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New Aspects of Polycyclisation

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The review deals with a comparative discussion of polycyclisation processes and the prospects of the polycyclisation method in the synthesis of thermostable polymers. The bibiography includes 221 references.

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I. INTRODUCTION

During the last 10–15 years, increasing attention has been devoted in many world scientific centres to an active search for new ways of synthesising polymers containing various cyclic groups in the macromolecules. The reason for this is, on the one hand, the ease of their formation due to the favourable thermodynamics and kinetics of such reactions (particularly of the formation of five- and six-membered systems) and, on the other hand, the importance and wide variety of their applications in man's practical activities.

The rapid development of these investigations is largely related to the fact that they are directed to the solution of one of the most urgent problems in the modern chemistry of macromolecular compounds presented by modern engineering techniques now being developed, namely the creation of materials with special properties.

The development of new macromolecule formation reactions led to the appearance of the class of polyheteroarylenes—polymers the macrochains of which consist of aromatic carbocycles and heterocycles. Many of these polymers have a high heat resistance and thermal and chemical stability, useful deformation-strength characteristics, satisfactory electrical conductivity and photoconductivity, etc.

A significant role of the same reactions in natural processes can be postulated with a high degree of probability, since, for example, cyclic forms are known to be important in the structure of protein. The pathways leading to the formation and decomposition of macromolecular compounds in nature are still obscure. However, the synthesis of high polymers which are the most important biologically—proteins, higher carbohydrates, and nucleic acids—and the study of their nature, metabolism, etc. are virtually impossible without simulating the functions of these natural compounds by synthetic polymers.

Studies in the field of cyclic polymers have been very numerous; the reactions used for their synthesis have also been extremely varied. Nevertheless, despite the different nature of these reactions, they can be combined under the single concept of polycyclisation, because they lead to polymeric structures the final form of which is in fact determined by cyclisation processes. The synthesis of a cyclic polymer can occur in a single-stage or via the formation in the first stage of an intermediate linear macromolecule containing fragments capable of subsequent cyclisation.

Processes already familiar, such as cyclopolymerisation and cyclocopolymerisation, the Diels–Alder reaction, 1,3-dipolar cycloaddition, polycyclotrimerisation, and polyheterocyclisation, are also polycyclisation reactions. The reactions enumerated above can be divided into two groups: (1) processes in which chain propagation is coupled to the formation of rings, as, for example, in Butler cyclopolymerisation and in polycycloaddition reactions and (2) single- or two-stage polyheterocyclisation processes (including the synthesis of ladder and parquet structures) and polycyclotrimerisation in which the stages involving the formation of linear and cyclic polymers may be separated.

The formation of polycyclic compounds constitutes an irreversible process and may be regarded as an example of non-equilibrium polymerisation reactions. The energy relations of these reactions and also their feasibility are mainly determined by the structural changes in the chemical bonds and by the appearance of qualitatively new bond systems.

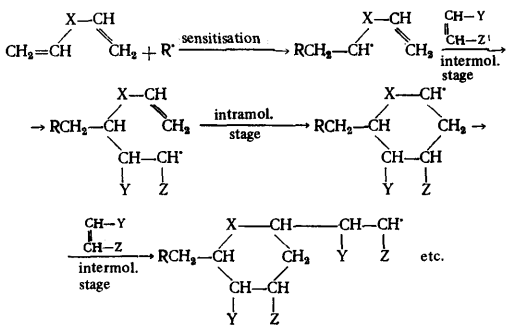
In the course of studies on these reactions, there has been a significant change in traditional ideas about functionality, introduced into polymer chemistry by its founder (Staudinger [1]), according to which it was believed that linear macromolecules can be formed only by the interaction of bifunctional polymers, while monomers with a large number of functional groups give rise to the formation of branched and cross-linked products. Polycyclisation is virtually based on tetrafunctional starting materials and leads ultimately to cyclolinear polymers.

In recent years investigators have paid increasing attention to the mechanism and kinetics of the formation of cyclochain polymers and also to a more detailed study of the properties of the latter. The results of the investigation of cyclochain polymers are described in an extensive original literature, in many review articles [2-14], and monographs [15-20].

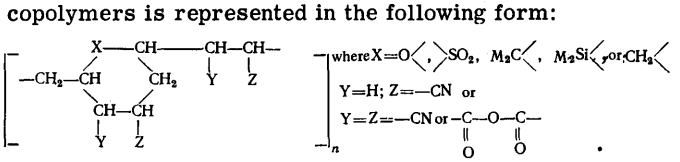
This review deals with a comparative discussion of polycyclisation processes and their influence on the properties of polymers, attention being concentrated on methods whereby thermostable polymers may be synthesised.

II. CYCLOPOLYMERISATION AND CYCLOPOLYMERISATION

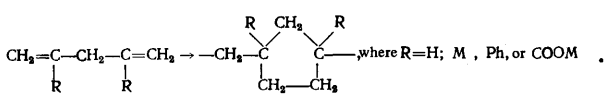
In 1951 Butler and Ingley [21] established that, contrary to theoretical predictions [1], dialkyldiallylammonium salts form non-cross-linked linear polymers and, in order to account for these results, put forward an intramolecular–intermolecular mechanism, which proved to be common to reactions involving the conversion of 1,6-dienes into cyclopolymers [22,23]. Later Butler [24,25] reported the copolymerisation of certain dienes with mono-olefins proceeding via an alternative intramolecular–intermolecular mechanism:



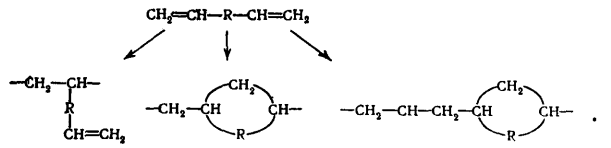
The first example of this kind was the cyclopolymerisation of vinyl ether and maleic anhydride; subsequently the reaction was extended to a wide range of dienes, alkynes and SO_2. [26-29] The general structure of the resulting copolymers is represented in the following form:



Apart from the fundamental work of Butler and coworkers, mention should be made of the wide range of studies by Marvel's school and many other investigators in which the scope of cyclopolymerisation was greatly extended and its kinetics and mechanism were investigated. Thus it was shown that symmetrical 1,5-dienes are polymerised similarly to 1,6-dienes with a high degree of cyclisation, forming polymers containing five-membered rings in the macromolecules [30-32]:

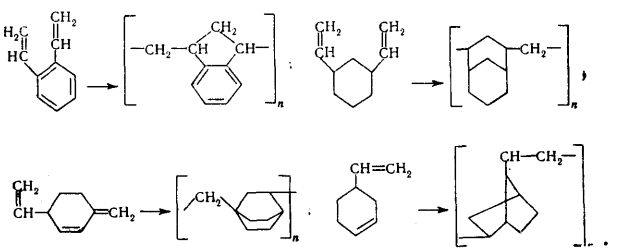


Asymmetric 1,5- and 1,6-dienes and other non-conjugated dienes are capable of homopolymerisation and cyclisation, particularly in those cases where the reactivities of the two double bonds are comparable; otherwise cyclopolymerisation, branching, and cross-linking reactions compete and the contribution of each to the overall process may vary considerably [33-35].



It was noted that the polymerisation of asymmetric dienes and the copolymerisation of two monomers have many features in common and the relation between the cyclisation and copolymerisation parameters is determined by the nature of the multiple bonds of the monomers [35]. Polymers containing different macrorings in the chain were obtained by the cyclopolymerisation of higher $\alpha\omega$-diolefins in which the double bonds are separated by 4–18 methylene groups [36-40].

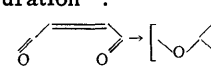
The polymerisation of dienes containing cyclic groups, which leads to the formation of bicyclic structures in the absence of steric hindrance, has been described. Thus *o*-divinylbenzene [41], *cis*-1,3-divinylcyclohexane and *cis*-1,3-divinylcyclopentane [42], and 1-methylene-4-vinylcyclohexene and 4-vinylcyclohexene [43] polymerise according to the following equations:



The formation of bicyclic and tricyclic structures is also possible in polymerisation of branched open-chain trienes and tetraenes; thus Trifan and coworkers [44] reported the synthesis of soluble polymers with a low degree of unsaturation from triallylethyl- and tetraallyl-ammonium bromides and also from 3-vinylhexa-1,5-diene.

The polymerisation of monomers containing double bonds between carbon atoms and heteroatoms, for example, dialdehydes [45-50], di-isocyanates [7,51], dinitriles [7,52], and epoxy-compounds, has been investigated in recent years.

Systematic studies on the effect of temperature, solvents, catalysts, and monomer concentration on the rate of polymerisation and on the molecular weight of the polymer formed have shown that the mode of reaction, its rate, and the polymer structure are determined not only by the nature of the monomer, but also to a considerable degree by the type of catalyst employed, its amount, the presence of water, and other factors [7]. Thus the studies of the structure of the polymer obtained by the cyclopolymerisation of maleic aldehyde by infrared and NMR spectroscopy have shown that, in contrast to cationic and Ziegler catalysts, anionic catalysts promote the formation of the *cis*-configuration [45]:

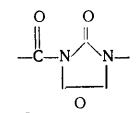
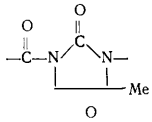
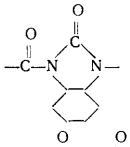
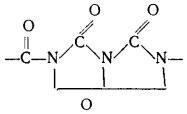
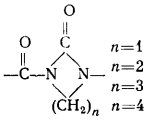


In the case of *o*-phthalodialdehyde, the amount of the *cis*-form is also determined by the catalyst employed,

decreasing in the following sequence: γ-irradiation > cationic catalysts ≥ anionic catalysts > coordination catalysts [50].

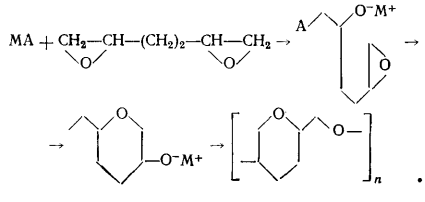
Anionic catalysts, polar solvent, and a temperature in the range between −50° and −75°C are most suitable for the cyclopolymerisation of di-isocyanates [7]. Polymers of this type are listed in Table 1.

Table 1. Cyclopolymers of aliphatic di-isocyanates [7].

