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The formation of linear and three-dimensional polymers by polycyclisation

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ABSTRACT. **The influence of the functionality of the starting materials, their isomerism, method of synthesis, process kinetics, and other factors on the structure (microstructure of copolymers), molecular weight, degree of cyclisation, and properties of polymers obtained by reactions involving the polycyclisation of polyfunctional monomers and oligomers are analysed.**

The bibliography includes 77 references.

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I. Introduction

Polycyclisation (polycyclocondensation) is a method of synthesis of numerous new generation polymers, mainly highly thermostable and heat resistant.[1] A characteristic feature of polycyclisation is that the reactions leading to the formation of macromolecules (both linear and network) are accompanied by the formation of small rings—intramolecular cyclisation. Such cyclisation can follow polymer formation or can be kinetically indistinguishable from the latter. One should not think that polycyclisation is yet another method of synthesis of polymers different from polymerisation and polycondensation, because these two processes constitute the basis of the formation of polymers. The essential feature of polycyclisation is that at the beginning of polymerisation or, more frequently, polycondensation one obtains macromolecular precursors (called in a number of instances, incorrectly in our view, pre-polymers), and then (frequently simultaneously) cyclic structures are produced:

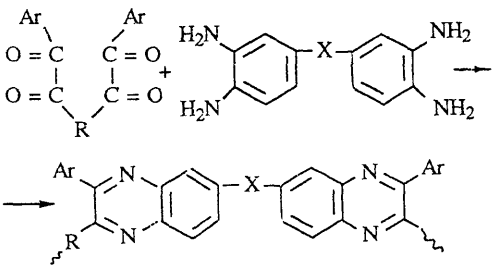
Monomer (s) ⟶	Intermediate polymer ⟶	Final polymer–
Oligomer (s)	Precursor	polyarylene,
Polymer (s)		linear or network
		polyheteroarylene

The final products, containing cyclic fragments which determine the physicochemical and operational properties of polymers, can be obtained also by the traditional procedure involving the initial synthesis of the corresponding monomers or reactive oligomers, incorporating such rings, and then the synthesis of polymers from the latter by the usual methods. This procedure is widely used for the creation of particular polyheteroarylenes, but it is important to note that these processes are no longer polycyclisation. The properties of the polymers formed can then differ markedly from those of the analogous polymers produced by polycyclisation.

Thus the simple interchange of the sequence of reaction stages ("components") alters the "sum", which is understood as the final polymer, its structure and properties. The present review is devoted to the analysis of the influence of various factors (the structure of the monomers and reaction conditions) on the formation during the polycyclisation process of polymers with a definite set of properties.

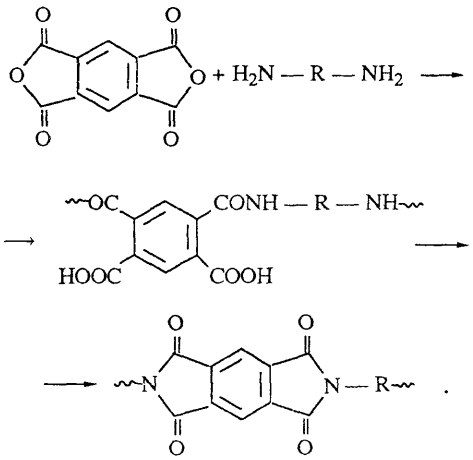
II. Polycyclocondensation of polyfunctional monomers

A series of new polymers of practical values has been obtained by polycyclisation. Here it was found essential to re-examine certain postulates of the chemistry of high-molecular-weight compounds, which have already become classical, in particular the question of the interrelation between the functionality of monomers and the structure (linear or three-dimensional) of the polymers formed.[2] If the monomers used in polycyclisation processes contain, apart from the functional group necessary for the propagation of the polymer chain, also other functional groups capable of forming cyclic fragments, linear polymers are formed also from polyfunctional polymers (trifunctional and tetrafunctional). One of the striking examples of this kind is the synthesis of polyquinoxalines from two tetrafunctional monomers: tetra-amines and tetraketones. In the presence of two amino groups in the *ortho*-positions and keto-groups in the α- positions, arranged in pairs, the six-membered quinoxaline ring is readily formed and linear high-molecular-weight polyquinoxalines are formed quantitatively under mild conditions:

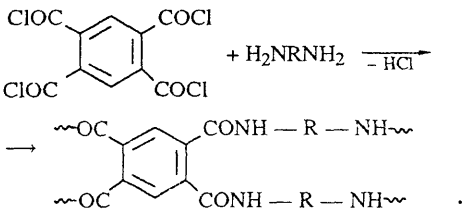


The formation of polyimides from diamines and tetracarboxylic acids is more complex and more ambiguous in this sense. When derivatives of the acids such as dianhydrides, formally regarded as bifunctional monomers, are used, linear high-molecular-weight

polyamidoacids are formed, but this entails the "appearance" of a further two functional groups—carboxy-groups, which participate in the formation of the imide ring in the next stage:



If one begins with derivatives of tetracarboxylic acids with two pairs of carboxy-groups in the *ortho*-positions, such as their acid tetrachlorides, then one obtained cross-linked network polymers instead of linear polymers:



(Naturally if the reaction centres in the polyfunctional monomers are located in positions unfavourable for ring closure, then the polymer formation reaction obeys the "classical" rules of polymer chemistry.)

Network polymers based on traditional bifunctional monomers can also be obtained by polycyclisation, for example by the polycyclotrimerisation of various monomers, which we shall consider below.

Polycyclisation processes proceed in one or several stages, frequently with formation of the corresponding intermediate polymer. As already mentioned, they are a variety of the polymerisation and polycondensation methods of synthesis of polymers and obey many of the rules governing the latter.

We shall consider certain features of linear polycyclisation occurring via the polycondensation mechanism. Thus, when the polycyclisation reactions consist of two stages, the mechanism and kinetics of the first stage hardly differ from those of the corresponding polycondensation reactions leading to the formation of linear polymers—frequently polyamides with other functional groups. Such processes can be reversible or irreversible, equilibrium or non-equilibrium, and are accompanied by the formation of low-molecular-weight products or there are no products. The methods used to carry out the reaction are also similar, although polycondensation in solution is so far usually employed for this purpose. The single stage polycyclisation reactions widely used at the present time, in which the propagation of the polymer chain and intramolecular cyclisation are kinetically indistinguishable, have much in common with the usual polycondensation processes.

