot 2NaBH_4;$$

$$Ni(CO)_2\cdot[P(OC_6H_5)_3]_2\ ;\quad Al\ (iso\text{-}C_4H_9)_3—[TiCl_4]_n.$$

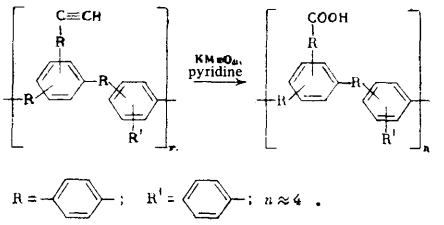
This involved preliminary preparation of complexes of the catalytic systems—the triethyl-phosphite complex of cobalt and the mixed organometallic catalyst based on triphenylphosphine, nickel chloride, and sodium tetrahydroborate—with *p*-diethynylbenzene and phenylacetylene followed by examination of their structure. In the presence of the first catalytic system above the rate of polycyclotrimerisation could be controlled by the introduction of electron-donor additives such as tertiary amines into the reaction mass or of electrophilic substituents, e.g. chlorine, bromine, etc., into the aromatic ring of the phenylacetylene. Copolycyclotrimerisation is strongly activated by electron-donor additives: the rate increases sharply, the induction period disappears, and the range of simultaneous conversion of the initial monomer mixture is enlarged.

High yields (~70%) of copolymers are obtained by copolycyclotrimerisation in the presence of the catalytic system $NiCl_2.2(C_6H_5)_3P.2NaBH_4$ under comparatively mild conditions with high rates of conversion of the initial monomers. The yield of soluble products increases considerably with increase in the phenylacetylene content of the initial mixture, and completely soluble oligophenylenes free from terminal ethynyl groups are formed when its molecular ratio to *p*-diethynylbenzene is 4 : 1. Use of a *p*-halogenophenylacetylene in copolycyclotrimerisation

enabled[43,44] the relative activities of acetylenic monomers in the reaction to be assessed and in most cases highly halogenated soluble copolymers to be synthesised.

Thus it follows from the above results that the nature of the catalytic complexes has a significant influence on the conditions of polycyclotrimerisation, on the relative reactivities of mono- and di-yne, and on the structure and properties of the resulting copolymer.

A method of oxidising toluene-soluble oligophenylenes obtained in the presence of a Ziegler–Natta type of catalyst (iso-$C_4H_9)_3Al-(TiCl_4)_n$, a mixed organometallic catalyst $NiCl_2.2(C_6H_5)_3P.2NaBG_4$, and also $(C_8H_7O_2)_2Ni.(C_6H_5)_3P$ and $[(C_2H_5O)_3P]_4CoBr$ has been devised[45,46] in order to make a comparative assessment of the efficiency and ascertain the influence of different catalytic systems on copolycyclotrimerisation, as well as to establish the structure of the polymeric products. Since multiple (double and triple) carbon–carbon bonds are readily oxidised in the presence of chromic and nitric acids or potassium permanganate, and their rupture produces organic acids or ketones[47–49], oxidation of the oligophenylenes followed the scheme




The oxidation products were pale grey powders soluble in pyridine, dioxan, dimethylformamide, and oxolan.

Properties of oxidised oligophenylenes[47–49].

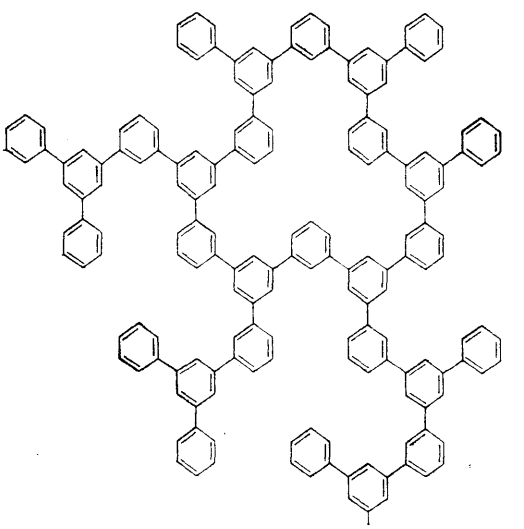
| Catalytic system | Acid value, mg KOH $g^{-1}$ | M.p., °C | Yield, % |
|---|---|---|---|
| Al (iso-$C_4H_9)_3$—$[TiCl_4]_n$ | 63.0 | 207–213 | 60.0 |
| Al (iso-$C_4H_9)_3$—$[TiCl_4]_n$ | 75.5 | 250–260 | 60.6 |
| $NiCl_2 \cdot 2P(C_6H_5)_3 \cdot 2NaBH_4$ | 71.5 | 130–139 | 34.2 |
| Ni $(C_8H_7O_2)_2 \cdot P(C_6H_5)_3$ | 71.2 | 275–279 | 21.0 |
| $[(C_2H_5O)_3P]_4CoBr$ | 80.0 | 178–193 | 23.6 |

The Table shows that the acid values and the melting points of the oxidised products depend on the conditions of formation and the structure of the initial oligophenylenes. Thus oligophenylene obtained in the presence of the sodium tetrahydroborate catalyst melted at 130–139°C after oxidation, whereas the corresponding temperatures obtained with a Ziegler–Natta type of catalyst were 250–260°C. The highest yield of oxidised product was found for a *p*-diethynylbenzene-phenylacetylene oligophenylene obtained in the presence of the Ziegler–Natta type of catalyst. From the molecular weights of the methyl ester of this copolymer (1800) and the content of methoxy-groups (6.3%) it follows that the macromolecule of the oxidised oligophenylene contains ~4 carboxy-groups. Alcohol-soluble lower oxidation products were isolated by precipitates in water; they had molecular weights of 300–450, acid values 100 to 160, and melting points 120–160°C depending on the structure of the initial oligophenylenes.

Decarboxylation of the oligophenylenecarboxylic acids at 400°C gave high yields of products having molecular weights close to those of the initial oligophenylenes (before oxidation) and with an elementary composition close to that calculated theoretically for oligophenylenes free from groups and bonds other than aromatic rings. Furthermore, acid values and infrared spectra indicated that the products contained no carboxy-groups and were almost devoid of multiple bonds, since the iodine values were close to zero. Since the initial oligophenylene, the methyl oligophenylenecarboxylate, and the product of decarboxylation of the oligophenylenecarboxylic acid had molecular weights of the same order, it was concluded[47–49] that the higher the yield of oxidised product (oligophenylenecarboxylic acid) the greater the extent of copolycyclotrimerisation of *p*-diethynylbenzene and phenylacetylene, the dominant process in the presence of the Ziegler–Natta catalyst (iso-$C_4H_9)_3Al-(TiCl_4)_n$.