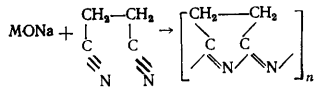
Monomer [a]	Structure of polymer unit	M.p., °C	β_{int} [b]	Solvent
1,2-Diethylene di-isocyanate [c]		365	0.85	H_2SO_4, TCE–phenol (40:60)
1,2-Triethylene di-isocyanate		287	1.35 0.56 [c] 0.72 [d]	HCOOH, DMSO, DMF, nitromethane
1,2-Cyclohexylene di-isocyanate		303	0.38	Pyridine, nitromethane, DMSO
1,2,3-Triethylene tri-isocyanate		365—400	0.28 [e]	H_2SO_4
αω-Polymethylene di-isocyanate		350 270—280 350 350		DMSO DMSO *m*-Cresol Ethylene carbonate

[a] Polymerisation in DMF between −30° and −50°C with NaCN as catalyst.
[b] β_{int} of 0.5% solution in 40 : 60 TCE–phenol mixture at 30°C.
[c] Polymerisation without catalyst.
[d] The molecular weight, determined osmometrically in nitromethane solution, is 45 000.
[e] Polymerisation in bulk at 0°C in a stream of nitrogen.
[f] In sulphuric acid.

The cyclopolymerisation of diepoxy-compounds can be achieved in the presence of a wide range of catalysts, which may include tri-isobutyl and tri-isopropyl-aluminium, PF_5–H_2O, diethylzinc, and others. Depending on the structure of the initial monomer, tetrahydrofuran or pyran rings are formed. The polymer having the highest molecular weight (η = 0.45 dl g^{-1}) but with limited solubility is that of 1,2,5,6-diepoxyhexane obtained in the presence of the $ZnEt_2$–H_2O system; the author suggested an anionic polymerisation mechanism [52]:



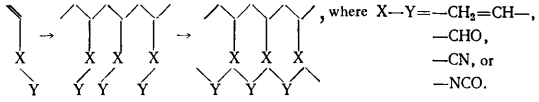
The cyclopolymerisation of various dinitriles in methanol in the presence of sodium methoxide via the mechanism



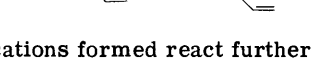
has been described [52]. n may vary, depending on the reaction conditions, from 6 to 65. There is a possibility of the incorporation in the polymeric skeleton of other structures, including the triazine structure.

Interesting results have been obtained in the study of the cyclopolymerisation of three types of bifunctional monomers with fixed (in the 2-position of the six-membered ring) double bonds [54]: (a) monomers with two C=C bonds (*o*-divinylbenzene, *cis*-1,2-divinylcyclohexane); (b) monomers containing two C=O bonds (*o*-phthalodialdehyde, *o*-formylphenylacetaldehyde); (c) monomers containing one C=O bond and one C=C bond (*o*-vinylbenzaldehyde). Although the structural characteristics of the monomers favour cyclopolymerisation, chain propagation in these polymers is different and is determined in the present case by the nature of the monomer. A stepwise chain propagation has been suggested for the cationic polymerisation of *o*-divinylbenzene; the polymerisation of monomers such as *cis*-1,2-divinylcyclohexane and *o*-phthalodialdehyde takes place, according to the author, via a concerted mechanism, while in the cationic polymerisation of *o*-vinylbenzaldehyde both mechanisms operate [53].

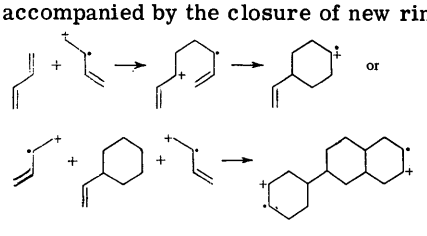
A very interesting and important aspect of the cyclopolymerisation reaction from the standpoint of the synthesis of thermostable and semiconducting materials is its employment for the synthesis of ladder and doubly cross-linked structures. Polymers of this type may be obtained both by the cyclopolymerisation of the corresponding linear polymers containing terminal multiple bonds within the framework (for example *cis*- and *trans*-polybuta-1,4-dienes [54], polyisoprenes [55,56], polyacrylonitrile [57], and polycyanoacetylene [58]) and directly by the cyclopolymerisation of diene or diyne monomers in the presence of cationic catalysts [59–65], which may be represented as follows in a general form:



The most probable mechanism of the conversion of conjugated diene monomers (or polymers) into ladder structures is one of the cationic-radical type [63,64], according to which the formation of active centres takes place via the transfer of one electron from the monomer molecule to the electron-accepting component of the catalyst A^+:



The radical-cations formed react further either with a monomer molecule or with a double bond of the polymer, this being accompanied by the closure of new rings:



It was established that identical structures are formed as a result of the cyclopolymerisation of *cis*-1,4-, *trans*-1,4-, *cis*-3,4-, and *trans*-3,4-polyisoprenes by a Ziegler-Natta catalyst[62]. At the same time, depending on the structure of the radical-cation (1,2- or 1,3-), the polymers formed have the perhydroanthracene or perhydrophenanthrene structures respectively[63,64].

In principle, cyclopolymerisation can be achieved by radical, ionic, or coordination mechanisms depending on the catalyst employed (Tables 2 and 3) and also under the influence of ultraviolet light or γ-radiation. Under these conditions, monomers containing non-conjugated double bonds show a greater dependence on the catalyst, since the different reactivities of the double bonds require more favourable conditions for the intramolecular reaction. Thus allyl acrylate reacts with azobisisobutyronitrile to form polymers containing 60 mole % of lactone groups[39], whereas anionic catalysts give rise exclusively to polymerisation involving the double bond of acrylic acid[92,93]. At the same time, a monomer such as 2,6-diphenylhepta-1,6-diene forms only a cyclopolymer in the presence of catalysts of any type[68].

Table 2. Cyclopolymerisation of symmetrical 1,6-dienes.

No.	Monomer	Polymerisation	References
1	$CH_2=CR-CH_2-CH_2-CH_2-CR=CH_2$ (R=H; Ph)	Anionic	66–69
2	$CH_2=CR-CH_2-CH_2-CH_2-CR=CH_2$ (R=COOM; COOH; COOEt, COCl; CN; $CONH_2$)	Radical Anionic	63–68
3	$CH_2=C(Ph)-CH_2-CH_2-CH_2-C(Ph)=CH_2$	Radical Anionic Cationic	68,69
4	$CH_2=CH-C(=O)-CH_2-C(=O)-CH=CH_2$	Radical Anionic	70
5	$CH_2=CH-C(=O)-O-C(=O)-CH=CH_2$	Radical	34,71
6	$CH_2=C(M)-CO-O-CO-C(M)=CH_2$	Radical	72
7	$CH_2=CH-O-CH(R)-O-CH=CH_2$ (R=H; M; *n*-Pr; Ph; CN)	Radical	73,74
8	$CH_2=CH-CH_2-\overset{+}{N}(R)(R)-CH_2-CH=CH_2$ (R=H; M).	Radical	20,75,76
9	$CH_2=CH-CH_2-N(-CH_2-CH=CH_2)-C_3H_2N_3(NH_2)_2$	γ-Irradiation Radical	77
10	$CH_2=CH-S-C(=O)-S-CH=CH_2$	Radical	78
11	$CH_2=CH-S-CHR-S-CH=CH_2$ (R=H; M; Ph)	Radical	78
12	$CH_2=C(M)-CH_2-P(=O)(R)-CH_2-C(M)=CH_2$ (R=Ph; M; Et)	Radical	79
13	$CH_2=CH-CH_2-M(R)(R)-CH_2-CH=CH_2$ (M=Sn; Ge; Si; R=M, Et; Ph)	Ziegler-Natta catalyst	80–82

Usually the cyclopolymerisation of monomeric compounds is carried out in an emulsion or in dilute solutions (at a concentration of about 0.1 M), which tends to increase the yield of soluble polymers; only a few examples of the cyclopolymerisation of monomer in the solid state are known[83].

Interesting results have been obtained in the study of the controlled and directed cyclopolymerisation of butadiene[89] and the anhydride of methacrylic acid[93,94] with radical sensitisation of the process. On the basis of data for the mechanism of free-radical polymerisation at different temperatures and after a comprehensive investigation of the specimens obtained[95–97], it was concluded that the intermolecular stage of the cyclopolymerisation process takes place stereoselectively. Reaction temperature and the predominance of one of the pyramidal structures of the strained cyclic radical formed are then of decisive importance; the axial mode of addition leads to syndiotactic stereoregularity which in the ideal case involves the presence of *ddll*-sections throughout the chain[98].

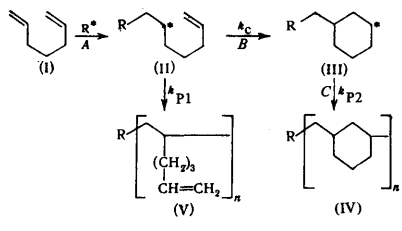
Table 3. Radical cyclopolymerisation of asymmetric dienes.

No.	Monomer	References
1	$CH_2=CH-CH_2-O-C(=O)-CH=CH_2$	83,84
2	$CH_2=CH-CH_2-O-C(=O)-CH=CHR$ (R=COOH; COOM; M)	37,85–88
3	$CH_2=CH-CH_2-NH-C(=O)-C(R)=CH_2$ (R=H; M)	84
4	$CH_2=CH-CH_2-NH-C(=O)-CH=CH-CH_3$	38
5	$CH_2=CH-O-C(=O)-CH=CH-Ph$	88,89
6	$CH_2=C(M)-C(=O)-O-C(=O)-CH=CH-M$	89
7	$CH_2=CH-O-C(=O)-CH=CH-M$	86
8	$CH_2=CH-CH_2-O-SO_2-CH=CH_2$	90,91

Numerous studies, particularly on cationic and radical systems, have been undertaken to elucidate the cyclopolymerisation mechanism. Nevertheless there is at present no theory which would yield a clear explanation of the alternation of intramolecular and intermolecular "cyclopolymerisation" steps. The latest advances in the field of anionic cyclopolymerisation and their comparison with the results quoted in a number of publications concerning radical and cationic systems, enabled Butler and coworkers[7] to make certain generalisations concerning the cyclopolymerisation mechanism.

In a general form, the cyclopolymerisation mechanism can be represented by the following scheme:

Scheme 1



where R* may be a radical, cationic, or anionic catalyst.