The specific features of polycyclisation are manifested in the stage of the cyclisation reactions proper, which can be defined in a general form as reactions in polymer chains. Since many of the polymers formed under these conditions are infusible and insoluble, the processes are carried out on solid polymers. The main procedure involves heat treatment of the intermediate polymers over a wide temperature range. The effectiveness of the process is inferred from the degree of cyclisation of the final polymer. The "kinetic inhibition" with increase in the degree of cyclisation has been noted. It is due to the increase in the glass point of the polymer. A similar phenomenon has been observed in a number of studies in relation to the cyclisation of poly-*o*-carboxyamides, polyhydrazides, polyhydroxyamides, etc.[3–5]

At the same time, cyclisation frequently proceeds effectively in the vitreous state of the polymer and this permits the claim that the influence of the glass point of the polymer being cyclised (noted above), although significant, does not determine fully the kinetics of the cyclisation and the degree of completion of the process. The chemical structure of the cyclised group and the reactivity of the fragments which they contain are very important. The intramolecular cyclisation of polyamidoacids and their esters, which proceed effectively in the solid state, may serve as a clear example.[6–8] Although the esters are not degraded on conversion into imides, in contrast to the acids, the degree of polymerisation of the polyimides synthesised by the cyclisation of polyamidoacid esters is usually higher than that of the corresponding polyimides obtained by the thermal cyclisation of polyamidoacids. However, by virtue of the lower reactivity of the ester group compared with the carboxy-groups, the cyclisation of polyamidoacid esters is usually completed at higher temperatures in order to achieve complete conversion.

Table 1. The properties of polyimides obtained by thermal and chemical cyclisation.

Property	Ph/PM		E/PM		Ph/BP		Ph/Bphn	
	T	Ch	T	Ch	T	Ch	T	Ch
E, GPa	—	8.0	2.7	4.0	8.6	4.6	5.4	5.0
σ, MPa	—	162	112	139	321	129	154	143
ε, %	—	15	35	56	23	7	4	40
CTR, p.p.m. K^{-1}	—	5.5	31.9	22.3	31.9	8.2	18.1	25.3

Note. Ph = *p*-phenylenediamine; PM = pyromellitic dianhydrides; E = di(4-aminophenyl) ether; BP = dianhydride-3,3′,4,4′-tetracarboxylic acid; Bphn = dianhydride of benzophenone-3,3,′4,4′-tetracarboxylic acid; *E* = modulus of elasticity on extension; σ = tensile strength; ε = elongation at rupture; CTR = coefficient of thermal expansion; T = thermal cyclisation; Ch = chemical cyclisation.

Together with the degree of cyclisation, an important factor for the attainment of the optimum properties of the polymers formed on polycyclisation is their molecular weight.[9] In this sense, thermal cyclisation of the intermediate polymers, both in the solid state and,

especially, in solution, is in many instances complicated by various side reactions and leads to a decrease in molecular weight, which impairs the deformation-strength properties of the final polymeric materials. In order to eliminate or suppress the undesirable processes, the so called chemical methods, in which the aim is to carry out catalytic cyclisation under milder conditions, have been frequently used in recent years.[10–13] It is then possible to reduce to a minimum the degradative processes and to obtain polymers of a much higher quality. The improvement of the deformation-strength characteristics (Table 1) is in our view mainly a consequence of the higher molecular weight of the polymer.

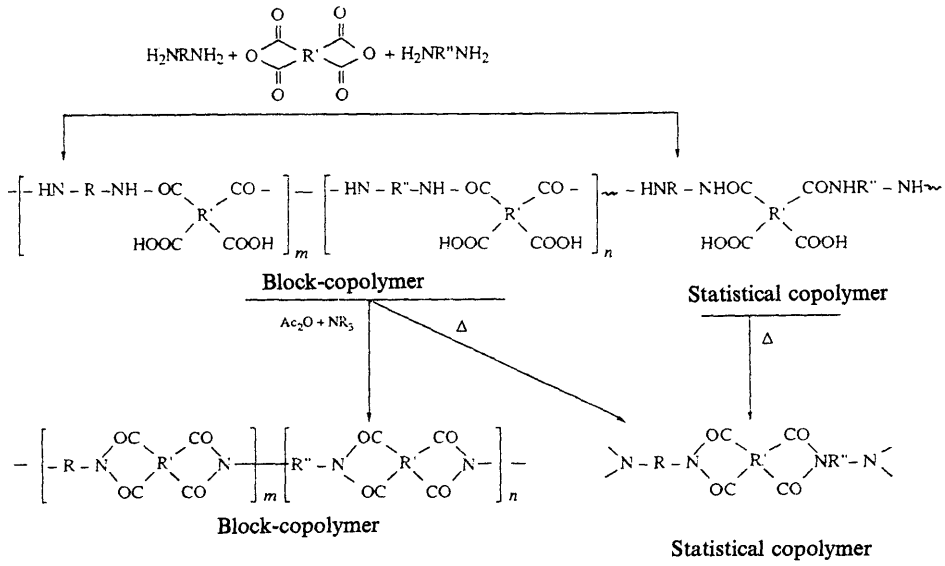
Thus in the synthesis of polymers by polycyclisation it is necessary to endeavour not only to achieve a quantitative degree of cyclisation, on which depend primarily the thermal stability, heat resistance, and other physicochemical properties of the polymers, but also it is essential to maintain a high molecular weight, which is important for the attainment of optimum deformation-strength properties of the corresponding polymeric materials. It is likewise necessary to bear in mind that the cyclisation conditions affect also the morphology of the polymers formed. Thus it has been noted that the polyimides obtained by thermal cyclisation are much less soluble in organic solvents than the corresponding polymers obtained in the presence of catalytic systems.[9] The densities of the former are lower than those of the latter.[13]

There is no doubt that the relations obtained for the cyclisation of polyamidoacids to polyimides are in general valid also for many other polymers formed as a result of the intramolecular cyclisation of intermediate polymers.