Synthesis of soluble branched polyphenylenes of high molecular weight by polycyclotrimerisation of a mixture of *m*-diethynylbenzene and phenylacetylene in chlorobenzene solution was accomplished[50] in the presence of a Fischer catalyst, the active principles of which are complexes $TiCl_2.(AlCl_3)_n$, where $n = 1$ or 2. Examination of the effect of the molecular ratio of the initial monomers on the properties of the products revealed that soluble polyphenylenes were obtained with up to 50% excesses of the diyne. The yield of methanol-insoluble fractions was 88%; gas chromatography revealed neither of the initial monomers in the lower fractions. The resulting polyphenylenes were cream-coloured powders soluble in chlorinated hydrocarbons and cyclic ethers. They softened at ~320°C and had number-average molecular weights up to 70 000 (measured osmometrically in chlorobenzene solution at 30°C). The ultraviolet and infrared spectra of the polymers contained absorption bands characteristic of mono-, di-, and trisubstituted aromatic rings, but none indicating terminal ethynyl groups.

Thus the resulting polymers probably had a branched structure with macrocyclic polyphenylene fragments in the chain



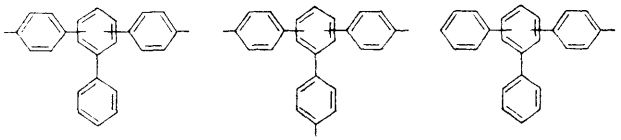
The formation of macrorings within a polymer molecule explains also the appearance of soluble polyphenylenes of high molecular weight when excess of *m*-diethynylbenzene is present (up to 1.5 moles per mole of phenylacetylene).

Soluble copolymers have been obtained[51] by heating an equimolecular mixture of phenylacetylene with a 9 : 1 mixture of *m*- and *p*-diethynylbenzenes in the presence of a catalyst $Ni(CO)_2.2(C_6H_5)_3P$ in benzene. Infrared bands characteristic of triple bonds ⋮CH and C⋮C (3300 and 2100 $cm^{-1}$ respectively) were absent, but the appearance of an absorption band in the region of 965 $cm^{-1}$, typical of terminal *trans*-disubstituted double bonds, was regarded as attributable only to linear telomerisation of acetylenic compounds[52]. Solid cross-linked products separated when solutions of the copolymers were allowed to stand in the air.

Copolymers readily soluble in aromatic solvents have been obtained[51] by the copolycyclotrimerisation of the above diethynylbenzene mixture with phenylacetylene or *m*-ethynyltoluene in the presence of a $(C_2H_5)_2AlCl-(TiCl_4)_n$ catalyst (with Al : Ti = 3 : 1), which converts[53] phenylacetylene into a high (up to 80%) yield of triphenylbenzene with only slight quantities of linear products. Infrared and $^1H$ and $^{13}C$ nuclear magnetic resonance data indicate that the copolymers contain predominantly aromatic groups with very minute quantities of double and triple bonds. The reactions of these triple bonds are not those typical of terminal acetylenic compounds, since attempts to increase the molecular weight of the products by oxidative dehydropolycondensation were unsuccessful. Comparison of the n.m.r. absorption areas due to aromatic and aliphatic protons in the diethynylbenzene–*m*-ethynyltoluene copolymer indicated a ratio of mono- to di-functional initial compounds of 1.2–1.0.

Polycyclotrimerisation of diethynylbenzene with phenylacetylene or *m*-ethynyltoluene gave high yields of soluble copolymers having molecular masses of 10 000–50 000 and softening points of 200–300°C depending on the reaction conditions. Gel-permeation chromatography established that the degree of polydispersity and the molecular mass of the copolymers were almost unaffected by the initial catalyst concentration (over a fivefold range)[51]. The good solubility of the copolymers in organic solvents, the low viscosity of their solutions ($[\eta] = 0.089–0.288$), and also the very great brittleness of films based on them (independently of molecular mass) provide convincing evidence of the branched structure of the copolymers. Furthermore, the value $\alpha \approx 0.5$ in the Mark–Houwink equation $[\eta] = KM_\omega^\alpha$ found experimentally also confirms a branched structure.

Because the effect of the catalyst is relatively non-specific the three possible aromatic groupings



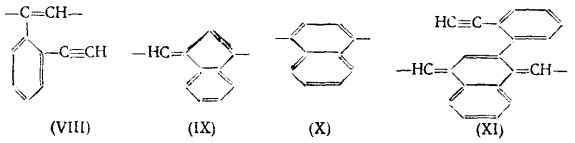
(V) (VI) (VII)

may be formed during cyclotrimerisation[51]. Group (V) arises from the interaction of one monofunctional and two difunctional molecules, and results in a linear polymer. Actually, however, groups (VI) and (VII) may also be formed, and give rise respectively to branched polymers and chain termination. Each of the groupings may in turn contain 1,2, 4- and 1,3,5-substituted aromatic rings. Two mathematical models have been suggested for theoretical calculation of the probability of formation of a particular structure at various stages of polycyclotrimerisation, and these establish foundations for conducting the process under optimum conditions and obtaining polyphenylenes having specified properties[51].

Furthermore, the statistics of branching processes based on the cascade theory has been applied[54] to the polycyclotrimerisation of *p*-diethynylbenzene and its copolycyclotrimerisation with phenylacetylene on the hypothesis of equal and constant reactivity of the ethynyl groups, with the aim of determining the degree of conversion at the point of gel formation and the mean molecular weights under random reaction conditions. The statistical estimations for the diyne indicated that the gelation point is determined by the condition $\alpha_{cr} = 0.5$: i.e. the critical degree of conversion of ethynyl groups is in this case 0.5, as for the random polycondensation of a trifunctional polymer. The values of $\alpha_{cr}$ calculated for the copolycyclotrimerisation increased from 0.5 to 1 with increase in the proportion of phenylacetylene in the initial mixture from 0 to 2 moles per mole of *p*-diethynylbenzene.