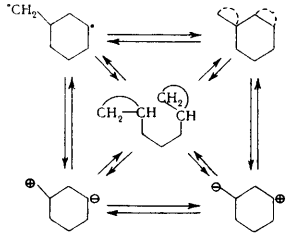
The initiator R* reacts with the terminal carbon atoms of the diene yielding the structure (II), the remaining double bond of which is involved in a further intramolecular cyclisation. The cyclic structure (III) then reacts intermolecularly with another diene molecule, this being continued until the formation of the polymer (IV). Nor can one rule out the possibility of the conversion of structure (II) via intermolecular propagation into a linear polymer (V). Therefore the most important factors here are the stability of structures (II) and (III) and the relative rates of reactions B and C.

Evidently, if the intramolecular process takes place more slowly than intermolecular reactions, the polymer will contain a large number of unsaturated groups; on the other hand, if the intramolecular process is faster than the intermolecular process, a linear and saturated polymer is obtained. It was found that the cyclisation constant k_c is then independent of the concentration of monomers and the degree of cyclisation of the polymer is determined by the ratio k_c/k_p.

Statistical calculations on the cyclopolymerisation reactions carried out by Butler and Raymond [99] for 1,6-dienes selected as model compounds showed that theoretically the monomer concentration required for the attainment of 95% cyclisation must be reduced to 0.10 M. However, in practice, polymers with 95–100% cyclisation have been obtained at a monomer concentration of 1.9–8.0 M. To account for this contradiction, the authors proposed two schemes taking into account electronic effects and steric factors; however, none of these can provide an answer to questions such as, for example, why the activation energy for cyclisation is equal to or greater than the activation energy for linear chain propagation and why the reactivity of diolefinic monomers is frequently higher than that of the analogous mono-olefins.

Therefore the only possible conclusion has now been reached that steric and entropy effects, the probabilities of the intramolecular and intermolecular steps, thermodynamic stability, and electronic effects in the transition states make a contribution to the cyclopolymerisation mechanism. The ease of cyclisation may be due to the electronic interaction between the double bonds of the 1,6-dienes or between the reaction centres formed on attack by the sensitiser and the intramolecular double bond, as can be seen from the scheme below [3,100]:

Scheme 2



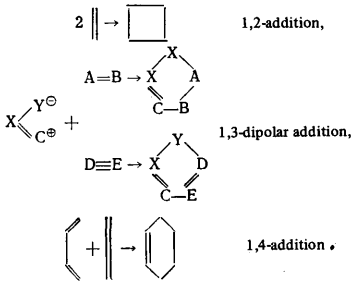
The steric resonance interaction, which constitutes the driving force of the cyclopolymerisation reaction, leads to a bathochromic shift in the ultraviolet spectra.

Similar investigations carried out on allylsilanes showed that the magnitude of the shift is satisfactorily consistent both with calculations by the molecular orbital method and with experimental observations on the polymerisation of diallyl-, [80,81,101] triallyl- and tetra-allyl-silanes [102]. The activation energy for the cyclopolymerisation of allylsilanes calculated per double bond is 9 kcal mole^{-1}. [103]

Further development of hypotheses concerning the cyclopolymerisation mechanism involves the accumulation of new data in the field of anionic processes and also the verification with the aid of new experimental techniques of the results obtained in radical and cationic systems.

III. POLYCYCLOADDITION

The use of cycloaddition reactions, which are well known in organic chemistry, for the synthesis of polymers may be regarded as a further development of methods for the synthesis of macromolecules [15];



The 1,2-addition reactions are little used in the synthesis of polymers owing to difficulties in the synthesis of the monomers and because the strain in the resulting cyclobutane ring gives rise to instability of the polymers.

1. 1,3-Dipolar Cycloaddition

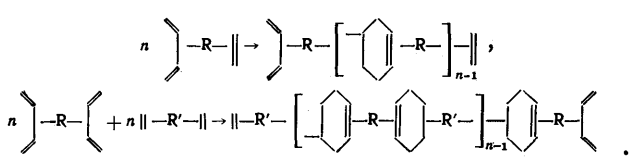
1,3-Dipolar cycloaddition reactions have found some application in the synthesis of polymers, since the bifunctional monomers are relatively easily synthesised and the majority of dipolar addition reactions take place quantitatively. Moreover, the above method is interesting because it makes it possible to introduce into the polymer chain the greatest variety of five-membered heterocyclic systems and is frequently used in those cases where other methods are less effective; if the dipolarophiles contain triple bonds, for example acetylenes or nitriles, and the dipole has an atom Y with a lone electron pair, the resulting heterocycle is aromatic (it includes a π-electron sextet), which is the reason for the high thermal stability and heat resistance of the corresponding polymers.

The main types of polymers synthesised by the 1,3-dipolar addition reaction are listed in Table 4. It is noteworthy that the formation of a mixture of polymeric products with different positions of substituents in the heterocycles is possible in many cases.

2. The Diels–Alder Reaction

The Diels–Alder reaction is achieved by the interaction of a diene and a dienophile; the latter include maleic anhydride, acrolein, vinyl monomers, and also various quinones. The Diels–Alder polymerisation can be achieved starting with monomers containing in a single molecule both diene and dienophile functional groups or via

the copolymerisation of bisdienes with bisdienophiles according to the following mechanisms [11]:



Polymers with high softening temperatures have been obtained by the interaction of 1,5-di-(9-anthryl)penta-1,4-diene and anthryl azine with benzidine-bismaleimide [11]:

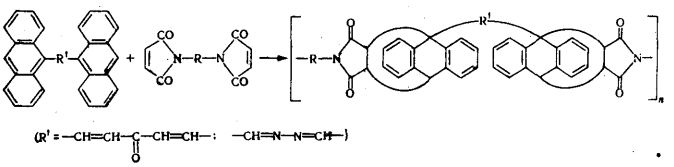
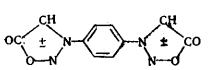
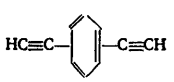
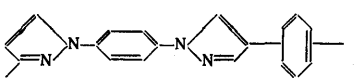
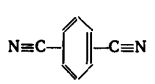
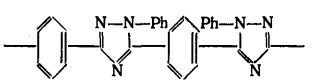
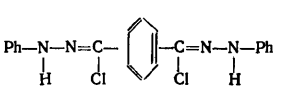
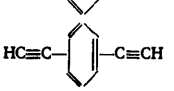
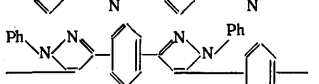
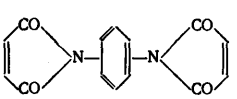
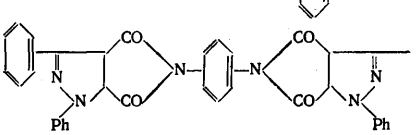
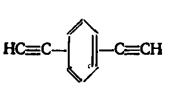
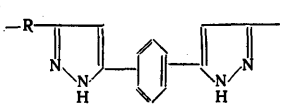
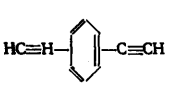
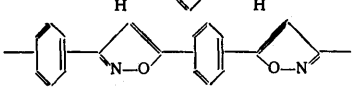
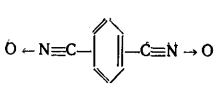
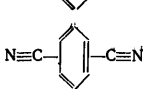
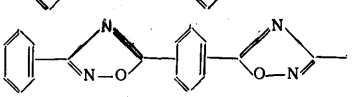
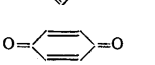
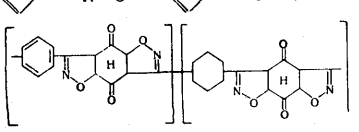
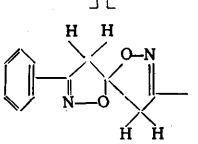
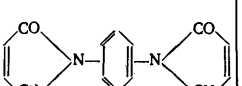
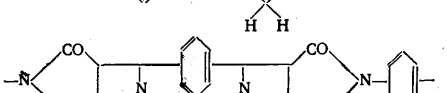
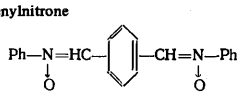
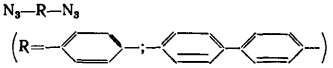
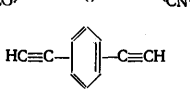
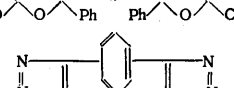
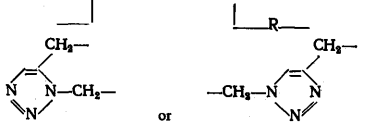
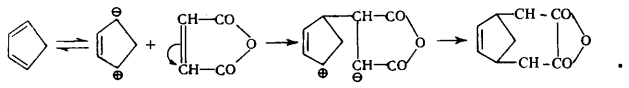


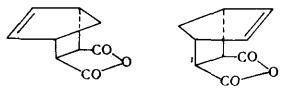
Table 4. Types of polymer synthesised by the dipolar 1,3-addition reaction.

1,3-Dipole	Dipolarophile	Polymer unit	References
Bis-sydnones 			104 105
Bisnitrileimines			
			106
			
Bisdiazoalkanes $N_2CH—R—CHN_2$ $R=(CH_2)_4; (CH_2)_3; C_6H_4.$			107
Bis(nitrile oxides)			
			108
			
	$H_2C=C=CH_2$		
Bisphenylnitrone			
			109
Diazides $N_3—R—N_3$ 			110
$HC\equiv C—CH_2—CH_2—N_3$			111
(mixed dipole-dipolarophile)		or	

Although the Diels–Alder polymerisation includes reactions of unsaturated compounds and the resulting polymers do not have a structure typical for condensation products, the synthesis of the polymer itself resembles polycondensation. In a general form, this reaction involves the π electrons of both components and the formation of a dimeric product according to the mechanism



In the interaction of cyclopentadiene with maleic anhydride, two forms of addition are possible, but the *endo*-form is produced preferentially [11]:



exo-form *endo*-form

In many cases, the synthesis of polymers with regular structures has been achieved by the Diels–Alder reaction [11]. Thus the polymers obtained by the reaction of cyclopentadienes, α-pyrones, or thiophen dioxides with bismaleimides contain bicyclo[2,2,2]octene rings in which the imide groups are in the *exo*-position. Even reactions in which both these forms are produced should lead to chains with a certain degree of order in the distribution of *endo*- and *exo*-groups in relation to the chain.

Polymers obtained by the Diels–Alder reaction are as a rule amorphous, but their amorphous nature does not rule out the possibility of stereoregularity [11].

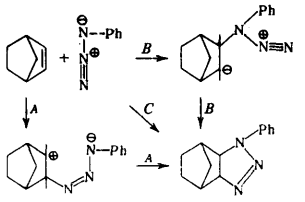
Kinetic studies have shown that polymerisation includes a number of individual reactions and is a stepwise and not a chain process. Therefore, the equation for second-order reactions $-dc/dt = KC^2$, where C is the concentration of the terminal diene and dienophile groups, should hold for the Diels–Alder reaction. The decrease of the rate on dilution of the solutions and on decrease of the molecular mobility of the reactants is typical for the Diels–Alder reaction.