There is undoubted interest, from the standpoint of the recognition of the specific features of the polycyclisation and formation of polymers with the required set of properties, in studies directed towards the elucidation of the stereochemical and conformation characteristics of this process,[14,15] its statistics,[16] etc. However, it may be that the difficulties associated with the cyclisation processes on high-molecular-weight polymers noted above have in fact been responsible for the preferential development of single-stage polycyclisation processes, particularly in the preparation of thermoplastic and/or soluble polyheteroarylenes.

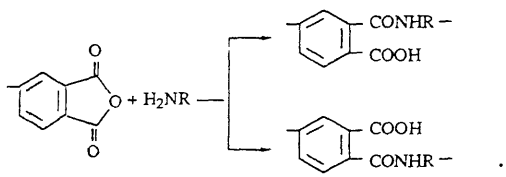
The polymers obtained by the single-state method, frequently in the presence of catalysts, are characterised by a high molecular weight and a virtually quantitative degree of cyclisation. Polycyclisation in various solvents† (high boiling organic solvents, polyphosphoric acid, etc.) have come to be most widely used. Depending on the solubility of the polymer formed, its synthesis proceeds throughout the process in solution[17,18] or is accompanied by the precipitation of the polymer at a specific stage (precipitation polyheterocyclisation), which does not prevent an increase in the molecular weight and/or degree of cyclisation of the polymer.[19–21]

Additional data concerning the specific features of polycyclisation have been obtained in the study of the formation of linear copolymers with a cyclochain structure.[22,23] In a multistage synthesis, the microstructure of such copolymers (statistical, block, or alternating) is laid down in the first stage of the reaction—the formation of the polymer chain—and is determined by factors, familiar from the polycondensation theory, namely the reversibility of the polycondensation, the ratio of the reactivities of the comonomers, the relation between the reactivities of the two reaction centres of the intermonomer, and the reaction conditions. However, by virtue of the characteristics of the second polycyclisation stage (see above), the microstructure of the copolymers can be retained or can break down. Thus in the thermal conversion into imides of copolyamidoacids with various microstructures, accompanied by their degradation, only statistical copolyimides are almost always formed. On the other hand, as a result of the catalytic cyclisation of copolyamidoacids, where there is no degradation of the polymers, the microstructures of the copolyimides formed do not differ from those of the initial copolymers:



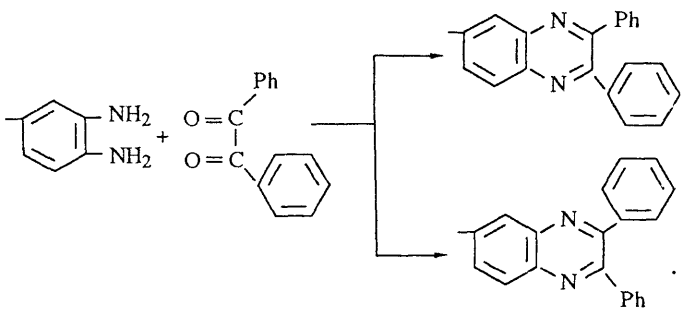
† There has been a recent growth of interest also in the synthesis of polyheteroarylenes in the melt and in the solid phase.

Proceeding now to the analysis of the relation between the physical and chemical structures and properties of polymers obtained by polycyclisation, we may note that the general laws of polymer chemistry are naturally valid for them too. The most important factor is the nature of the monomers and hence the structure of the polymers formed. The influence of various types of isomerism in polyheteroarylenes is unusual. Thus, in view of the multiplicity of the reaction centres in the monomers used in polycyclisation and a not unduly striking difference between their reactivities, the intermediate and final polymers formed contain various isomers which affect the physical structure and properties of the polymers. Striking examples are provided by the syntheses of polyamidoacids from the dianhydrides and diamines[24–26] and of polyphenylquinoxalines from bis-α-diketones and tetramines.[27–29] In the former case, the possibility of nucleophilic attack by the amine on both carbonyl carbon atoms of the anhydride ring is responsible for the formation of two isomeric fragments in the chains of the polyamidoacids:

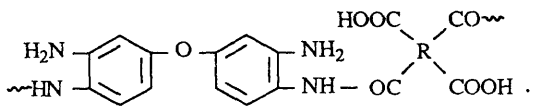


It is striking that it is not possible to obtain only one isomer by introducing different electron-donating and electron-accepting substituents even when there is a significant difference between the electrophilic properties of the above carbon atoms.[25] The heterounit structure arising in the polyamidoacids as a result of such isomerism affects their stability towards degradation.[25]

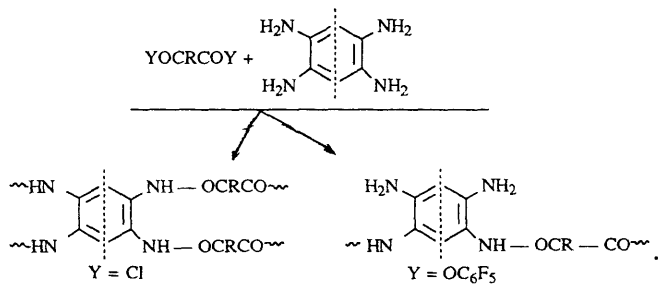
Similar factors are responsible for the appearance of isomeric fragments in the chains of polyphenylquinoxalines and hence for their amorphous structure and inadequate heat resistance, which may affect the strength parameters of the materials formed from them:



The nearly statistical distribution of different isomers in polyphenylquinoxalines as well as in many polyamidoacids is probably caused by the similar electrophilic properties of the corresponding carbonyl carbon atoms. At the same time even comparatively small differences between the basicities of the *p*- and *m*-amino-groups in tetramines (differing by approximately one order of magnitude) are found to be sufficient to ensure their selective acylation by carboxylic acid anhydrides with formation of virtually only the isomer having amide groups in the *para*-position relative to the bridging electron-donating group;[30,31]

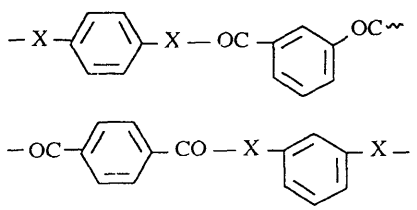


This example is also of interest because, by varying the reactivity of the acylating agent (the nature of its leaving group), it is possible to obtain both linear and network polymers. Thus, when carboxylic acid chlorides are used (as more reactive derivatives), the reaction involves all four amino-groups even under mild conditions and leads to gel formation. On the other hand, linear high-molecular weight polymers are formed on polycondensation of tetramines and activated esters (nitrophenyl, pentafluorophenyl) of dicarboxylic acids:[32]



A similar picture is observed also in acylation by tetracarboxylic acid dianhydrides. Depending on the reactivity of the latter, the mutual influence of the anhydride groups, and the nature of the bridging groups, both linear polyaminoamidoacids (reactions with relatively unreactive dianhydrides having bridging electron-donating groups—see above) and three-dimensional polymers (when the reactive pyromellitic dianhydride is used) are formed.