The possibility of controlling polycyclotrimerisation at the gel point, at which formation of a three-dimensional network begins, has been confirmed experimentally[54], and the reactivity of the ethynyl groups is shown to diminish during the reaction, probably owing to slow diffusion or steric hindrance. In discussing the properties of the resulting polyphenylenes, however, the authors unfortunately do not consider such an effect of polyenisation processes, which in some measure govern the formation of polymer molecules and their properties.

Study of the polymerisation of *o*-diethynylbenzene in the presence of various catalysts has established[55], that, in contrast to the behaviour of the *para*- and *meta*-isomers, 30–50% of the second ethynyl groups are not involved in coordination polymerisation in the presence of the catalytic systems $R_nAlCl_{3-n}-(TiCl_4)_n$ and $R_nAlCl_{3-n}.(C_5H_7O_2)_3Ti$ (where $n$ = 1,2, or 3), 70% of these groups remain uninvolved in radical polymerisation in the presence of azoisobutyronitrile, and only one ethynyl group in the *o*-diethynylbenzene molecule reacts in cationic polymerisation in the presence of titanium tetrachloride. From these results it is assumed that polymers containing groupings of the types

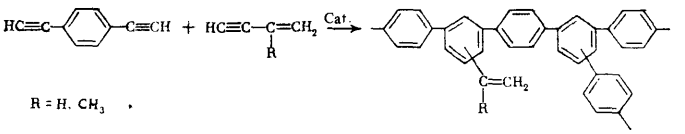


(VIII) (IX) (X) (XI)

may be formed from the *ortho*-isomer. Methyleneindane and naphthalene cyclic structures can be formed only in the presence of catalysts for coordination or radical polymerisation. However, a study of molecular models indicates[55] that formation of the six-membered cyclic structures (X) and (XI) is sterically more probable than the successive arrangement of five-membered structures (IX) in a chain, although formation of the latter is not excluded by the mechanism.

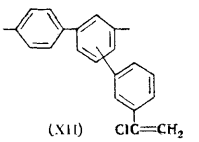
Reports have appeared[56–60] on the synthesis of branched oligophenylenes from *p*-diethynylbenzene and butadiyne or certain other monoacetylenes by polycyclotrimerisation in the presence of $(iso-C_4H_9)_3Al-(TiCl_4)_n$ (Al : Ti = 3 : 1). Polycyclotrimerisation of butadiyne or its mixture with phenylacetylene[57] gives branched oligophenylenes readily processed by hot moulding into infusible and insoluble polymeric materials distinguished by high thermal stability. This method of obtaining polyphenylenes is of definite practical interest, since butadiyne, in contrast to *p*-diethynylbenzene, is a by-product in the production of acetylene by the pyrolysis of hydrocarbon raw materials. Copolycyclotrimerisation of *p*-diethynylbenzene with hex-1-yne gives copolymers whose content of triple bonds diminishes with

increase in the proportion of the latter monomer[59]. Oligophenylenes containing free double bonds have been obtained[56] by partial or complete substitution of an alkenylacetylene—butenyne or 2-methylbutenyne—for phenylacetylene in its reaction with *p*-diethynylbenzene:



Increase in the quantity of unsaturated groups in such oligophenylenes increases their tendency to set, and plastometric tests reveal no deformation changes in hardened *p*-diethynylbenzene–2-methylbutenyne specimens even at 400°C and above, which indicates the high density of cross-linking and the enhanced thermal stability of such specimens.

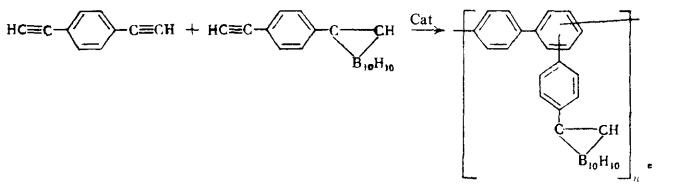
Oligophenylenes containing chlorovinyl groups



(XII)

have been obtained[60] from a mixture of *p*-diethynylbenzene, phenylacetylene, and *m*-ethynyl-1-chlorovinylbenzene. These groups not only increase the unsaturation of the resulting oligophenylenes but also confer on the polyphenylenes greater thermal stability than in the absence of this third monomer. Phenylacetylene is found to be more active than the chlorovinylethynylbenzene in polycyclotrimerisation.

Results of the model reaction of *p*-*o*'-dicarbadodecaboranylphenylacetylene in the presence of $(iso\text{-}C_4H_9)_3Al$–$(TiCl_4)_n$ and $NiCl_2.2(C_6H_5)_3P.2NaBH_4$, with the separation of *tris*-*p*-*o*'-dicarbaboranylphenylbenzene, suggested[58] that copolycyclotrimerisation of the former compound with *p*-diethynylbenzene could follow the scheme



Equimolecular proportions of the initial monomers gave a 75% yield of completely soluble copolymers having a boron content of 19%. They were amorphous yellow powders having $M_n$ = 3350. With the aim of controlling the boron content in copolymers of *p*-diethynylbenzene, phenylacetylene, and *p*-*o*'-dicarbaboranylphenylacetylene in the molecular proportions 1 : 1 : 0.5 a 73% yield of a mixed copolymer having a boron content of 12% was obtained. Formation of an insoluble fraction in 20% yield was due to some inhibition of copolycyclotrimerisation of the components[58]. Thermogravimetric analysis under dynamic and isothermal conditions indicated that copolymers containing carbaboranes were highly resistant to thermal oxidation in air[58].

Polymers containing 1,2,4-substituted aromatic rings are obtained[61] by the polycyclotrimerisation of diethynyldiphenylsilane or its mixture with phenylacetylene in heptane solution in the presence of $(iso\text{-}C_4H_9)_3Al$–$(TiCl_4)_n$. Such polymers have smaller elastic moduli than have polyphenylenes obtained from *p*-diethynylbenzene. This is attributed to greater elasticity of the "hinge" bond in the silicon-containing polymer.

In conclusion it must be noted that a distinguishing feature of the polycyclotrimerisation of acetylenic compounds is the formation mainly of trisubstituted aromatic rings in the polymer structure[3]. The rigidity of a polymer molecule increases with the content of aromatic groups, while the polymer as a whole is characterised by high heat resistance and thermal stability[4,5]. Therefore polyphenylenes obtained by the copolycyclotrimerisation of diynes with monoynes are of definite practical interest, since they can readily be processed by the usual methods of chemical forming into articles that withstand high temperatures for a long time[30,36,51].