The degree of polymerisation in the Diels–Alder reaction depends on its duration, since at the beginning oligomers accumulate in the reaction mixture and are gradually converted into products with a higher molecular weight. However, one should bear in mind that the Diels–Alder reaction is reversible and that at high temperatures the polymeric products may decompose into dienes and dienophiles. It is postulated that the dissociation takes place more readily in the centre of the molecular chain than at its ends, which leads to a narrowing of the molecular weight distribution [11].

Despite the fact that in many cases a biradical mechanism has been postulated for the Diels–Alder reaction [113], the vast majority of experimental data are consistent only with a synchronous mechanism [114] of the $[\pi 4 + \pi 2]$-cycloaddition type with retention of orbital symmetry [115,116].

The mechanism of the 1,3-dipolar cycloaddition reaction involving polymers has not yet been investigated. However, since there is sufficient information about 1,3-dipolar addition reactions of low-molecular-weight substances, certain comparisons may be made and conclusions reached [112]. 1,3-Dipolar polyaddition has much in common with polymerisation via the Diels–Alder reaction: it is an example of ionic [4 + 2]-cycloaddition, because, although the molecules of 1,3-dipolar compounds involved in cycloaddition reactions are formally neutral, they usually behave as three-orbital 4π-electron species [117].

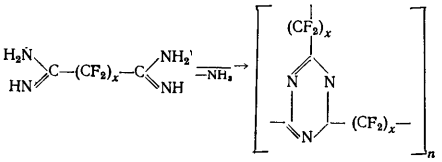
Analysis of 1,3-dipolar addition [115–118] and Diels–Alder reactions on the basis of the rule of conservation of orbital symmetry [119] has demonstrated the similarity of these two processes, which makes it possible to classify the former as pseudo-Diels–Alder reactions and suggests that they have similar kinetics and mechanism. Of the three theoretically possible mechanisms for the addition of a 1,3-dipole to double and triple bonds, illustrated for the interaction of phenyl azide with bicycloheptene as an example, the most likely is mechanism (*C*) with cyclic electron transfer and simultaneous formation of two new bonds [117]:



[(*A*) the positive end of the dipole initiates attack; (*B*) the negative end of the dipole initiates attack; (*C*) the addition takes place simultaneously]. According to mechanism (*C*), the synchronous electron shift leads to the formation of two new σ bonds and enables all three nitrogen atoms to reach octet stability without carrying a formal charge.

IV. POLYCYCLOTRIMERISATION

Polycyclotrimerisation can be achieved both as a polycondensation and a polymerisation process, which results in the formation of carbocyclic or heterocyclic polymers. The polycyclotrimerisation reaction was used for the first time to synthesise polymers by Brown [120–122], who described the polycondensation of diamidines with evolution of ammonia and the formation of cross-linked polytriazines:

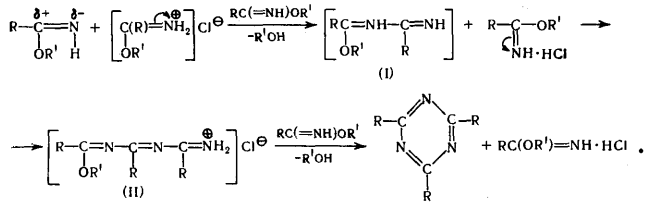


The addition of monoamidines appreciably suppresses the structure-formation process but nevertheless does not altogether rule it out owing to the considerable difference between the reactivities of mono- and bi-functional monomers.

In the course of further studies, the characteristics of this reaction and of the polycyclotrimerisation of fluorinated and non-fluorinated iminoesters were investigated in the presence and absence of catalysts, namely the dependence of the thermal degradation and other properties of the polymers obtained on the nature of the group linking the triazine rings; much attention has been devoted to problems of the processing and applications of triazine rubbers [123–134].

Yakubovich et al. [131] believe that the condensation of iminoester groups into triazine rings proceeds via a series of consecutive stages leading to the formation of a

linear "dimer" (I) and "trimer" (II). The resulting hydrochloride of the linear "trimer" (II) cyclises into the more stable *s*-triazine systems via the mechanism [135]



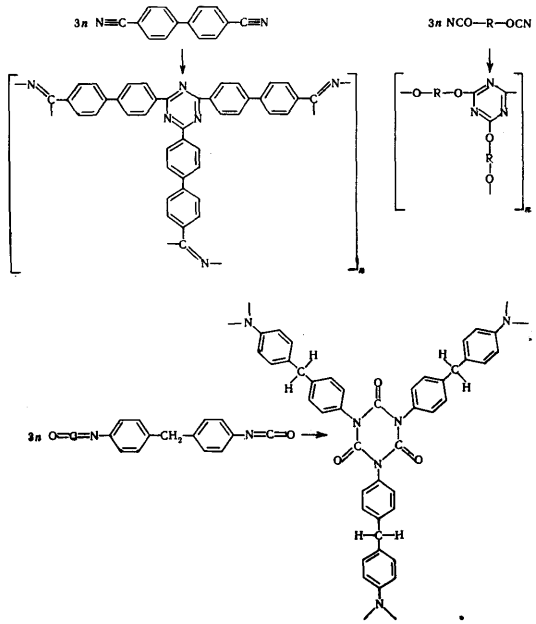
Presumably the electrophilic properties of the carbon atom in iminoesters are insufficient to ensure the effective addition of a second iminoester molecule to the C=N double bond; therefore the cyclisation of the free bases of the iminoesters takes place only in the presence of the iminoester hydrochloride, in which the electrophilic properties of the carbonyl carbon atom are enhanced owing to the presence of 'onium nitrogen and the associated shift of the π-electron density of the double bond:



The substitution of hydrogen atoms in the alkyl group of bisiminoesters by fluorine increases the electrophilicity of the carbonyl carbon atom to such an extent that the triazine ring is formed also in the absence of a catalyst [134]. In order to obtain linear polytriazines under these conditions, it is necessary that one position in the triazine ring should be substituted by a non-reactive side group and the remaining two should be involved in the formation of the polymer chain.

Examples of polycyclotrimerisation are provided by the formation of polymers with triazine rings from aromatic dinitriles, aryl cyanurates, or aryl di-isocyanates [14].

Scheme 3

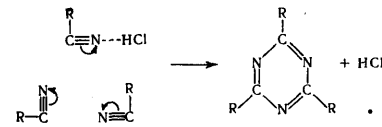


The reason for the tendency of compounds containing C=N bonds to form stable cyclic trimers is that, on conversion of monomers into trimers, the enthalpy of the π bond is lost; moreover, the cyclic trimer is stabilised owing to the combination of the most favourable valence angles (120°) and the planarity of the resulting ring, which makes possible the existence in the trimer of a stable aromatic system [136-139]. The inclusion of stable aromatic systems between triazine rings is responsible for the high thermal stability of the polymers [138].

The cyclotrimerisation of nitriles may be accelerated by many catalysts, for example, by the halides of coordination-unsaturated metals. The presence of a lone electron pair and of π bonds in the C≡N group promotes the formation of highly electrophilic molecular complexes with Lewis acids. It is suggested that the addition of more than one equivalent of the electrophilic compounds to a nitrile is due to the formation of the so called π complexes [140].

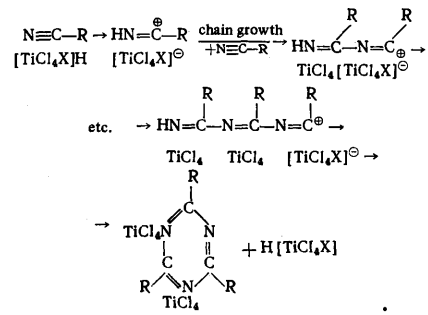
Hydrogen halides are used most often among compounds inducing the cyclotrimerisation of nitriles [141], but reactants such as sulphuric and chlorosulphonic acids, Lewis acids, and others can also serve as catalysts [142-145]. The ease of formation of the *s*-triazine ring in the presence of HCl is probably due to the possibility of a cyclic electron transfer via Scheme 4: [146,147]

Scheme 4



According to Scheme 4, both the free nitrile and its complex with the hydrogen halide is involved in the formation of triazines.

Interesting results have been obtained by Kargin and coworkers [148-153] in a study of the mechanism and kinetics of the polymerisation of benzonitrile with compounds such as $TiCl_4$, $ZnCl_2$, and BF_3. [149] They also showed that triphenyltriazine is an intermediate in the formation of a linear polymer with a polyene structure and that the complex $[TiCl_4X]H$, formed in the interaction between the complex-forming agent and proton-containing additives, serves as a centre for chain initiation [152]:



Petrov et al. [154] studied the kinetics of the cyclotrimerisation of di-isocyanates by infrared spectroscopy using as a test object the polymer obtained by the interaction of one mole of low-molecular-weight polybutadiene (mol. wt. 4000) containing terminal OH groups with 2 moles of 2,4-tolylene di-isocyanate in the presence of a catalytic system including glycidyl phenyl ether and dimethylbenzylamine in different proportions. It was shown that the cyclotrimerisation of isocyanate groups corresponds to a quasi-monomolecular reaction up to 70–90% conversion; the rate of cyclotrimerisation is directly proportional to the product of the initial concentrations of the tertiary amine and the epoxyalkane. The author suggested that the cyclotrimerisation reaction is a special case of anionic polymerisation [154].

The results have been explained in terms of the stepwise Beitchman mechanism [155], according to which the addition of the first, second, and third isocyanate (M) molecules to the catalytic complex (N) takes place in the same way:

$$N + M \xrightarrow{k} NM,$$

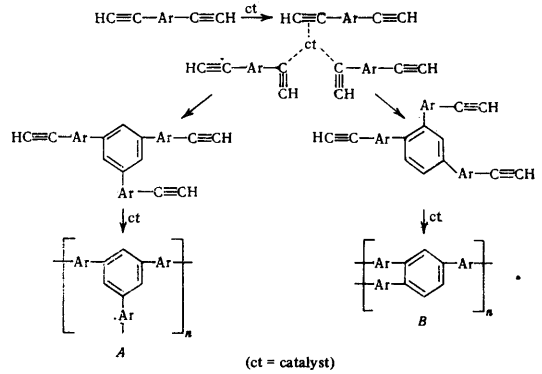
$$NM + M \xrightarrow{k} NM_2,$$

$$NM_2 + M \xrightarrow{k} M_3 + N.$$

Although the closure of the isocyanate ring, accompanied by the elimination of the catalyst, is most likely in the trimer stage, in principle the formation of a linear polymer or the arrest of reaction at the dimer stage are possible.