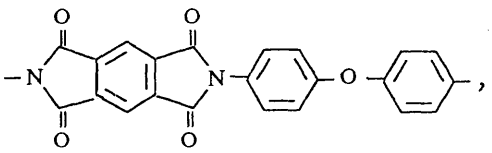
Another type of isomerism, which is manifested in an extremely unusual manner in polyheteroarylenes, is caused by the position of the bridging groups in the polymers relative to the heterocycle. In principle, this question is not new as regards heterochain polymers,[33,34] although in our view it has not been adequately considered. Thus the polyamide formed from *p*-phenylenediamine and isophthalic acid and correspondingly the polyarylate derived from hydroquinone and isophthalic acid are more crystalline than the isomeric polyamide derived from *m*-phenylenediamine and terephthalic acid and the isomeric resorcincol polyterephthalate:

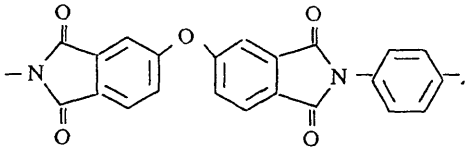


(a) X = NH
(b) X = O .

On the other hand, in the case of polyheteroarylenes the difference between the structures and properties of a series of isomeric polymers, containing bridging groups in the residues of a

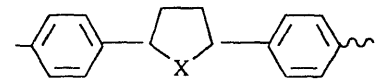
particular monomer, is in many respects associated with the different capacities for condensation of the heterocycle with fragments other than benzene rings.[35] Thus the polypyromellitimide derived from di(4-aminophenyl) ether and the polyimide obtained from *p*-phenylenediamine and di(3,4-dicarboxylphenyl) ether contain the same number of various fragments, but in the former there is a condensed system comprising three rings, while in the latter the polymer containing the phthalimide rings is a system comprising only two condensed rings:

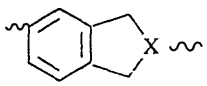


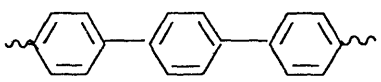


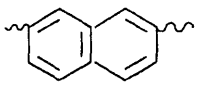
As a result, the first polymer is significantly superior to the latter as regards heat resistance (by 50–70 °C),

It is noteworthy that the degree of condensation of the heterocycle and other fragments of the macromolecule is a most important factor, which determines many properties of polyheteroarylenes. The latter can be arbitrarily divided into two types.[36] In the first, the heterocycles are joined by single bonds to other groups and they can be regarded as analogues of polyphenylenes. In the second, the heterocycles are condensed with other elements of the polymer chain and polynaphthalene may be regarded as their analogue. The limiting case of polymers of the second type is ladder polymers:



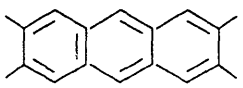






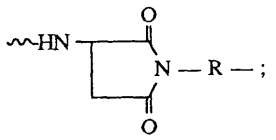
X = heteroatom

(I)

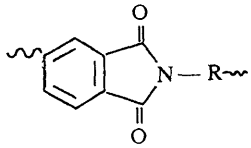


(II)

Polymers of the first type (I) include poly-1,3,4-oxadiazoles, polytriazines, and polythiadiazoles, while those of the second type (II) include aromatic polyimides, polybenzimidazoles, polyphenylquinoxalines, and polybenzoxales. One may quote examples where the heterocycle enters into the composition of both types of polymers. Thus poly(asparagine imides) (A) contain isolated imide rings, in contrast to the aromatic polyimides (B), the characteristic feature of which is systems comprising two, three, and more condensed imide rings, benzene rings, and other heterocycles:



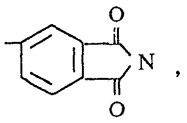
A

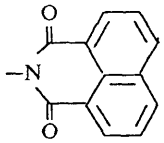


B

Naturally, by varying the degree of condensation of the benzene rings and the heterocycles, it is possible to vary different properties of the polymers and primarily their heat resistance.

An important factor which determines the creation of linear cyclochain polymers with the required set of properties is the size of the heterocycle in such polymers. Polyheteroarylenes with five-membered heterocycles are commonest. They include polybenzimidazoles, polybenzoxazoles, polybenzothiazoles, poly-1,3,4-oxadiazoles, and the majority of polyimides. However, representatives containing six-membered imide rings, i.e.





whose closure proceeds much more readily than that of the analogous phthalimide rings, are known for the polyimides. A specific feature of the formation of polyimides with six-membered rings is in fact that the polycyclisation cannot be arrested at the stage of the intermediate polymer—the polyamidoacid. A striking example of polymers with six-membered rings is polyphenylquinoxalines. In this case too polycyclisation proceeds in such a way that the polymer chain propagation and the closure of the six-membered quinoxaline ring occur almost simultaneously. The greater ease of closure of the six-membered ring compared with the five-membered ring (exceptions are naturally known) predetermines a series of advantages in properties, particularly the increased chemical stability. The high degree of cyclisation should have a positive effect also on the thermal stability of the polymers.

Hitherto, very many polymers have been obtained by polycrystalline reactions, polyimides being commonest among them. It is noteworthy that this is apparently due to the successful combination of thermal and mechanical properties in such polymers, the availability of the monomers, and the comparative simplicity of the synthesis. As a result of this, a vigorous development of imide-containing polymers, which already belong to the class of mass-scale polymers, can now be observed. New types of monomers for polyimides are being created and new methods of their synthesis (including catalytic methods) are being developed.

III. Polycyclotrimerisation and other methods of synthesis of polyheteroarylenes

A second important variety of polycyclisation involves the formation of linear and network poly(hetero)arylenes by the polymerisation method. This procedure has in our view a series of characteristic features, which distinguish it from both the traditional

methods of synthesis of polymers and from polycondensation. In this case polycyclic polymers are synthesised in several ways.