## III. POLYCYCLOTRIMERISATION OF MONOMERS WITH MULTIPLE CARBON–NITROGEN BONDS

The polycyclotrimerisation of several compounds containing multiple carbon–nitrogen bonds was already known in the nineteenth century, but most research in this field has been undertaken during recent years. At the present time a number of cyanogen compounds—such as hydrocyanic acid, cyanogen chloride, cyanamide, acetone cyanohydrin, β-hydroxypropionitrile, acrylonitrile, etc.—are large-tonnage industrial products. Several 1,3,5-triazines (cyanuryl chloride, cyanuric acid, melamine, and their derivatives), obtained by the cyclotrimerisation and cyclocondensation of appropriate compounds, are also produced industrially on a large scale.

Research on the polycyclotrimerisation of monomers containing multiple carbon-nitrogen bonds has been widely developed only during the past decade in connection with the need for highly heat-resistant and thermostable polymers and composition materials for various branches of modern technology, especially for air and space travel. As already noted above, this method has several advantages over well known syntheses of thermostable polymers and is distinguished by the simplicity of its technical organisation, the availability of the starting materials, the absence of separation of secondary products, etc. A considerable number of publications have now appeared on the cyclotrimerisation and polycyclotrimerisation of monomers containing multiple carbon–nitrogen bonds, the synthesis and the properties of the polymers, the laws of their formation, etc.

We do not intend to discuss in detail all aspects of the problem, since several reviews have already been published in this field during recent years[3,4,7,62–66]. We shall consider recent studies of the polycyclotrimerisation of monomers with cleavage of multiple carbon–nitrogen bonds, e.g. in aliphatic, aromatic, and hetero-organic nitriles, cyanates, cyanamides, etc. Attention will be paid mainly to work on the mechanism, kinetics, and thermodynamics of polycyclotrimerisation, gel formation, the molecular weight characteristics of the polymers, the influence of the structure of the monomers on the properties of the polymers, and specific features of this synthesis of cross-linked polymers.

During recent years Korshak[7,67] has developed the concept of the heterounit character of polymers consequent on several secondary processes accompanying the main polymerisation reaction. Such structural "defectiveness" of a particular polymer leads in most cases to diminished heat resistance, thermal stability, physicomechanical indices, etc. For example, the polycyclotrimerisation of isocyanates, nitriles, and other monomers is accompanied by many secondary reactions (chain polymerisation,

dimerisation, etc.)[3,4,7,67–79]. The production of polymers of almost perfect structure is therefore an urgent problem, whose solution will improve considerably many characteristics of the polymers and may lead to materials having qualitatively novel properties.

Recent papers by Korshak and his coworkers have shown that cyanates and cyanamides are potentially the most promising and convenient compounds for studying this new field in polymer chemistry[62,64,65]. These monomers are more reactive than nitriles, which makes them convenient for investigating the laws of polycyclotrimerisation. The cyclotrimerisation of cyanates and cyanamides, in contrast to that of isocyanates, is uncomplicated by dimerisation, carbodi-imidisation, or linear polymerisation, and these compounds are considerably less subject to hydrolysis of functional groups and are stable on storage. Furthermore, cyanates and cyanamides are non-toxic, and are less volatile than isocyanates [64,65]. They can be prepared simply, in high yields from readily available starting materials[64,66]. Their great synthetic possibilities have permitted the establishment of various systematic series of initial monomers and oligomers, detailed study of the influence of their structure on the properties of the resulting polymers, and formulation of principles governing the directed synthesis of networks having specified properties[62,64,65].

## 1. Laws of Polycyclotrimerisation

Research on the kinetics and mechanism of the cyclotrimerisation of nitriles has been discussed in detail in several reviews[3,4,62–65], and therefore will not be considered here.

A series of papers of Korshak et al. [3,4,80–90] has been devoted to a detailed investigation of the kinetics and the mechanism of the cyclotrimerisation and polycyclotrimerisation of aryl cyanates. Since the polycyclotrimerisation of arylene dicyanates yields insoluble, infusible, highly cross-linked polymers, it is more convenient to use monofunctional cyanic esters for investigation of kinetics, heat of reaction, and also the effect of the structure of cyanic esters on reactivity. The cyclotrimerisation of phenyl cyanate into triphenyl cyanurate — a reaction that models the formation of a polymer by polycyclotrimerisation and is not complicated by such processes as gel formation, etc. — was studied first. The reaction was conducted in ditolylmethane solution in the presence of chromium acetylacetonate $(acac)_3Cr$, one of the most active catalysts for this process. The rate of cyclotrimerisation was measured by means of a double calorimeter from the quantity of heat evolved in a certain time. The reaction was found to be autocatalytic[81–90]. The heat of cyclotrimerisation of phenyl cyanate is $-27.9 \pm 1.4$ kcal mole$^{-1}$. The energy of stabilisation of the 1,3,5-triazine ring has also been estimated (as 26 kcal mole$^{-1}$); this ring is stabilised both by delocalisation of electrons with formation of a system analogous to the $\pi$ system of the benzene ring and also by partial polarisation of a cyclic nitrogen–carbon bond[81].

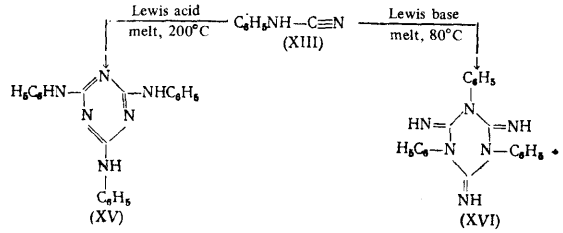
The kinetics of the conversion of various substituted aryl cyanates have been studied and the enthalpies measured to ascertain the effect of the structure of cyanic esters on their reactivity and the heat of cyclotrimerisation[89]. The nature of substituents has a significant influence on the rate. Thus electron-donor substituents (*p*-methoxyl, *p*-methyl) lower the rate of cyclotrimerisation, whereas electron-accepting substituents (*p*-chloro) increase it in comparison with that of unsubstituted phenyl cyanate. The maximum rate, the time of its achievement, and the heat of reaction are linear functions of the $\sigma$ constants of the substituents[89].