Korshak, Sergeev, and coworkers [156,157] achieved the polycyclotrimerisation of diethynyl compounds in bulk and in solution in the presence of complex catalyst which consisted of various complexes of cobalt, nickel, and other transition metals capable of catalysing the cyclisation of acetylenes into benzene and its derivatives. The overall mechanism of the polycyclotrimerisation of diethynyl compounds may be regarded as involving the consecutive trimerisation of ethynyl groups leading to chain propagation, branching, and cross-linking (see Scheme 5).

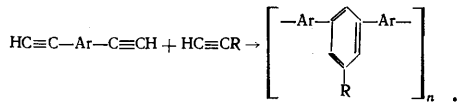
Scheme 5



(ct = catalyst)

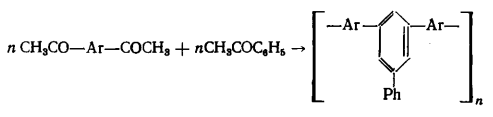
The study of the infrared and NMR spectra showed that polycyclotrimerisation results in a decrease of the intensity of the absorption band corresponding to the stretching vibrations of the ≡C–H linkages (3300 cm^{-1}) and an increase of the vibration frequency of the hydrogen atoms linked to the benzene ring.

The formation of 1,3,5- and 1,2,4-substituted benzenes depends on the nature of the catalyst metal and the ligand [156,157]. The use of a mixture of diethynyl and monoethynyl compounds make it possible to regulate the degree of branching of the polymer formed:



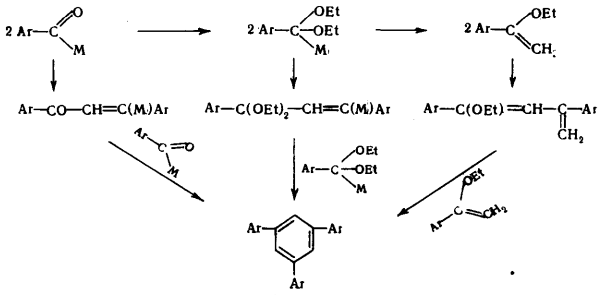
On heat treatment, oligomeric polycyclotrimerisation products are converted into an infusible and insoluble state.

Korshak, Teplyakov, and coworkers [158,159] proposed a new method for the synthesis of polyphenylenes via the polycondensation of aromatic diacetyl compounds according to the mechanism



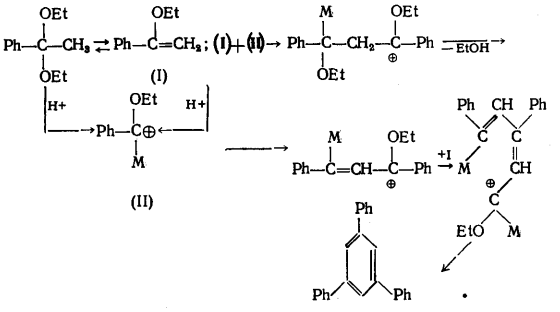
However, as in the trimerisation of acetylenic compounds, it was found that the use of diacetyl monomers alone leads rapidly to the formation of three-dimensional products. Therefore, one usually employs equimolar mixtures of di- and mono-acetyl compounds, although in this case too gel formation is observed in the course of the reaction.

The authors showed that the formation of the benzene ring is a fairly complex process including as an intermediate stage the crotonic condensation of the acetyl groups, resulting initially in the formation of a dimer and then a trimer, the intramolecular cyclisation of which yields 1,3,5-substituted benzene rings. The catalytic effect on the reaction by ethyl orthoformate, which apparently promotes the conversion of acetyl compounds in an acid medium into more reactive ketals, has been noted. In this case, the mechanism of the possible fundamental steps in the formation of polyphenylenes can be represented as follows [158]:



A detailed study has been made of the cyclocondensation of acetophenone ketal, which can serve as a model for the synthesis of polymers. Mass-spectrometric analysis established that a certain amount of α-ethoxystyrene, dypnone [1,3-diphenyl-2-buten-1-one], and 1,3,5,7-tetraphenylcyclo-octatetraene is formed in the course of the reaction together with triphenylbenzene [159]. Kinetic investigations established that the cyclocondensation of acetophenone ketal is described by the equation for second-order reactions with a rate constant of $(1.2-1.4) \times 10^{-1}$ litre $mole^{-1}$ min^{-1} at 20°C.

The authors proposed the following mechanism for the condensation of acetophenone ketal on the basis of the results obtained:



The employment of diacetylarylene bisketals together with acetophenone ketal makes it possible to achieve polycondensation and to obtain soluble linear polyphenylenes consisting of oligomers with a molecular weight up to 3000. The oligophenylenes are hardened by heat treatment in an inert atmosphere at 300°C using toluene-*p*-sulphonic acid as the catalyst; the hardened polyphenylenes are infusible and insoluble; they are decomposed vigorously in air at about 400°C. The infrared spectra

of the heat-treated polyphenylenes show no absorption whatever due to the vibrations of the terminal ketal groups.

V. POLYHETEROCYCLISATION

Polyheterocyclisation is a typical polycondensation process, which can be achieved in different ways. (1) In two stages (the first stage involves the formation of linear polymers containing in their macromolecules fragments capable of cyclisation and the second stage, the cyclisation proper, leads to a cyclochain polymer with repeating heterocycles in the chain); (2) in one stage—in polyphosphoric acid (PPA). The most interesting polyheterocyclisation products from the standpoint of thermal stability and heat resistance are polyheteroarylenes—polymers containing only aromatic carbocyclic and heterocyclic groups in the macrochains.

Certain polyheteroarylenes can be formed also on direct fusion of the starting compounds; however, this method is not preparatively useful, since it requires a high temperature at which secondary processes (degradation, cross-linking) may occur in the polymers and alter their properties.

The majority of polyheteroarylenes can be obtained by both methods; each of these has its advantages and disadvantages, largely associated with the properties of the final product. Since the majority of polyheteroarylenes do not melt and do not dissolve in the usual organic solvents, an advantage of the two-stage method is the formation in the first stage of soluble prepolymers, which can be worked into finished articles by the usual methods and then cyclised by heat treatment.

An advantage of the synthesis in PPA is primarily the occurrence of the process in a single stage, its relative simplicity, cheapness, and the ready availability of the starting compounds. Moreover, PPA, which provides a unique combination of the properties of an effective solvent for polymers, a proton donor (this promotes the condensation), and a cyclodehydrating agent, frequently makes it possible to synthesise polymers with a higher molecular weight and with a higher degree of cyclisation. In the two-stage process, the cyclisation usually occurs in the solid phase and, as the reaction proceeds, the macromolecular chains become increasingly rigid, which greatly hinders the occurrence of total cyclisation; PPA, which in this case behaves as a plasticiser, promotes the attainment of a higher degree of cyclisation.

A wide variety of different classes of polyheteroarylenes have been obtained by the above methods and the most important among them are the following: (1) *polyazoles*—polymers containing repeating five-membered heterocycles in the macromolecules: oxadiazole, triazole, pyrazole, thiadiazole, and other units; (2) *polybenzazoles*

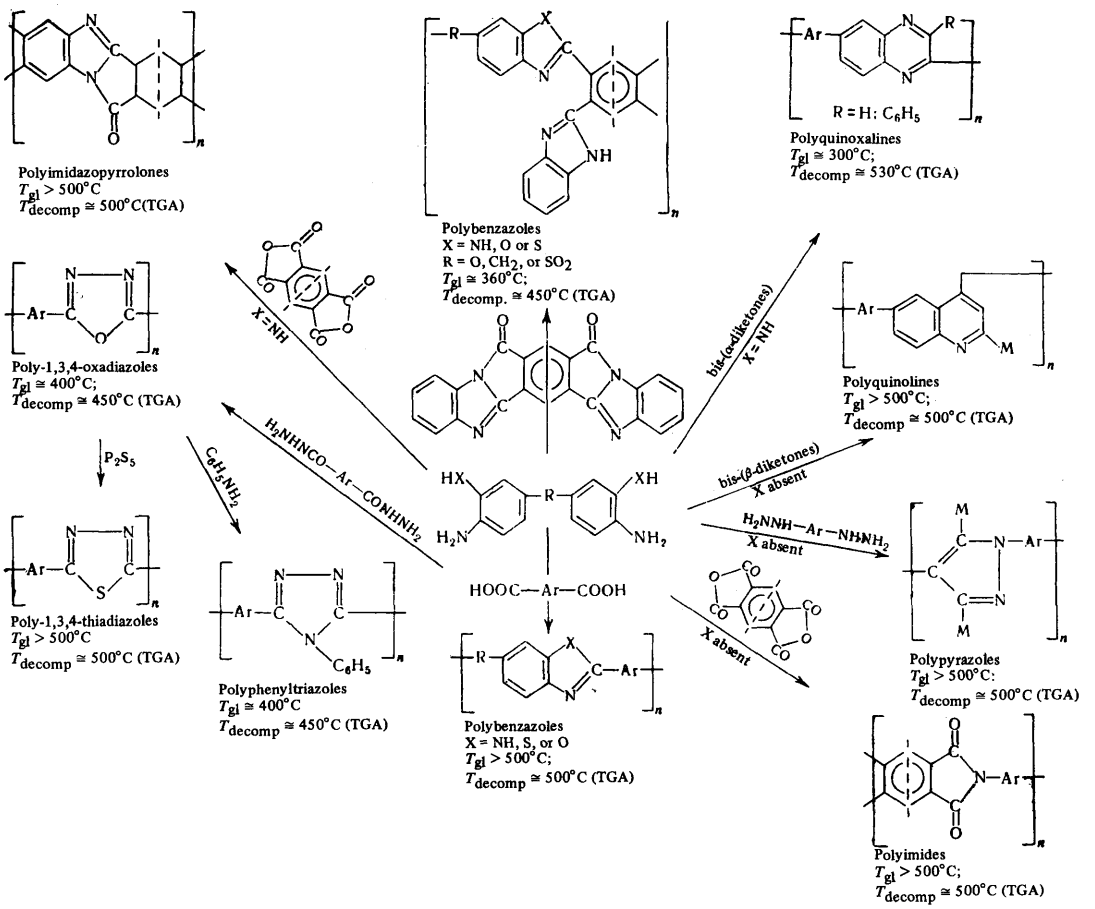


Figure 1. Scheme for the formation and main thermal characteristics of the principal types of polyheteroarylenes.