The first involves the polymerisation (copolymerisation) of different bi- and poly-functional compounds (monomers, oligomers, and polymers) involving the opening of multiple homo- and hetero-bonds, leading to the formation of carbocycles and heterocycles.

The second involves polycyclisation, the elementary step of which is the interaction of small (as a rule three-membered rings) with functional groups and multiple bonds, which results in the formation of new (usually five-membered) stable cyclic structures.

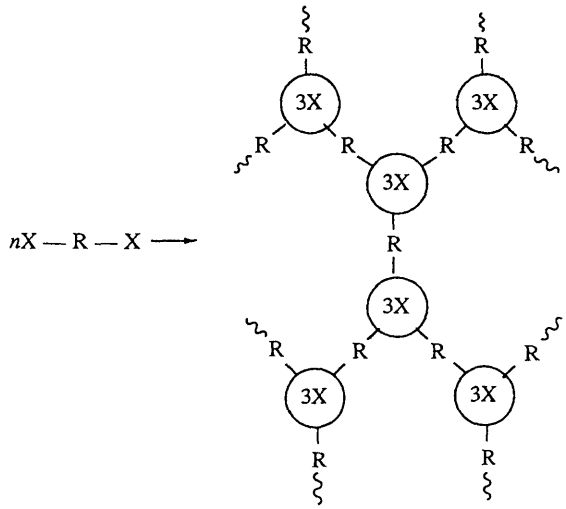
Examples of the procedures of the second type of polymerisation polycyclisation is provided by the copolymerisation of two different unsaturated rings with formation of a new cyclic structure (reactions of the Diels–Alder type), as well as the opening of unstable four-membered rings (for example, uretdione rings), with formation of stable six-membered fragments. The polycyclisation procedures listed above do not apparently exhaust the entire wide variety of the possible different versions of these reactions.

One of the most important differences between the polymerisation of different compounds with the opening of multiple bonds or strained rings and polycondensation consists in the absence of segregation of any products during the reaction. This factor determines the principal features of this polycyclisation method and makes it possible to solve the difficult problem of the processing of polycyclic polymers, which exhibit as a rule an enhanced heat resistance and thermal stability. Here not only linear cyclochain polymers but also network heat resistance structures can be made into articles directly from liquid or low-melting monomers and oligomers.

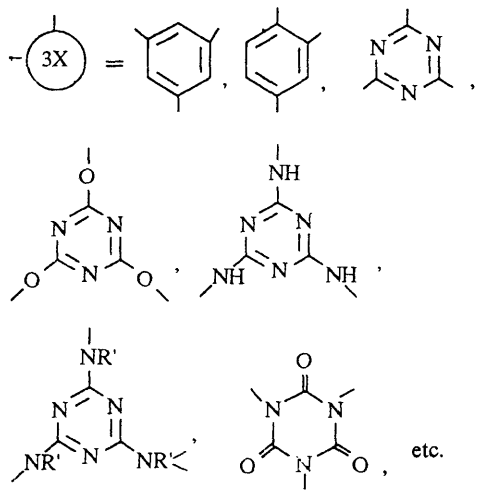
The cyclic fragments formed as a result of polycyclisation via the polymerisation mechanism may be four-, five-, and six-membered carbocycles and heterocycles, for example, polymers containing in the chain rings such as those of uretdione,[57] imino-derivatives of uretdiones,[38] 1,2,4-oxodiazole,[39] iminohydantoin,[40] oxazoline,[41], isoxazoline,[42] oxazolidinione,[43] iminooxazolidinone,[44] 1,3,5- and 1,3,4-phenylenes,[45] pyridine,[46] 2,4,6-triazine,[47] cyanurate,[48] isocyanurate,[47] etc.

Our aim was not to consider in a short review the numerous studies in this field and only certain most characteristic examples of such reactions will be surveyed with emphasis of their specific features. Polycyclotrimerisation is one of the reactions investigated in greatest detail.[47]

The polycyclotrimerisation of monomers (or oligomers and polymers) containing two and more functional groups with multiple bonds between homo- and hetero-atoms should lead to the formation of hypothetical network polymer structures with the same internodal fragments and stable six-membered aromatic carbocycles and heterocycles as network nodes:



where X = $-C\equiv CH$, $-C\equiv N$, $-O-C\equiv N$, $-NH-C\equiv N$, $-NH-C\equiv N$, $-N\equiv C=O$, $-N=C=N-$, etc,

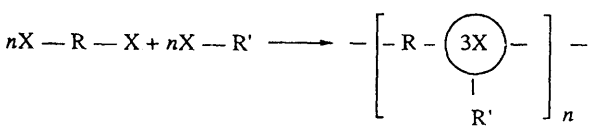


In the presence of thermostable aromatic or organoelement groups as internodal fragments in such polymers, one may expect a high thermal stability of these blends. In the case of small intermodal fragments (M_c), the thermal stability of such dense network structures should also be high.

It is noteworthy that the advantages of the polycyclotrimerisation reaction can be utilised provided that a number of conditions are fulfilled. For example, the reaction must take place stereoselectively with virtually complete conversion of the functional groups, since only in this case does the polymer structure remain undisturbed by the fragments formed as a result of side reactions of some kind or by residual non-cyclised functional groups.

There are literature data[47] on polymers obtained by the polycyclotrimerisation of compounds such as ethynyl derivatives (−R−C≡CH), nitriles (−R−C≡N), cyanates (−R−O−C≡N), isocyanates (−R−N=C=O), unsubstituted cyanamides (−R−NH−C≡N), *N*-substituted cyanamides (−R−NR′−C≡N), and carbodiimides (−R−N=C=N−R−). Other types of compounds containing multiple bonds between different atoms may be achieved in the future.

