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Polycyclotrimerisation of cyanamides

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ABSTRACT. The results of studies in the field of the synthesis of polymers with a network structure by the polycyclotrimerisation of cyanamides and oligomers containing cyanamide groups are surveyed and analysed. The prospects for the use of polymers based on compounds containing cyanamide groups in the preparation of various thermostable materials are discussed.

The bibliography includes 174 references.

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I. Introduction

The synthesis of structured polymers containing *sym*-triazine groups at the network nodes has recently attracted special attention since it is one of the promising ways of creating new polymeric materials.[1–17] The increase in thermal stability and the improvement of physicomechanical characteristics of such polymers are achieved as a result of the development of the highly selective polycyclotrimerisation and the elucidation of the influence of the heterounit structure of network systems on their properties. As a result of this, the polycyclotrimerisation reactions of monomers and oligomers containing the N ≡ C–NH and N ≡ C–NR functional groups are of great interest. They make it possible to obtain cross-linked polymers having a regular chemical structure with a definite specified size of the internodal fragments and stable *sym*-triazine rings at the network nodes. An advantage of this reaction, leading to the synthesis of network polymers, is that it proceeds without the evolution of low-molecular-weight products. Because of this, articles can be made from such polymers by polymerising monomers or oligomers prepared beforehand (which are as a rule low melting and are readily soluble in organic solvents), i.e. by the usual methods for the processing of thermoreactive polymers.

Numerous studies devoted to the characteristics of the cyclotrimerisation of cyanamides and related compounds, which merit a special survey in combination with earlier information,[1–4,8,10,11,13,15,16,18–21] have been published recently. Therefore the consideration of the advances in the synthesis, investigation, and applications of network polymers based on cyanamides and oligomers containing cyanamide groups has become the subject of the present review. Attention has been concentrated on the latest studies which have not been described in reviews published previously.[1–4,8,11,13,15,16,19–21]

II. The synthesis of N-substituted cyanamides

The commonest method of synthesis of cyanamides involves the interaction of the corresponding amines with halogenocyanogens (ClCN, BrCN):[8,11,19,21–30]

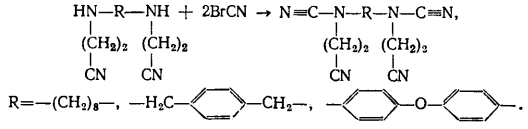
$$2\,R{-}NH_2 + HalCN \rightarrow R{-}NH{-}C{\equiv}N + R{-}NH_2 \cdot HHal,$$

R = alkyl or aryl.

It has also been suggested that cyanamides be synthesised in amide solvents, which play the role not only of solvents but also of acceptors of the hydrogen halides evolved, which makes it possible to increase by a factor of two the yield of cyanamides.[29] This method is convenient for the synthesis of cyanamides from primary amines.[11,28,29,31] In the synthesis of N-substituted cyanamides from secondary amines,[11,28,29] $NaHCO_3$ can be used as the acceptor.

Certain other methods of synthesis of substituted cyanamides are also known.[32–34] The preparation of lower aliphatic cyanamides by the interaction of calcium hypochlorite with amine salts followed by the treatment of the resulting alkyl-disubstituted chloroamines with a solution of KCN or NaCN has been described.[32]

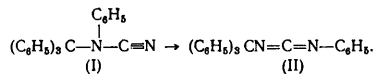
Cyanoethylated bis(cyanamides) have been obtained[35] by the interaction of cyanoethylated diamines with bromocyanogen in accordance with the scheme



The introduction of the cyanoethynyl group; as a substituent at the nitrogen atom lowers the melting point of the cyanoethylated bis(cyanamides) compared with the corresponding unsubstituted bis(cyanamides), which is especially important in the practical use of these compounds.

A specific property of cyanamides is the tendency towards tautomerisation,[36–40] which has a significant influence both on the chemical properties of cyanamides and on the mode of their cyclotrimerisation (on the structure of the products formed). Spectroscopic studies on cyanamide[41,42] have made it possible to establish unambiguously that this compound exists only in the form $NH_2{-}C \equiv N$ in the crystalline state, in aqueous solutions, and in certain organic solvents.