Direct calorimetry has been used[83–86,88,90], under conditions analogous to those of the model reactions, to make a more thorough kinetic study and measure the heat of the polycyclotrimerisation of di-2-*p*-cyanatophenylpropane. The kinetic features are mainly the same as in the cyclotrimerisation of phenyl cyanates. The mean heat of polycyclotrimerisation of the dicyanate is $\Delta H = -56.8$ kcal mole$^{-1}$, i.e. 28.4 kcal mole$^{-1}$ per N:C.O group. The close agreement between this value and the above heat of cyclotrimerisation of phenyl cyanate (−27.9) confirms the great selectivity of the polycyclotrimerisation of arylene dicyanates[83,84].

The rate of polycyclotrimerisation of di-2-*p*-cyanatophenylpropane, the heat of reaction, and also the effective activation energy depend on the nature of the solvent[88]. The solvents used can be arranged in the sequence ditolylmethane > nitrobenzene > anisole > diglyme in which the rate falls. Both physical and specific solvation of the arylene dicyanate by solvent molecules are responsible for the decreased rate and heat of polycyclotrimerisation[88]. Bonetskaya et al. [83,85,86] have found that the presence of water in the system has an appreciable effect on the rate. Gas–liquid chromatography reveals traces of pentane-2,4-dione after the reaction mass has been thermostatted at 140°C. The reaction velocity is increased by the addition of water, but diminished by that of the pentanedione. These results suggest[86,90] that an active form of the catalyst is formed by the action of water, and is present in equilibrium with the main form.

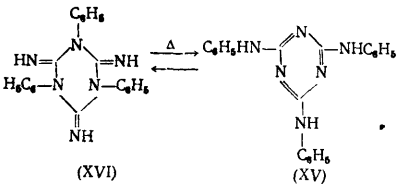
The kinetic features of the polycyclotrimerisation of arylene dicyanates established in the above studies reduce essentially to the following points. The process has a clearly defined autocatalytic character. Independently of the concentrations of catalyst and monomer, the maximum rate is observed at a definite extent of conversion (~40%) of the dicyanate. The maximum rate is proportional to the square root of the product of the concentrations of the catalyst and water, and varies linearly with the concentration of the arylene dicyanate. Addition of small quantities of pentane-2,4-dione in addition to the chromium acetylacetonate catalyst decreases the maximum rate, while the time of achievement of this maximum is sharply increased. In the absence of a catalyst additions of the final reaction products (triphenyl cyanurate or a polymer) do not catalyse the reaction[81,83–86,90].

Korshak et al. have made a series of studies[91–97] of the polycyclotrimerisation of cyanamides, another type of hetero-substituted nitriles. Phenylcyanamide (XIII) and *N*-ethylphenylcyanamide (XIV) were first chosen as model compounds. Either normal triphenylmelamine (XV) or triphenylisomelamine (XVI) could be formed depending on the conditions of cyclotrimerisation[91,92,94]:




Thus the cyclotrimerisation of (XIII) in the melt under mild conditions (20–80°C) gives (XVI), whereas at 200°C

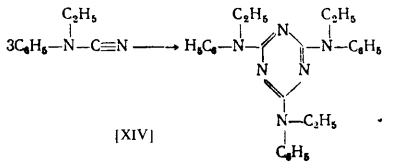
the main product is (XV). Hydrolysis of the isomeric products (XVI) and (XV) gave high yields respectively of triphenyl isocyanurate and cyanuric acid[91,92,94]. Study of the effect of temperature on the isomers showed that structure (XV) remains unchanged until it decomposes (above 400°C), whereas (XVI) isomerises into (XV) at temperatures above its melting point (185°C)[91,94]:



(XVI) (XV)

Isomerisation of (XVI) into (XV) takes place at considerably lower temperatures in solution. The normal melamine structure is more stable than the isomelamine structure at high temperatures, so that it is of greater interest for the development of thermostable polymers[91]. Korshak et al.[91,92,95,96] have investigated the action of various catalysts with the aim of directing the cyclotrimerisation of *N*-monosubstituted cyanamides to give a definite isomeric structure. They find that the formation of triphenylmelamine (XV) is favoured by catalysts such as Lewis acids (metal chlorides), but that of triphenylisomelamine (XVI) by Lewis bases.

To ascertain the effect of a substituent in the cyanamide group on the reactivity of an arylcyanamide and on the structure of the products the same workers have studied[93,94,96,97] the cyclotrimerisation of *N*-ethylphenylcyanamide (XIV)



[XIV]

The presence of the aliphatic substituent $\alpha$ to the nitrile group diminishes the reactivity of the cyanamide group, so that the process occurs only in the presence of such catalysts as Lewis acids. A substituted melamine of normal structure is formed: the iso-structure was not detected among the reaction products[94]. The above features of *N*-mono- and *NN*-di-substituted cyanamides and of the products of their cyclotrimerisation must be taken into account in preparing polymers from cyanamides and examining their properties.

Korshak et al.[93,94] have studied the polycyclotrimerisation of primary and secondary *N*-substituted biscyanamides. The highly reactive di-*p*-cyanamidophenylmethane begins to polymerise below its melting point of 162°C. Heating at 100°C for 2 h leads to 43% conversion. The rate of polycyclotrimerisation increases sharply at temperatures above the melting point, and at 180°C, for example, conversion reaches 87% after 30 min. As in the case of the model compound phenylcyanamide, two isomeric polymelamine structures can be formed depending on the temperature of polycyclotrimerisation of the biscyanamide: at 100 and 140°C, i.e. at temperatures below the melting point of di-*p*-cyanamidophenylmethane, the process results in formation of a polymer predominantly of isomelamine structure; at 180°C and above, i.e. above the melting point of the monomer, the main product is a polymer having the normal melamine structure[94].

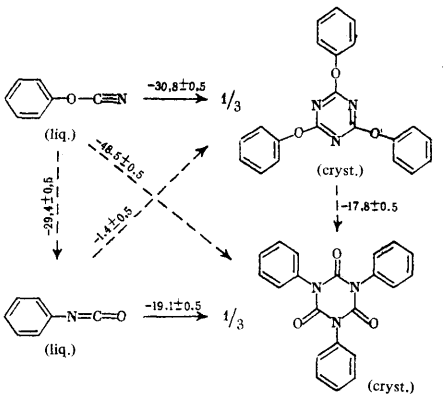
Di-*p*-*N*-methyl(and ethyl)cyanamidophenylmethane have been used as examples for kinetic study of the polycyclotrimerisation of secondary *N*-substituted cyanamides. As with the model compound (*N*-ethyl-*N*-phenylcyanamide) the presence of aliphatic substituents $\alpha$ to the nitrile group diminishes the reactivity of the cyanamide group in comparison with primary *N*-substituted cyanamides. Such compounds undergo polycyclotrimerisation in the presence of cationic catalysts such as Lewis acids, but hardly at all in the absence of catalysts under the same temperature conditions. An isomelamine structure was not detected[94] among the products of the polycyclotrimerisation of secondary *N*-substituted biscyanamides.