Polycyclotrimerisation is one of the examples confirming the necessity for the revision of certain classical postulates in the chemistry of high-molecular-weight compounds. Thus, whereas bifunctional monomers, for example diisocyanates form linear polyureas or polyurethanes on reaction with bifunctional amines or diols, the polycyclotrimerisation of the same diisocyanates affords dense network polymers with a regular chemical structure, illustrated in the polycyclotrimerisation scheme presented above. In "classical" polycondensation, the introduction of a monofunctional monomer leads to chain termination and the restriction (regulation) of the molecular weight of the polymer.[2] On the other hand, in polycyclotrimerisation the introduction of a monofunctional monomer can yield a linear polymer in accordance with the following scheme:



The similarity of a series of fundamental features of gel formation in the polycyclotrimerisation of dicyanates and diisocyanates, i.e. polymers of different classes, as well as the study of the molecular weight characteristics in the course of the reaction up to the gel point and of the sol fraction beyond the gel point made it possible to formulate general ideas concerning the formation of the topological gel structure in this method of synthesis of network polymers.[49−52] In a number of instances, the experimental data are close to the theoretical postulates[53] developed for the gel formation process in polycyclotrimerisation reactions. The existing differences can be explained by the failure of the theory to take into account the macrocyclisation associated with the appreciable branching of the macromolecules.[49,53]

The traditional methods of synthesis of network polymers from monomers, oligomers, or polyfunctional polymers are complicated by factors such as the differences between the reactivities of the functional groups which do not lead to branching, the proportions of the initial oligomers and polymers having different molecular weights and different types of functional groups, which are difficult to regulate, and many others. All this hinders the synthesis of network polymers with a chemically regular structure.

In the synthesis of polymers by the polycyclotrimerisation reaction, it is possible to overcome most of these difficulties and to obtain regularly cross-linked (at the molecular level) polymers. In this method of synthesis, the reaction of each functional group is accompanied by the branching of the macromolecule with the exception of the "losses" of the functional groups in macrocyclisation.

Detailed study of the gel formation process and of the molecular weight characteristics has shown[49−53] that the macrocyclisation reaction may be regulated by varying the conditions in the synthesis of the polymers. This determines in its turn the change of their topological structure. The possibility of influencing the topology (i.e. a higher level of structural organisation than the molecular level) of the networks leads to greater prospects for the directed regulation of the physical properties of network polymers.

An interesting feature discovered for a number of polymers obtained by polycyclotrimerisation is their capacity for crystallisation.[54−56] In the known[57−61] crystalline network polymers, the internodal segments are flexible aliphatic and siloxane fragments with M_c not below 2100.[57−59] The crystal structures of the cross-linked polymers is similar to that of the initial crystalline oligomers and is in essence determined by the latter.

Rigid-chain dense network polymers with a crystal structure completely different from that of the initial crystalline monomer, have been obtained in the case of polycyanurates. In other words, the crystal structure of the network polymer is formed in the course of its synthesis. In the study of the polycyanurate based on 1,4-dicyanatobenzene (M_c = 108), it was shown by X-ray diffraction that, by regulating the conditions in the synthesis, it is possible to obtain polymers with the same chemical structure but a different physical structure.[54]

A tendency towards crystallisation has been observed also in other polycyanurates based on aromatic dicyanates[47,55,56] and also in certain dense network polymers with a different chemical structure, obtained by the cyclotrimerisation of monomers with C−N multiple bonds.[47] By an appropriate selection of the initial monomers and the cyclisation conditions, similar structures can apparently be obtained in a highly crystalline state.

The capacity for crystallisation of network polyheteroarylenes obtained by polymerisation polycyclisation as well as many other unusual properties of these polymers are a consequence of their regular structure achieved as a result of the highly selective cyclisation of the functional groups of the initial monomers and its virtually quantitative completion.

When a series of polycyanurates based on dinuclear aromatic dicyanates differing in the nature of the bridging group between the phenyl groups are studied systematically, the most striking feature is that the polymers of dicyanates having a flexible bridging group and small substituents at the central carbon atom have anomalously high specific impact strengths (up to 30 kJ m^{-1}), in contrast to all the known dense network aromatic polymers. Furthermore, block specimens of aromatic and many organoelement polycyanurates have a high bending strength, a Brinell hardness of 100−170 MPa, a tensile strength of 100 MPa, a modulus of elasticity in the range 3000−5000 MPa, and a relative elongation on rupture of 3−6%. These polymers retain effective physicomechanical properties also at elevated temperatures.[47,48,63]

In order to elucidate the causes of the unusual mechanical properties of polycyanurates, a study was made of the formation of the super molecular structures of these polymers at different stages of their synthesis, starting with the initial monomer 2,2-bis-(4-cyanatophenyl)propane and ending with a regular network system and a virtually quantitative conversion of the functional groups.[64] It was found that, in the course of polycyclotrimerisation, the formation of a material with a globular structure is observed initially against the background of the characteristic cryptocrystalline structure of the monomer. The size of the globules did not remain constant in the course of the polymerisation and gradually diminished—from ~500 to 100−200 Å. The aggregation of globules, leading to fibrille-like formations in the final stage of the polymerisation (for a conversion of the N≡C−O group of ~98%) was subsequently observed under these conditions.

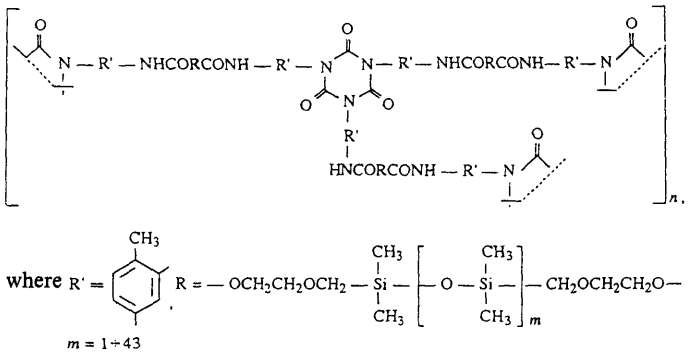
Simultaneously with the formation of the supermolecular structure of polycyanurates, the relaxation properties of the solid networks formed in different stages of the conversion of the NCO groups of the initial monomer were investigated. With increase in the degree of conversion, the relaxation curves initially shift towards higher stresses and then, beyond a ~90% conversion of the monomer, they begin to be displaced to the region of lower stresses.

The parameters of the Kohlrausch equation for different stages of the process were calculated. The data obtained show that, as the polycyclotrimerisation of aryl dicyanates advances and with the consequent increase in the regularity of the network formed, the nature of the supermolecular structure of the polymer changes, which leads in its turn to a steady variation of the mechanical properties of the network system—a decrease in brittleness and an increase in elasticity.[64] It may be that, if it becomes possible to obtain a regular defect-free network also in the case of the usual thermoreactive systems, then it will be possible to obtain also polymeric materials with increased resistance to impact influences and increased elasticity.