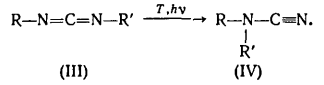
The isomerisation of *N*-phenyl-*N*-tritylcyanamide (I) to *N*-phenyl-*N'*-tritylcarbodiimide (II), observed both in the crystalline state and in solution, has been studied in detail:[43,44]



In both cases, the rate of the process depended on temperature: with increase in temperature, the isomerisation process was accelerated.

The rate of reaction also increases when a non-polar solvent is replaced by a highly polar one, which enabled the authors[43] to propose an ionic isomerisation mechanism.

The reverse isomerisation of disubstituted carbodiimides (III) to the corresponding cyanamides (IV) is accelerated both thermally and photochemically, which has led to the conclusion[45,46] that this process has a radical mechanism:

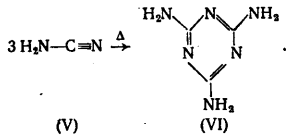


(III) (IV)

The possibility of finding the given compounds in different tautomeric forms depending on the reaction conditions has been confirmed by the results obtained in the study of the alkylation[43–48] and cyclotrimerisation of substituted cyanamides.[8,11,49–61] The alkylation of *N*-monosubstituted cyanamides afforded both *NN*-disubstituted cyanamides[43,44,47,48] and the corresponding carbodiimides[38,43,44,46,48] or mixtures of these products.[38,43,44,48]

III. Cyclotrimerisation of monocyanamides

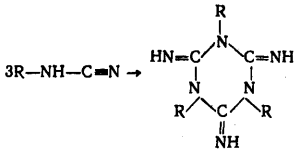
There are few literature data[62–64] on the cyclotrimerisation of cyanamide (V) (T_m = 42 °C) with formation of 2,4,6-triamino-1,3,5-triazine (melamine) (VI), because on heating above the melting point (80–130 °C) cyanamide as a rule dimerises with formation of dicyanodiamide $NH_2-C(=NH)-NHCN$:[50]



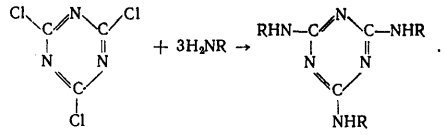
(V) (VI)

The cyclotrimerisation of cyanamide is carried out by heating the latter above 150 °C in solution in tetrahydronaphthalene, diphenyl ether, or a mixture of *m*- and *p*-cresols[62] and also in solution in dimethyl sulphoxide or sulpholan in the presence of an alkali metal or alkaline earth metal hydroxide.[63,64]

The cyclotrimerisation of substituted cyanamides has been frequently reported[49–57,65–67] but until recently the available literature data were contradictory. In some cases the cyclotrimerisation products were isomelamine derivatives,[51,52,55,56,65] whilst in others they were substituted melamines with the normal structure.[53,57,66,67] Thus the cyclotrimerisation of aromatic and aliphatic monocyanamides has been carried out in aqueous or alcoholic solution without a catalyst or in the presence of an alkaline catalyst.[22,49] In all cases, the trimerisation products were the corresponding trisubstituted isomelamines:

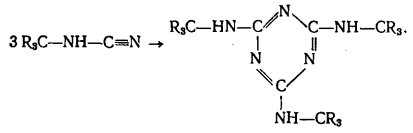


Substituted melamines with the normal structure could be obtained only by condensing cyanuric chloride with the corresponding amine:[22]



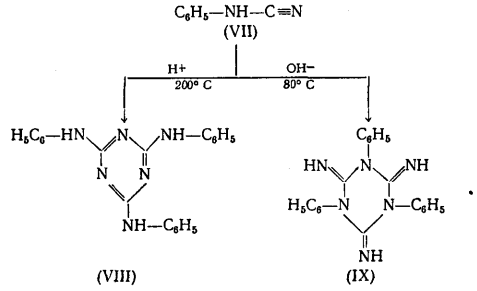
The formation of substituted isomelamines was also observed in the cyclotrimerisation of primary and secondary alkylcyanamides in solution in ethanol.[54] The cyclotrimerisation of compounds having the formula RCO–NR′–CN, where R, R′ = alkyl, arylalkyl, allyl, or methylallyl, in solution in aqueous ethanol in the presence of an alkaline catalyst also leads to the formation of substituted isomelamines.[65]

On the other hand, when the trimerisation of tertiary aliphatic cyanamides was carried out under similar conditions,[53] trisubstituted melamines with the normal structure were obtained:



These literature data permit the conclusion that 2,4,6-triamino-1,3,5-tri-azines are formed more readily if the substituting groups generate steric hindrance to attack by the NH group, as in the case of tertiary alkyls,[53,57,66] 1-adamantyl,[66] and *o*-substituted aryls.[67]

A series of studies have been published[8,11,13,58–61] in which the cyclotrimerisation of phenylcyanamide (VII) was investigated. It was found that, depending on the conditions in the cyclotrimerisation of compound (VII), triphenylmelamine (VIII) and triphenylisomelamine (IX) may be formed:

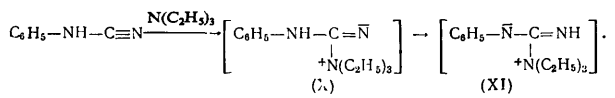


(VIII) (IX)

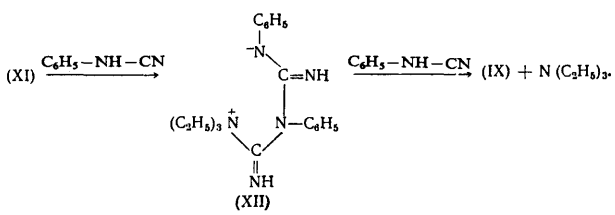
Thus compound (IX) is formed in the cyclotrimerisation of compound (VII) in the melt under mild conditions (20–80 °C), whereas at 200 °C the structure (VIII) is mainly produced.[52] The structure of the final product of the cyclotrimerisation of compound (VII) may be regulated also by the nature of the catalyst. Thus compound (VIII) is formed in the presence of Lewis acids ($SnCl_2$, $ZnCl_2$, $TiCl_4$, etc.), whereas on treatment with basic catalysts (triethylamine, pyridine, triphenylphosphine, etc.) the iso-form (IX) is produced. Lewis acids probably form adducts with compound (VII) having different degrees of substitution of the electron pair involved in the π-bond: ranging from molecular compounds of the type $C_6H_5-NH-CN.MX$ to the ionic structures $C_6H_5-NH-C \equiv N-\overline{M}X$. An increase in the polarisation of the $-C \equiv N$ group tends to accelerate the cyclotrimerisation of compound (VII) with formation of the structure (VIII).

The cyclotrimerisation of compound (VII) catalysed by triethylamine apparently gives rise to the complex of compound (VII) with $(C_2H_5)_3N$ as a reuslt of the nucleophilic attack by the carbon atom of

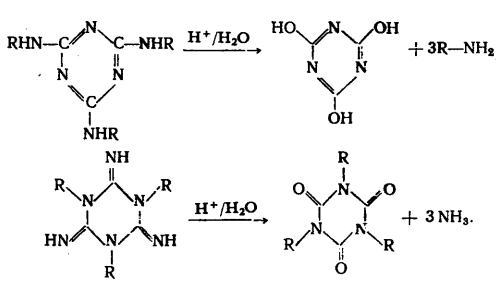
the nitrile group on the nitrogen atom of the tertiary amine:



Of the two tautomeric structures (X) and (XI), compound (XI) is probably more stable. This has been confirmed by IR spectroscopic data, since the intensity of the 2230 cm^{-1} absorption band, characteristic of the vibrations of the $-C \equiv N$ bond of cyanamides,[68] diminishes as triethylamine is added to a solution of compound (VII) in toluene and a band appears at 2130 cm^{-1}, corresponding to the vibrations of the carbodiimide group.[68] Subsequently the complex (XI) apparently combines with two further molecules of compound (VII), forming triphenylisomelamine (IX) via the transition state (XII):[60]



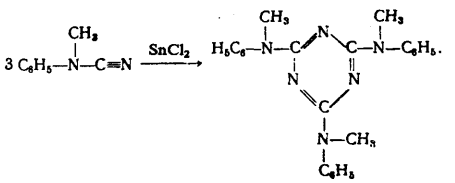
The fundamental difference between the compounds having the isomelamine and melamine structures, obtained as a result of the cyclotrimerisation reaction, is manifested in the products of their hydrolysis: melamine derivatives form, as a result of hydrolysis, cyanuric acid and the corresponding amine, while isomelamine derivatives give rise to the corresponding isocyanurate and ammonia:[11,50,58]