## 2. Thermodynamic Parameters of Cyclotrimerisation and Polycyclotrimerisation

Study of the thermodynamic parameters helps to elucidate the conditions under which polycyclotrimerisation is possible and is reversible, and will give information on the temperature range of thermodynamic stability, structural features of the resulting polymers, the relative stability of isomeric compounds, the possibility of their isomerisation, and other important aspects of the process.

Thermodynamic characteristics of the polycyclotrimerisation of dicyanates have been studied in greatest detail on di-2-*p*-cyanatophenylpropane[98]. Measurements have been made on the temperature dependence of the heat capacity of the polymer and of the initial dicyanate, as well as the enthalpies of combustion of these compounds. Calculations of enthalpy, entropy, and Gibbs free energy have been made for polycyclotrimerisation of the dicyanate into a regularly cross-linked amorphous polymer. Within the limits of experimental error the enthalpy of polymerisation $-\Delta H_{pol}$ found at 420 K coincides with the value determined by direct calorimetry (respectively 53.2 and 56.8 kcal mole$^{-1}$), which yet again confirms the unidirectional character of the polycyclotrimerisation of arylene dicyanates[98].

Great interest attaches to comparative estimates of the thermodynamic parameters of the cyclotrimerisation and polycyclotrimerisation of isomeric esters of cyanic acid—cyanates and isocyanates — into corresponding isomeric derivatives of cyanuric acid[99]. Because of the complexity of the investigation of cross-linked systems and the occurrence of numerous secondary processes accompanying the polycyclotrimerisation of di-isocyanates it is more convenient to examine model compounds (phenyl cyanate and isocyanate) and their trimers (triphenyl cyanurate and isocyanurate). Enthalpies of combustion of these compounds have been determined[99], and enthalpies calculated for cyclotrimerisation




and the hypothetical reactions indicated by the broken

arrows. Here the arrows indicate the directions of exothermic reactions and the numerals thereon their enthalpies (in kcal mole$^{-1}$) for the given physical states. Inspection of the values for the hypothetical isomerisations shows that the iso-form is considerably more stable than the normal form in both monomers and trimers. The validity of this conclusion, based on calculated values, is confirmed by published information on the isomerisation of aliphatic cyanates and alkyl cyanurates into high yields of the corresponding isocyanates and alkyl isocyanurates[64,73,100]. Despite the greater thermodynamic stability of the iso-form of the initial compounds and trimers, however, aromatic cyanates and cyanurates do not isomerise, and conditions have not yet been found which would permit such reactions[64,73,100].

A comparative thermodynamic study has been made not only on model compounds but also on di-isocyanates isomeric with arylene dicyanates[99]. The enthalpy of polycyclotrimerisation of di-*p*-isocyanatophenylmethane (-24 kcal mole$^{-1}$) was rather more than half the value for the dicyanate. The decrease in entropy accompanying polymerisation both of the dicyanate and of the di-isocyanate is ~36 e.u., exceeding by about 30% the value of linear polymerisation. This is a feature of polycyclotrimerisation resulting in the formation of regularly cross-linked polymers[99].

For the polycyclotrimerisation of di-2-cyanatophenylpropane over the range 100–420 K both $\Delta H_{pol}^0$ and $\Delta S_{pol}^0$ are negative[98]. The upper temperature limit to polymerisation of this dicyanate is 1480 K, much higher than the temperatures at which thermal decomposition of monomer and polymer begins. (Below 1480 K there is no thermodynamic hindrance to conversion of monomer into polymer, but above this temperature formation of the polymer is impossible). The absolute values of the Gibbs free energy show that the polycyclotrimerisation equilibrium for dicyanate and di-isocyanate ($-\Delta G_{pol}^0$ respectively 40.3 and 19.1 kcal mole$^{-1}$) is almost completely displaced towards formation of the polymer[98,99].

## 3. Gel Formation and Molecular Weight Characteristics in Polycyclotrimerisation

The investigation of gel formation and molecular-weight characteristics is a key to understanding the formation of three-dimensional structures. Knowledge of these processes will in turn enable the direction of the reaction to be controlled both in the initial stage of oligomerisation and following the gel point, and also polymers to be produced having a definite topological structure and thus their physicochemical and thermal properties to be influenced. Polycyclotrimerisation is a fundamentally new method for synthesising three-dimensional polymers, which enables networks of regular chemical structure to be built with segments of strictly specified size $M_c$ between cross-links. Such systems are ideal models for experimental investigation of gel formation.

Korshak et al.[101–103] have used aromatic dicyanates and the isomeric di-isocyanates to make a detailed investigation of the influence on gel formation of such factors as method of synthesis, nature of solvent, catalyst, and monomer, and also monomer and catalyst concentrations. Di-2-*p*-cyanatophenylpropane and di-*p*-isocyanatophenylmethane were used as initial monomers. The gel point and the dependence of yield of gel on degree of conversion are governed by the method of synthesis and the solvent employed. The type of catalyst affects these parameters only in certain solvents[101].

The influence of monomer concentration on the character of gel formation depends on the nature of the solvent. With decrease in concentration in a "good" solvent (nitrobenzene, chlorobenzene) the conversion at the gel point increases, whereas in a "bad" solvent (ditolylmethane) the dependence is "anomalous", i.e. the conversion at the gel point diminishes[101].

No appreciable effect of temperature on gel formation was observed. On polycyclotrimerisation in the mass of either of the above monomers the main parameters of gel formation were unaffected by nature or concentration of the catalyst[102].

The close agreement of several of the main rules of gel formation in the polycyclotrimerisation of dicyanates and of di-isocyanates, i.e. of different classes of monomers, together with investigation of the molecular weight characteristics during the reaction up to the gel point and the sol fraction after this point, has enabled general ideas to be formulated on the construction of a topological gel structure in this method of synthesising cross-linked polymers[102,103]. Comparison of the experimental results [102] with the theory of gel formation developed for polycyclotrimerisation reveals close agreement in several cases. Differences existing between calculated and experimental values are explained by the fact that the theory ignores the macrocyclisation resulting from the considerable branching of the macromolecules[102,103].