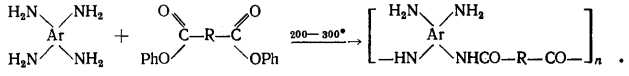
and *polybenzazines* —polymers containing condensed heterocycles: benzimidazole, benzoxazole, benzothiazole, benzimide, indole, quinoline, quinoxaline, benzoxazine, and other units; 3) ladder polymers of different structures.

Fig. 1 presents a general scheme for the formation of the main polyheteroarylenes indicated above and some of their thermal characteristics.

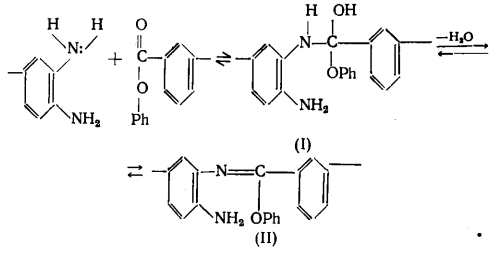
1. Two-stage Method of Synthesising Polyheteroarylenes

The first stage of this process has been investigated in many systems and such studies have led the majority of investigators to the conclusion that at this stage the reaction is reversible and obeys relations characteristic of equilibrium polycondensation [160–165]. Since the second stage is the cyclisation proper and the properties of the final polyheteroarylenes are to a large extent determined by the structure of the prepolymers, we shall consider in this section also the mechanism of the reactions occurring in the first stage.

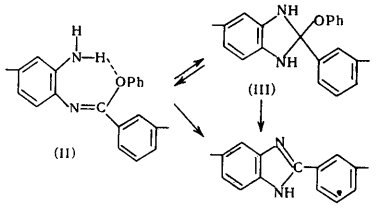
According to the literature [166,167], the formation of polybenzimidazoles on interaction of 3,3′-diaminobenzidine with diphenyl esters of dicarboxylic acid takes place via the formation of a polyaminoamide as an intermediate:



However, Wrasidlo and Levine [168] believe that such interaction begins with the nucleophilic attack by the amine on the carbonyl carbon atom of the diphenyl ester, leading to the formation of an intermediate aldol type product (I), which after dehydration gives rise to a new intermediate with the structure of a Schiff base (II):

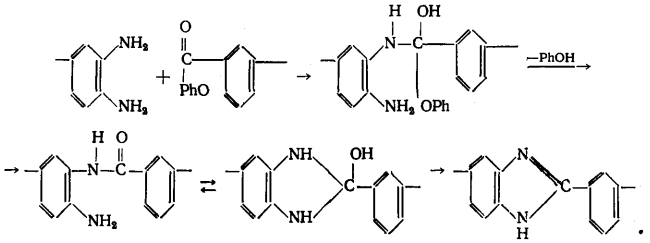


The *syn*-form of the intermediate (II) can produce intramolecular hydrogen bonds, which promote the intramolecular formation of phenol and prevent the formation of cross-linked and branched structures. The authors postulate the possibility of an equilibrium between the intermediate (II) and the benzimidazole structure (III):

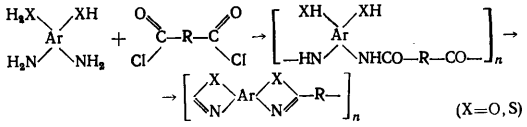


The consecutive elimination of phenol from structures (II) and (III) leads to the final benzimidazole. The electronic absorption spectra of the prepolymer and the fact that water is formed before the phenol are quoted in support of the proposed mechanism.

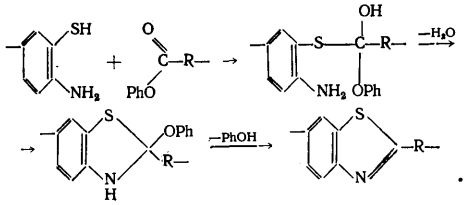
However, Grey et al. [169], who studied the reaction in a flow system in contrast to the earlier investigators, demonstrated on the basis of spectroscopic data and elemental analysis that water and phenol begin to form simultaneously and that half the theoretical amount of water and the entire phenol are produced in the first stage and only water in the second stage. This led them to the conclusion that the reaction intermediate has a hydroxyimidazoline structure formed via the following mechanism:



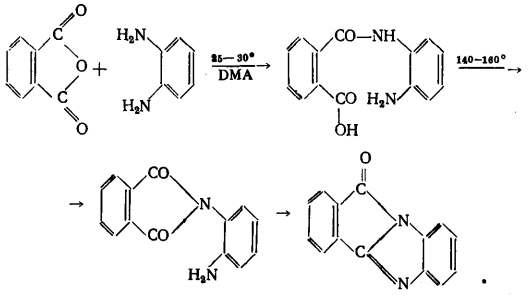
Many workers believe that polybenzoxazoles [170–172] and polybenzothiazoles [173] are formed via a polyhydroxamide and a polymercaptamide respectively as intermediates in the first stage:



It has been suggested that the reaction of 3,3′-dimercaptobenzidine with diphenyl esters in diethylaniline solution proceeds via a different mechanism [174]:



The synthesis of ladder polymers (for example pyrrone type polymers) by the two-stage method proceeds via the formation of a polyaminoamidoacid in the first stage, which has been demonstrated convincingly by Colson et al. [175], using NMR, for the reaction of phthalic anhydride with *o*-phenylenediamine:



The study of the reaction of bis-(β-diketones) with dicarboxylic acid dihydrazides by Korshak and coworkers [176] in order to synthesise polypyrazoles showed that polyacylhydrazones are formed as intermediates in the first stage. The kinetic data obtained by the authors for this stage contradict the earlier idea according to which the interaction of amines with carbonyl compounds is regarded as a bimolecular process, the rate-limiting stage of which is

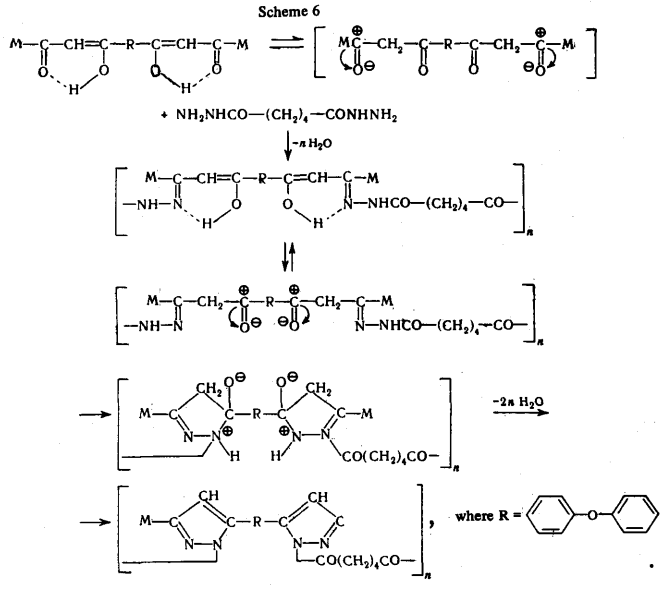
the formation of an intermediate adduct [177,178]. The interaction of 4-acetoacetylphenyl ether and adipodihydrazide under the chosen conditions was irreversible and obeyed the equations for first-order reactions. The activation energy was 17 kcal mole^{-1} and at first sight greatly exceeded the usual activation energy for a keto–enol transformation. Therefore, the hydrogen bond energy in 4-acetoacetylphenyl ether was determined by 1 H NMR and was indeed found to be 23 ± 4 kcal mole^{-1}. Such unusually marked stabilisation of the intramolecular hydrogen bond is probably due to the conjugation of the enol ring with the benzene rings, as in benzoylacetone and dibenzoylmethane [179].

On the basis of their results, the authors proposed a mechanism for the formation of polypyrozoles according to which bis-(β-diketones) and the intermediate hydrazones react in the keto-form (see Scheme 6).

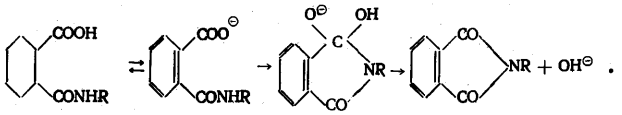
The second stage in the synthesis of polyheteroarylenes—dehydrocyclisation—consists in the intramolecular formation of water from the intermediate product with formation of a cyclochain polymer and may be achieved both in solution and in the solid phase. These processes are being vigorously investigated since they have a direct influence on the properties of the polymers [180–194].

A study of the kinetics of the imidisation of a polyamidoacid in solution in dimethyl acetamide at 80°C on the basis of the amount of water formed, both chromatographically and from the change of the absorption intensity in the region of 1780 cm^{-1}, showed that the process is first-order with a rate constant $k = 3.87 \times 10^{-3}$ litre mole^{-1} s^{-1}. The reaction is very rapid and after 11 min the degree of imidisation is 98.5%. [180] The reaction rate depends on the nature of the diamine and the dianhydride: polyamidoacids comprising more basic diamines and aromatic dianhydrides are cyclised more readily.

Scheme 6



It was observed that the cyclisation of a polyamidoacid in the form of the ammonium salt proceeds much faster (by a factor of 5–10) compared with the cyclisation of the free polyamidoacid. Therefore, it has been suggested that the mechanism of the cyclisation reaction includes a stage in which the carboxy-group is ionised [184]:



On the other hand, the cyclisation of the methyl ester of a polyamidoacid proceeds much more slowly than that of the acid itself [187], which constitutes indirect confirmation of the above hypothesis.

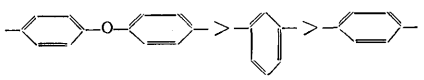
A characteristic feature of the kinetic curves for the cyclisation of polyamidoacids is the presence of two stages, the first of which corresponds to rapid cyclisation and the second to a very slow process. The activation energies for the two stages are almost the same, but the activation entropy for the second stage is significantly higher [184]. If the water formed in the cyclisation process is not removed from solution, then hydrolytic cleavage of the macromolecules and a decrease of the molecular weight of the polymer are possible at the reaction temperature [180]. Therefore, in solid-phase cyclisation, which takes place at higher temperatures (250–300°C), it is necessary to remove water rapidly from the reaction zone; consequently, the cyclodehydration of solid prepolymers is carried out in thin layers *in vacuo* [183–187].