By introducing various organic and organoelement groups (containing B, F, and Si) into the internodal fragment in polycyanates, highly thermostable rubbers with T_g = −120 °C and highly heat-resistant systems with T_g = ~400 °C were synthesised. Carbaborane-containing polycyanates retain a large amount (~100%) of coke residues up to 900–1000 °C.[47,48,63]

Heat-resistant network polymers based on dicyanates can be designed not only by altering the structure of the initial dicyanate but also by their copolymerisation with diisocyanates, bismaleimides, oligoepoxides, and other compounds.[47,63,65–67]

The synthesis of telechelic oligomers with flexible (aliphatic and siloxane) fragments between the isocyanate functional groups has been achieved. The polycyclotrimerisation of these oligmers yielded transparent network polymers with different specifically regulated lengths between the network nodes:[68]



The combination of rigid network nodes with an aromatic framework and of flexible siloxane chains of different lengths leads to the observation of two transition temperatures. The devitrification of the siloxane and subsequently of the rigid isocyanurate fragments is reflected in the temperature variation of the tangent of the mechanism losses angle (Fig. 1).

A phase separation takes place in this system, which has been confirmed by electron microscopy and X-ray photoelectron spectroscopy data. These results show that the contents of silicon and nitrogen on the surface and within the bulk of the glass specimen differ appreciably. This shows that the siloxane phase is forced out onto the surface of the glass.[68]

Whereas the usual organic glasses have a modulus of elasticity of the order of 10^3 MPa, in this instance monomers were obtained with a wide set of moduli of elasticity, ranging from 3×10^3 to 3 MPa depending on the value of n. On the other hand, these polymers behave similarly to vitreous (elastic) polymers. This factor opens the way to new possibilities in the photoeleasticity method and in other branches of engineering.[68,69]

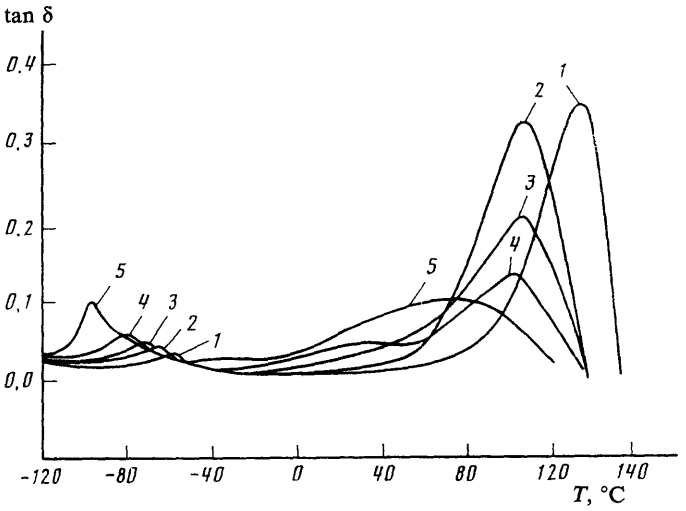


Figure 1. Temperature variation of tan δ for block specimens of polyisocyanurates with different lengths of the internodal organosilicon fragments m: *1*, 1.2; *2*, 2.1; *3*, 3.2; *4*, 5.4; *5*, 9.2.

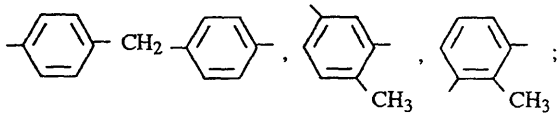
The synthesis of linear polymers and oligomers containing in the chain regularly alternating functional groups capable of entering into the polycyclisation reaction, namely ... −X−R−X−R−X−R−..., where X is the functional group and R are aromatic, aliphatic, or organoelement substituents, constitutes a promising way of designing new polymeric structures with interesting properties.

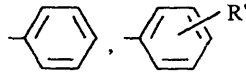
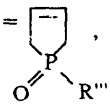
Polycarbodiimides are representatives of polymers of this type.[47,70,71] A series of infusible (T_{soft} = 50–150 °C) oligocarbodiimides, based on bis(4-isocyanatophenyl)methane and 2,4-tolylene

diisocyanate and soluble in organic solvents, have been synthesised:[47,70,71]

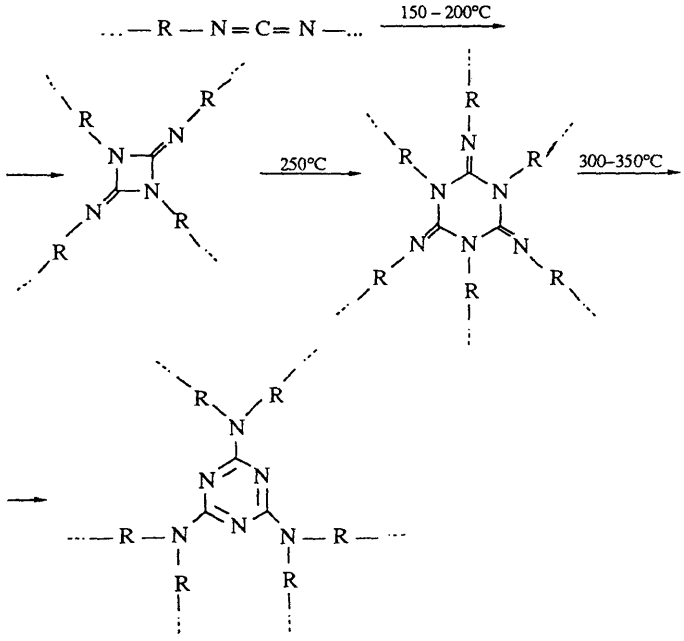
$$n\mathrm{O{=}C{=}N{-}R{-}N{=}C{=}O + 2R'{-}N{=}C{=}O \xrightarrow{\text{Cat.}}$$

$$\rightarrow R'{-}N{=}C{=}N{-}[{-}R{-}N{=}C{=}N{-}]_n{-}R' + (n+1)CO_2,$$

where R = ;

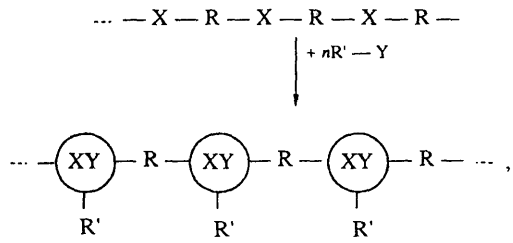
R' = ; Cat. = ; R''' = — CH_3, Ph.