Traditional methods of synthesising cross-linked polymers from monomers, oligomers, or polyfunctional polymers are complicated by such factors as differences in reactivity between functional groups not leading to branching, a difficultly controllable distribution among molecular weights and types of functionality for initial oligomers and polymers, and many others. All this makes it difficult to synthesise cross-linked polymers having a chemically regular structure. Polycyclotrimerisation eliminates most of these disadvantages and enables polymers to be obtained that are regularly cross-linked at a molecular level. In this method of synthesis the entry of each functional group into reaction is accompanied by branching of the macromolecule, except for the "loss" of functional groups on macrocyclisation.

The detailed investigation of gel formation and molecular weight characteristics made by Korshak and his coworkers[101–103] has shown that macrocyclisation can be controlled by varying the reaction conditions. This in turn affects the topological structure of the resulting polymers. The possibility of acting at a higher (than molecular) level of structural organisation of the networks opens up great prospects for controlling the physical properties of cross-linked polymers by changing their topology.

## 4. Structure and Properties of Polymers obtained by Polycyclotrimerisation

The main types of monomers that have been widely investigated in polycyclotrimerisation are isocyanates, nitriles, cyanates, and cyanamides. Many papers have been published on the cyclotrimerisation and polycyclotrimerisation of isocyanates, and the results have been summarised in several exhaustive reviews[3,4,68–75,77–79]. Discussion of the polycyclotrimerisation of monomers of this type lies outside the scope of the present Review; we note merely that several interesting studies have recently appeared on

the mechanism of the cyclotrimerisation of isocyanates[104,105]. However, polycyclotrimerisation of isocyanates with formation of cross-linked structures has been little studied, and published views on its mechanism are often contradictory[3,4,68–75,77–79,106–111].

Most of the information on polymers based on isocyanates comes from the patent literature, from which in most cases it is difficult to assess the structure of the polymers or the presence of secondary structures. Among the known groups of compounds that form cyclotrimers isocyanates are most likely to undergo various secondary reactions—dimerisation, carbodi-imidisation, linear polymerisation, chain termination by hydrolysis of isocyanato-groups, etc.—accompanying cyclotrimerisation. The occurrence of these numerous secondary processes, which are extremely difficult to eliminate, is the main hindrance to investigation of the polycyclotrimerisation of isocyanates and a correct interpretation of the results in relation to the reaction mechanism and the structure of the resulting cross-linked polymers.

Nitriles are usually unreactive in comparison with isocyanates, and their polycyclotrimerisation requires severe conditions (high temperatures, pressures, catalyst contents, etc.), which hinders their processing into articles. A considerable content of catalysts (usually highly active compounds) in the cross-linked polymer also affects adversely the thermal stability and other properties of materials obtained from such polymers[3,4,7,62,63,65]. Furthermore, the cyclotrimerisation of nitriles may be accompanied by several secondary processes—linear polymerisation of cyano-groups with formation of azomethine structures, chain termination by various reactions of nitrile groups in the presence of a high content of catalytic systems, formation of cyclic products by aliphatic nitriles, etc.—especially under severe conditions. The presence in such polymers of various "defect" structures makes difficult the formation of a chemically regular network, which in turn diminishes their thermal and physicochemical characteristics[3,4,7,62,63,65]. In the Reviewers' opinion necessary conditions for overcoming these disadvanatages of the synthesis of cross-linked polymers by the polycyclotrimerisation of nitriles are— the discovery of highly active catalysts for polycyclotrimerisation, development of convenient and cheap methods for obtaining the initial monomers, and also synthesis of nitriles containing electron-accepting groups to strengthen polarisation of the N⋮C bonds.

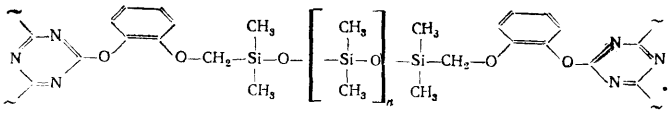
Korshak and his coworkers[3,4,62,64,65,80–99,101–103] have shown that, in contrast to isocyanates and nitriles, cyanates and cyanamides undergo highly selective polycyclotrimerisation under certain conditions with almost quantitative conversion of functional groups. The resulting polycyanurates and polymelamines are highly cross-linked heterochain polymers with 1,3, 5-triazine rings as branch points separated by segments of aromatic and heterorganic diols, glycols, and diamines[80–99,101–103,112–152]. Such polymers, especially those having highly cross-linked aromatic structures, were not known previously. In contrast to randomly cross-linked systems, polymers having a chemically regular network should exhibit a qualitative change in several properties of cross-linked polymers. Thus polycyanurates surpass in heat resistance and thermal stability the similarly constructed polyisocyanurates obtained from di-isocyanates, although the study of model compounds shows that the isocyanurate ring is thermally more stable than the cyanurate ring[73,74,113,118,120]. The presence of numerous "defect" structures—urea groups, linear structures, dimers, etc.—probably has a considerable influence on the thermal stability of polymers obtained by the cyclotrimerisation of di-isocyanates. In contrast to all known highly cross-linked aromatic polymers block polycyanurate specimens have abnormally high specific impact resistance (up to 30 kgf $cm^{-1}$ $cm^{-2}$) and are distinguished by good physicochemical indices both at room temperature and at high temperatures[112,113,122].

In order to ascertain the causes of the unusual mechanical properties of polycyanurates electron microscopy has been used to monitor the formation of a supermolecular structure at various stages of synthesis[123]. The product of the early stages of polycyclotrimerisation has a globular structure, and then aggregation of the globules is observed, leading in the final stage (on 98% conversion of cyanato-groups) to fibrillar organisations. Parallel with the investigation of the super molecular structure of polycyanurates a study was made of the relaxation properties of the solid networks formed at various stages of conversion of the cyanato-groups of the initial monomer (di-2-*p*-cyanatophenylpropane). With increase in the degree of conversion the relaxation curves first moved to higher stresses, but after ~90% conversion of the monomer they then began to move into the region of lower stresses. The results indicate that, as the polycyclotrimerisation of arylene dicyanates progresses, and hence the network becomes more regular, the character of the supermolecular structure changes from the simplest globular form to fibrillar structures, which in turn leads to a regular variation in the mechanical properties of the cross-linked systems, to diminished brittleness and enhanced elasticity[123]. Perhaps obtaining in the usual thermosetting systems a regular network free from defects might also yield polymeric materials of enhanced elasticity and impact resistance.