The studies showed that the mechanism of solid-phase cyclisation is more complicated in solution. Regardless of the prepolymer cyclised (polyamidoacid, polyhydroxamide, polyhydrazide, and others), the kinetics of these reactions have the following common feature: regardless of the fact that all such reactions are unimolecular and are treated as first-order processes, the rate constant calculated from the first-order kinetic equation decreases monotonically with conversion. Thus, with increase of the degree of cyclisation of a polyamidoacid from 0.2 to 0.8, the absolute reaction rate constant increases by a factor of 10–12. The decrease of the imidisation (and in general cyclisation) rate constant with increase of the degree of reaction may be accounted for by the fact that the energy and time parameters of the constant k in the Arrhenius equation do not remain constant in the solid-phase process [183]. The decrease of the reactivity of the macromolecules in consequence of the increased rigidity of the polymer chains and their decreased mobility with increase of the degree of cyclisation may be regarded as one of the causes of this phenomenon.

An attempt has been made to estimate quantitatively the change in mobility (increase of rigidity) of polymer chains during cyclisation using as an example the polyhydrazide obtained from the dihydrazide of 4-carboxyphenyl ether and the dichloride of diphenylphthalide-4,4′-dicarboxylic acid [188]. It was shown that the glass temperature of the resulting intermediate exceeds the experimental temperature, the solid-phase reaction is sharply inhibited and virtually comes to a stop; under these conditions, the degree of cyclisation does not reach the maximum possible value. In this case, one observes "self-inhibition" of the reaction owing to a continuous change in the mobility of the polymer chains during the solid-phase polycyclisation caused by the increase of their rigidity due to the increase in the content of cyclic fragments.

The authors suggest that the specific behaviour of these polymers is due to the non-indentity (according to the thermodynamic parameters) of the polymer chains involved in the reaction; this is responsible for the change in the reactivity of the hydrazide groups in the cyclisation [188–190].

The cyclodehydration of polyhydroxamides takes place at 250–300°C. Despite the fact that the decrease of molecular weight during cyclisation corresponds to the calculated values, amide units may persist under these conditions in the polymer, as shown by the presence in the infrared spectra of a weak absorption band at 1660 cm^{-1}. This band disappears only after heating the polymer at 420–430°C, which is accompanied by the formation of a small amount of water and carbon dioxide and the loss of solubility of the polymer in sulphuric acid [192]. The study of the kinetics of the cyclisation of polyhydroxamides showed that the chemical structure of the initial polyhydroxamide influences the rate of the process in a manner similar to that observed for other polymers: with decrease of the mobility of the macromolecular chains in the cyclisation process (i.e. with decrease of the number of units capable of rotation), the cyclisation rate constant falls and the pre-exponential factor increases. It has been established that the rate of cyclisation decreases in the following sequence as a function of the groups linking the benzoxazole rings [193]:

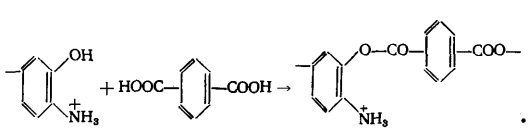


The authors suggest that the mechanism of the cyclodehydration of polyhydroxamides does not include a preliminary amide–imidoyl rearrangement, as shown by the formation of 2-phenylbenzoxazole from *o*-hydroxy-*N*-methylbenzanilide in which such tautomerism is impossible. The presence of a strong intramolecular hydrogen bond, which probably plays an important role in cyclodehydration, has been detected in the infrared spectra of *o*-hydroxamides [194].

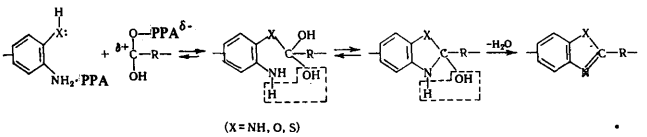
2. Single-stage Method of Synthesising Polyheteroarylenes in Polyphosphoric Acid

The elucidation of the mechanism of polyheterocyclisation in PPA was preceded by a detailed study of the acid properties of PPA itself as the P_2O_5–H_2O system [195-198] and also of the mechanism of the ring closure of a number of low-molecular-weight compounds [198,199], which led to the hypothesis that PPA acts simultaneously as a protic acid, a Lewis acid, and a phosphorylating agent [200]. This is the reason for the change in the reactivity of various compounds when the reaction is carried out in PPA.

Thus, it has been shown that, being a strong Lewis acid, PPA increases the positive charge on the carbon atom of the carbonyl group and thereby leads to an increase of its electrophilic reactivity. It is also interesting to note that, in reactions in PPA, the basicity of the hydroxy-group is higher than that of the amino-group; therefore, the reaction of bis-(*o*-aminophenols) with dicarboxylic acids in PPA involves the initial selective formation of a polyester [170]:



Taking these facts into account, Iwakura and coworkers [170] achieved for the first time the synthesis of polyheteroarylenes in PPA and proposed the following general mechanism for the formation of polybenzazoles:

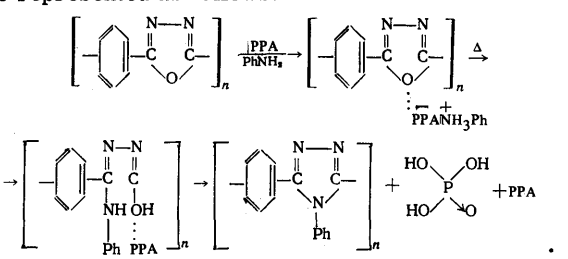


(X = NH, O, S)

It has been suggested that the intermediates formed are hydroxyimidazolines in the synthesis of polybenzimidazoles in PPA and the corresponding hydroxy-derivatives in the synthesis of polybenzoxazoles and polybenzothiazoles. It was noted that a high molecular weight is attained more rapidly in the last two cases than for polybenzimidazoles. According to the authors, this is due to the higher basicity of the hydroxy- and mercapto-groups in PPA compared with the amino-group and this is in fact the reason for the higher rate of formation of the polymer [201,202].

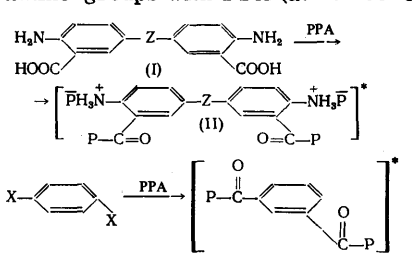
Probably the mechanism of the formation of poly-1,3,4-oxadiazoles from dicarboxylic acids and hydrazine derivatives in PPA is analogous to that quoted above [203], but this requires experimental proof.

The data obtained by Meiboom and coworkers [204] in a study of the rate of proton transfer in an acid medium to substituted ammonium ions proved to be important for the elucidation of the mechanism of their reactions in PPA. It was shown that the formation of the free base is the rate-limiting stage in this process. Later Holsten and Liliquist [205-207] determined by NMR spectroscopy the temperature range in which the aniline–PPA salt dissociates into the free acid and aniline. Accordingly, the mechanism of the formation of polyphenyltriazoles by the reaction of a polyhydrazide or polyoxadiazole with aniline may be represented as follows:



Kurihara and coworkers [208-210] made a detailed study by spectroscopic and chemical methods of the mechanism of the formation of polybenzoxazinones in PPA by the polycondensation of bisanthranilic acids and their copolycondensation with dicarboxylic acid derivatives. They demonstrated convincingly that the synthesis of polybenzoxazinones in PPA proceeds via the formation of phosphorylated intermediates in the following way.

First stage—phosphorylation of both initial compounds with formation of mixed anhydrides and the interaction of the amino-groups with PPA (at 40–80°C):

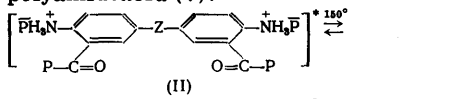


where Z = CH_2 or O, X = COOH, COCl, CN, C(=NH)OR,

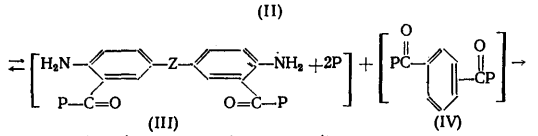
COOR, $\overset{O}{\overset{\|}{C}}NH_2$, or CHO, R = CH_3, C_2H_5 or C_6H_5,

P = $H[O\overset{O}{\overset{\|}{P}}(OH)_n]O$, and [ ]* = activated complex.

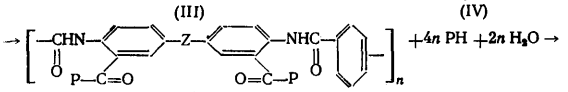
Second stage—the formation of the polyamidoacid (V). At 150°C the salt (II) dissociates and an equilibrium is established between the salt and the free amino-form of the phosphorylated product. The reaction is initiated by the nucleophilic attack by the free-amino groups on the carbonyl group of the mixed anhydride and leads to the formation of the polyamidoacid (V):



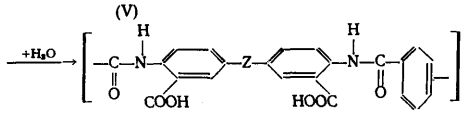
(II)



(III) (IV)

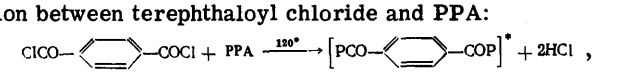


(V)



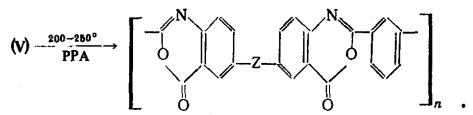
(VI)

The presence of the mixed anhydride (IV) in the reaction mixture has been demonstrated by carrying out the reaction between terephthaloyl chloride and PPA:



which resulted in the formation of a stoichiometric amount of hydrogen chloride. The carbonyl group in such a mixed phosphorylated anhydride is more sensitive to nucleophilic attack by amino- or phosphoramido-groups. The presence of free NH_2 groups, which appear as a result of the dissociation of the amine salt (II) in PPA, has been demonstrated by NMR. The polyamidoacid (V) was isolated from the reaction mixture and characterised by elemental analysis and infrared spectroscopy.