Their polymerisation at elevated temperatures yields polycyclic network structures with temperatures for the onset of decomposition of 420–450 °C and temperatures for the onset of deformation of 350–450 °C:[47,72–75]



Polycarbodiimides (polyfunctional linear polymers), used as polymer matrices for high-strength heat-resistant composite materials, combine the advantages of thermoplastics and reactoplastics.[76] Oligocarbodiimides are multipurpose thermoreactive oligomers capable of being processed into various heat resistant and thermostable composite materials for use in modern branches of engineering (Table 2).[76]

Oligomers and polymers containing functional groups of the type of carbodiimide groups alternating in the chain are capable not only of homopolymerising with formation of network polyheteroarylenes but also of entering into copolymerisation reactions with various compounds to form linear cyclochain polymers in accordance with the scheme



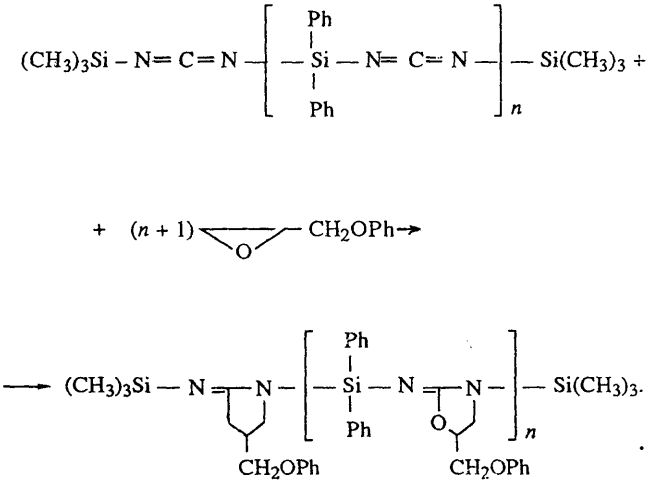
where X and Y are functional groups.

Table 2. Properties of composite materials based on oligocarbodiimides.

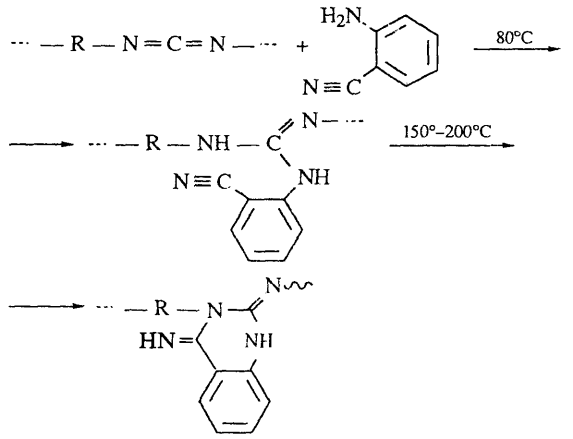
Property	T, °C	Carboplastic	Glass plastics	Adhesive
σ_{bend}, MPa	20	962	440	—
	300	466 (after 200 h)	390	—
	350	765	—	—
	400	452	—	—
σ_{comp}, MPa	20	900	400	—
ε	20	—	3.8—4.2	—
	300	—	3.9—4.7	—
tan δ	20	—	0.009—0.01	—
	300	—	0.020—0.025	—
τ_{sh}, MPa	20	—	—	15—18
	250	—	—	12—13

Note. ε = dielectric constant.

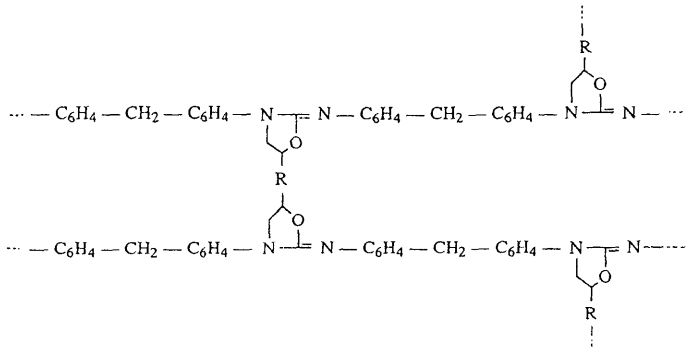
Thus polysilylcarbodiimides react with glycidyl phenyl ether to form polymers with iminooxazolidine fragments in the chain:[77]



Linear polyheteroarylenes with iminoquinazoline rings in the chain have been obtained by the reaction of aromatic polycarbodiimides with anthranilic acid nitrile:



The reaction of di- and poly-epoxides with polycarbodiimides results in the formation of network polyaminooxazolidines:[44]



It has been shown[44] that, together with iminooxazolidine fragments, other heterocyclic fragments (isomelamine, uret diimine) are also obtained as a result of the homopolymerisation of the carbodiimide groups. By altering the ratio of the carbodiimine and epoxide groups in the initial mixture of oligomers, the contents of different heterocyclic fragments in the final products were regulated.[44] In the presence of an excess of oligocarbodiimides, the uret diimine rings predominate in the polymer structure, being converted into isomelamine units at high hardening temperatures (250 °C). With increase in the content of the epoxide component in the initial mixture, reactions involving the formation of iminooxazolidine rings predominate.[44]

IV. Conclusion

Since the appearance of the first publications on polyheteroarylenes, whose synthesis is based on polycyclisation reactions, more than 30 years have elapsed, but the possibilities of this interesting aspect of polymer chemistry are far from being exhausted. New monomers are being synthesised for the preparation of polymers with a specified set of properties and new methods of their synthesis, primarily catalytic methods, are being developed. Polycrystallisation processes involving parallel-consecutive reactions proceeding via the polymerisation and polycondensation mechanisms are of interest. Processes of the monomers (oligomer)—finished article and of the RIM-technological type have attracted particular attention. Finally, recent years have been marked by the appearance of data on the synthesis of polymers of the type of polycatenanes and polyrotaxanes, which are again based on polycyclisation processes.

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