Another interesting feature of, regular highly cross-linked polymers obtained by the polycyclotrimerisation of monomers containing multiple carbon-nitrogen bonds is their ability to crystallise. Although crystalline cross-linked polymers had been known[153–158], they contained as segments $M_S$ between cross-links flexible aliphatic and siloxane fragments with $M_S \geqslant 2000$, and their crystalline structure was completely analogous to that of the initial oligomers. Korshak et al.[124] have been the first to obtain highly cross-linked rigid-chain polymers (for a polycyanurate based on *p*-phenylene dicyanate $M_S = 108$) of completely different structure from that of the original crystalline monomer. A tendency to crystallise has been observed in several polycyanurates and polymelamines obtained from various aromatic dicyanates and biscyanamides[93,94,112,113]. The ability of polycyanurates to crystallise, like many other usual properties of these polymers, is a consequence of their regular structure resulting from highly selective cyclotrimerisation of the cyanato-groups in the initial monomers and almost complete quantitative polycyclotrimerisation of the dicyanates.

In order to assess the density of packing of macromolecules in cross-linked polymers and establish the influence of the chemical structure of the initial monomers Korshak et al.[122] have been the first to calculate packing coefficients for such systems. Values for cross-linked polymers of diverse structure are found to lie within the narrow limits 0.673–0.698, close to the mean value 0.681 for linear polymers[159]. An exception is provided by polycyanurates containing dimethylsiloxane segments of various lengths

between junction points of the network



These polymers have abnormally low packing coefficients $K$, which decrease as $M_S$ increases, from 0.651 to 0.587 with increase in $n$ from 0 to 100.[131,152] Special determination on these systems showed zero porosity, so that these abnormally low packing coefficients can be attributed to loose packing of the macromolecules of the organosilicon polycyanurates[131,152].

Control of the chemical nature and length of the network segments has permitted monitoring of the influence of these parameters on the properties of cross-linked polymers obtained by the polycyclotrimerisation of monomers containing multiple carbon–nitrogen bonds, which in turn has led to directed improvement of the heat resistance, thermal stability, and physicomechanical indices of polymeric materials.

Besides aromatic polycyanurates and polymelamines, polymers of this type have been synthesised from organofluorine, organoboron, and organosilicon monomers. The presence of perfluorinated segments between cross-links in the structure of polycyanurates leads to glass points from −40 to +350°C.[116,134] Such polymers can be used as thermostable films, adhesives, and elastomers possessing improved flame resistance[134].

Polymers containing carbaborane fragments possess several unique properties, among which the most interesting is the high carbon residue at high temperatures (up to 1000°C), often with retention of definite strength properties[115,135,137,141,142,149]. Korshak, Andrianov, et al. have prepared organosilicon polycyanurates[127–131,145–147,152], which have glass points from −120 to +180°C depending on the length of the siloxane chain between the cross-links. These polymers possess high thermal stability with a wide temperature range of the hyperelastic state, from −120 to +340°C, i.e. up to the temperatures at which they begin to degrade[145–147,152].

The influence of the length of network segments on the properties of polycyanurates and polymelamines has been investigated also on the products of the polycyclotrimerisation of oligoarylates, oligo(arylene sulphones), and oligoamides with terminal cyanato- or cyanamido-groups[64,65].

A method based on the statistical theory of hyperelasticity has been used to examine the main parameters of the network structure of polymers obtained from oligodicyanates[131,152]. It involves measuring the stress relaxation at constant deformation on uniaxial extension of the polycyanurate films. The experimental number-average molecular masses and concentrations of active chains in unit volume of the cross-linked polymers are similar in magnitude to those calculated theoretically, which is evidence of selectivity of polycyclotrimerisation and quantitative conversion of the cyanato-groups of the oligodicyanates[131,152].

The size of the cross-linked segment influences also several other physicomechanical indices of the polycyanurates. Thus polymers containing dimethylsiloxane segments show a sharp increase in tensile strength and higher elastic moduli with increase in the frequency of cross-linking[131,152]. Enhancement of tensile, bending, and compressive strengths with increase in network frequency has been found also with polycyanurates containing aromatic oligoester segments[152].

In addition to the wide modification of properties of polycyanurates and polymelamines by the use of particular initial dicyanates and biscyanamides, several studies have shown that physicomechanical and thermal properties can be varied by synthesising copolymers of dicyanates and biscyanamides with monocyanates, nitriles, cyanamides, isocyanates, and acid anhydrides[64,65,94,117,125,126,133,134,138,151,152].

The very promising outlook for polycyclotrimerisation as a method for synthesising cross-linked systems having a regular chemical structure has been demonstrated by the combined study by Korshak and his collarborators[80–99, 101–103,112–152] of the synthesis of monomers and polymers and the physical properties of cross-linked systems obtained from monomers containing multiple carbon-nitrogen bonds. Thus several polycyanurates formed from aromatic and hetero-organic dicyanates possess high physicochemical indices, considerably surpassing in this respect most known highly cross-linked rigid-chain polymers[64,112,113,122]. The majority of cross-linked polymers obtained are characterised by high heat resistance and thermal stability: they begin to lose mass at about 400°C or above; and highly cross-linked systems do not soften right up to their decomposition temperature[64,65,93,94,112,113,119,122].

From the above account it may be concluded that polymers based on cyanates and cyanamides are of great practical interest. All the reagents required to prepare the initial monomers (phenolic diols, diamines, cyanogen chloride, triethylamine, acetone) are multitonnage industrial products. The monomers are obtained at temperatures of 0–20°C by technically simple processes. The yields of cyanates and cyanamides are close to theoretical. The products possess great stability, can be stored at room temperature for a long time, and are non-toxic. Their processing into goods via an oligomerisation stage is accomplished by gradually heating the initial monomers, does not require special equipment, and can be undertaken directly at the site at which the goods are obtained from the polymers[64,65]. Materials based on polycyanurates and polymelamines (adhesives, coatings, filled plastics, insulating compounds, etc.) possess excellent physicochemical properties and thermal stability[64,65,93,94,112,113,122,132–152].

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