Third stage—cyclodehydration in PPA. This occurs on further heating and leads to polybenzoxazinones:



(VII)

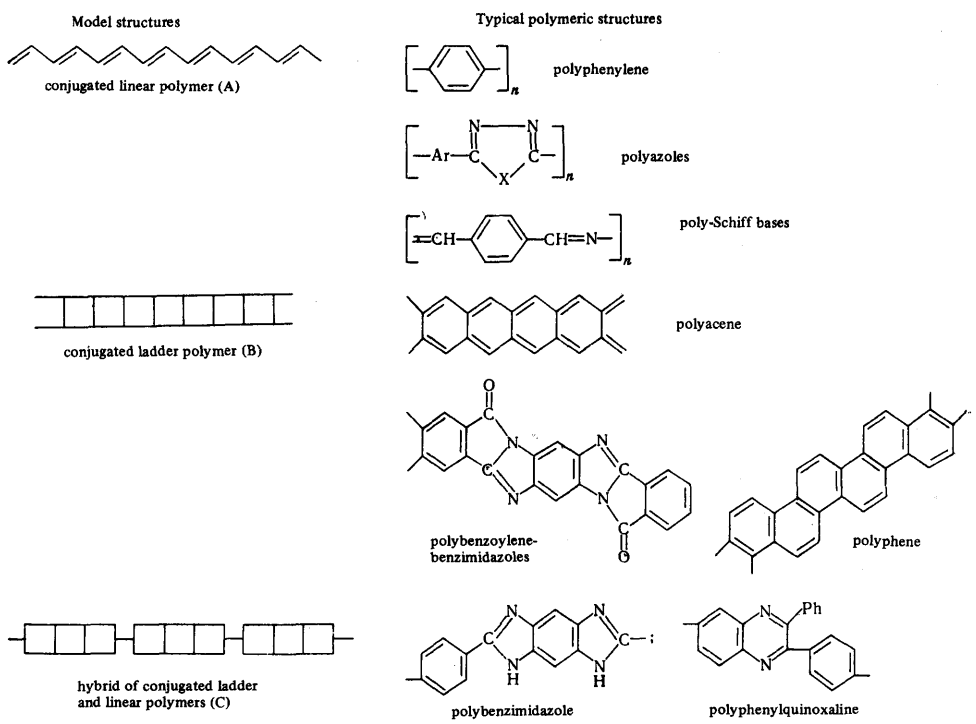
VI. LIMITS OF THE APPLICABILITY OF THE POLYCYCLISATION METHOD

Examination of the above data permits the following conclusions.

1. Despite the apparent wide variety of methods described, they are all based on well known polymerisation and polycondensation processes.
2. Methods leading to polymers with continuous conjugation or pseudo-conjugation of the aromatic (carbocyclic and heterocyclic) structural skeleton, i.e. polyheterocyclisation, polycyclotrimerisation, and 1,3-dipolar addition, are the most suitable for the synthesis of thermostable and heat-resistant organic polymers.
3. The two-stage method of synthesising polyheteroarylenes, whereby it is possible to obtain in the first stage soluble polymers capable of being worked, has nowadays been developed to the greatest extent.

All the above types of polyheteroarylenes can be represented by models [211] (see Scheme 7).

Scheme 7



The presence in the polymer macromolecules of aromatic carbocyclic and heterocyclic groups alone, which are responsible for the rigidity of the main chain and the strong interchain interaction, should lead to high softening temperatures (heat resistance) and resistance to high temperatures (thermal stability) and chemical reagents; when the molecular weight is fairly high, all these qualities give rise to satisfactory operational properties of polymers of this class.

The softening temperatures of polymers, which constitute the upper limits of the region where they can be employed, are related to thermal stability as follows [212]:

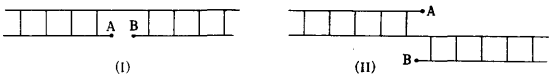
$$T = \frac{\Delta Q}{\Delta S} ,$$

where T is the melting point (or the phase transition temperature), ΔQ the amount of heat absorbed on decomposition of the polymer (or in the transition), and ΔS the entropy of decomposition of the polymer (or the entropy of the transition).

This formula takes into account the following factors: the intermolecular interaction, which determines Q, and the rigidity of the polymer chain responsible for the change in the entropy of the system.

Examination of the thermal stability of polyheteroarylenes of different structures from these standpoints suggested that aromatic polymers with a ladder structure should be more resistant to high temperatures and should be degraded more slowly, since this requires the dissociation of not one but two single bonds [212]. At the same time it was found that despite the differences in structure all the known polyheteroarylenes have similar thermal stabilities, according to dynamic thermogravimetric analysis, which are appreciably lower than suggested. The majority of the polymers begin to decompose in the temperature range 450–500°C with a simultaneous loss of mechanical and other valuable properties (Fig. 1).

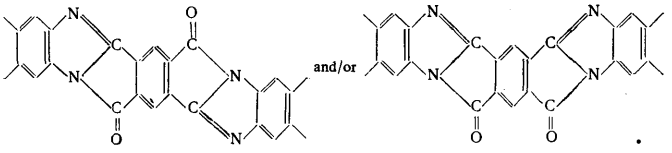
This apparent contradiction between the expected and actual thermal stabilities can evidently be accounted for by the presence of single bonds in the macromolecules, i.e. structural defects in the polymer due to incomplete cyclisation. Analysis of data for the properties of polyheteroarylenes and the study of the process in which they are formed (polyheterocyclisation reactions) showed that it is extremely difficult to attain complete polycyclisation in the polymer macromolecules. This applies particularly to the two-stage synthesis of polyheteroarylenes, in which the cyclisation process takes place in the solid phase, and also to the synthesis of ladder polymers.



In order that the reactive groups A and B should react with formation of a completely cross-linked (ladder) structure, it is necessary that they should be coordinated as in Scheme (I). When Scheme (II) obtains, the formation of a bond requires rotation by 180°, which is extremely difficult for polymers with a high softening temperature owing to the low mobility of the main chain segments. This difficulty increases with increase of the degree of cyclisation.

The study of the polycyclisation kinetics in the solid phase demonstrated differences between the initial and final rates of cyclisation, which is consistent with the entropies of the initial and final stages; the process activation energy does not change appreciably under these conditions [188].

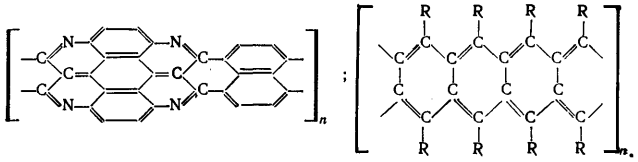
The lower than expected thermal stability of polyheteroarylenes may be caused, apart from the defects in the structure containing non-cyclised sections, by the branching of the polymer, which lowers the packing density and reduces the interchain interaction and also by the configurational and conformational disorder arising in polymer chains owing to the possibility of geometrical isomerism, which also leads to a loss of crystallinity and a decrease of interchain interaction. This can be illustrated using as an example polybenzoylenebenzimidazole obtained from pyromellitic dianhydride and 3,3′-diaminobenzidine, which consists of a mixture of *cis*- and *trans*-isomers (in relation to the benzene ring of pyromellitic acid) [175]:



Among the known polyheteroarylenes, phenylated polyquinoxalines have been attracting special attention; the closure of the quinoxaline ring is apparently favoured so much by thermodynamic and kinetic factors that these polymers are formed extremely readily at room temperature, have high molecular weights, and are fully cyclised, being at the same time fusible and soluble, i.e. capable of being worked [213–215].

A comparative study of the thermo-oxidative degradation of polyphenylquinoxalines and some of the most thermostable polymers—polybenzothiazoles—(under isothermal conditions, since the oxidation processes develop over a period of time) demonstrated a clear advantage of the phenylated polyquinoxalines both over polybenzothiazoles and over unsubstituted polyquinoxalines [215] (Fig. 2). The latter finding confirms the earlier hypothesis that the C–H bonds are very readily activated on heating and are the most susceptible to oxidation, particularly in heterocycles [216].

Such high thermal stability of polyphenylquinoxalines is probably related to the freedom from defects in the polymer chains, which can probably be regarded as the maximum attainable for true linear organic polymers. A further improvement of the thermal characteristics of polymers can be partly achieved by creating more condensed polymeric structures of the type



In this case chain termination at one point cannot cause any appreciable changes in the adjacent regions; under these conditions, there is also a high probability of the destruction of the radicals formed, which increases the resistance of the polyconjugated polymer to thermal oxidation [217–220]. However, the thermal characteristics of condensed polymers of this kind are not markedly improved either; this is probably because, with increase in the complexity of polymer structure, it is increasingly more difficult to attain a high degree of cyclisation and freedom from structural defects.

At the same time the requirements of modern engineering for articles based on thermostable polymers (for example, fibres, fabrics, coatings, plastics, etc.) are increasing continuously. Therefore further heat treatment

of finished articles is being employed to an increasing extent. With the aid of structure-forming processes such as carbonisation and graphitisation, it is possible to increase appreciably the thermal stability and heat resistance of the articles. Consequently, for the formation of satisfactory polycyclic structures, it is very important that the heat-treated cyclopolymers should have a defect-free structure, which makes it possible to avoid undesirable degradative processes [221].

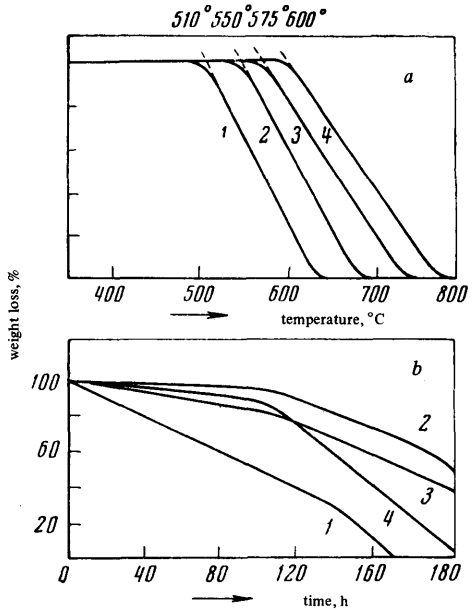


Figure 2. a) Weight loss according to dynamic thermogravimetric analysis in air at a heating rate of 6.67 deg.min^{-1}; particle size 140–240 mesh [1) diether polyquinoxaline; 2) diether polyphenylquinoxaline; 3) polybenzothiazole of type AA–BB; 4) polybenzothiazole of type A–B]; b) weight loss according to isothermal thermogravimetric analysis of the polymers in air at 371°C.

Graphitisation, which involves a more far-reaching heat treatment than carbonisation, leads to materials which should approach, to some extent, carbon structures which also consist of polymers with a very high molecular weight, a two-dimensional and three-dimensional network, and an infinite C/H ratio [218–220].

Thus, depending on the purpose of the final article, an appropriate method should be used for the synthesis of the polymer and for its subsequent heat treatment.

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