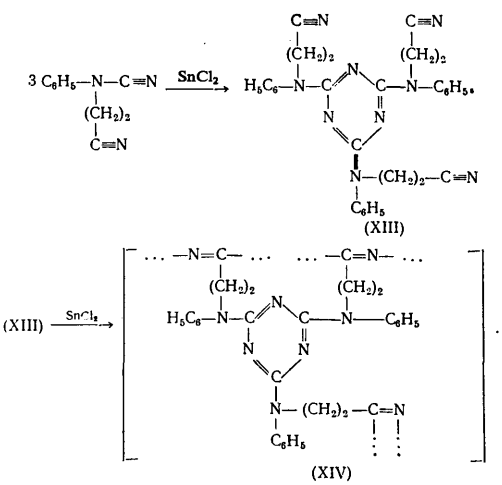
The trimerisation of disubstituted cyanamides was first described by Weith[69] in connection with the synthesis of hexaphenylmelamine by the reaction of diphenylamine with chlorocyanogen, which should proceed via an intermediate stage involving the formation of diphenylcyanamide. 2,4,6-Tri(1-pyrrolyl)-1,3,5-triazine has also been obtained by treating pyrrole with chlorocyanogen.[70]

The kinetics of the cyclotrimerisation of *N*-ethyl-*N*-phenylcyanamide have now been investigated[29] and it has been shown that the presence of the aliphatic substituent in the α-position relative to the nitrile group diminishes the reactivity of the cyanamide group, as a result of which the cyclotrimerisation of this compound proceeds only in the presence of cationic catalysts of the Lewis acid type and leads to the formation of 2,4,6-tris(*N*-ethylphenylamino)-1,3,5-triazine.

The cyclotrimerisation of *N*-methyl-*N*-phenylcyanamide and *N*-cyanoethyl-*N*-phenylcyanamide has also been investigated.[71,72] The cyclotrimerisation of *N*-methyl-*N*-phenylcyanamide[71] was achieved in the melt in the presence of $SnCl_2$:

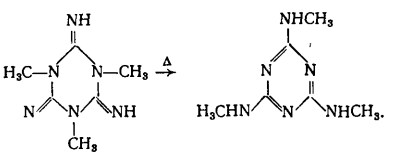


By studying the cyclotrimerisation of *N*-cyanoethyl-*N*-phenyl cyanamide in the presence of $SnCl_2$, the authors[71] showed that, depending on the reaction conditions, not only the corresponding trimer—2,4,6-tris(*N*-cyanoethylamino)-1,3,5-triazine (XIII)—but also the cross-linked polymer (XIV) is formed as a result of the polymerisation of compound (XIII) via the nitrile groups:

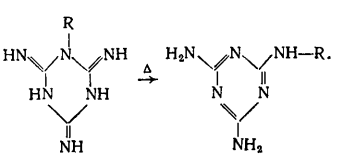


At 30 °C, compound (XIII) is formed preferentially, while at 150 to 280 °C the main product is compound (XIV). Heating of compound (XIII) in the presence of $SnCl_2$ affords compound (XIV).

Data concerning the isomerisation of isomelamine derivatives are of great interest.[11,19,56,58] Thus the isomerisation of trimethylisomelamine, synthesised by Hofmann's method,[73] to trimethylmelamine was carried out by heating trimethylisomelamine at the melting point:[56]



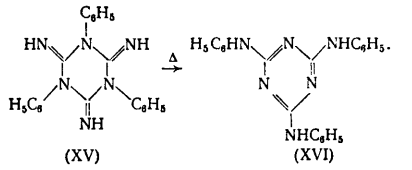
In a study of the influence of elevated temperatures on the reactivity of monosubstituted isomelamines, their conversion into monosubstituted melamines was observed:[74]



The isomerisation occurred in solution in a hydroxylated solvent at a temperature above 80 °C in the presence of 0.1 – 10% of an alkaline catalyst, the yield of the monosubstituted melamine being 95 – 97%.

It has been shown in a study[11,58] of the isomerisation of triphenylmelamine that the substituted isomelamine (XV) isomerises to the melamine (XVI) with the normal structure at a temperature above the

melting point (185 °C); the structure of compound (XVI) does not change on heating to the decomposition temperature. It has also been found that in solution the isomerisation of compound (XV) to (XVI) proceeds at appreciably lower temperatures:[58]



(XV) (XVI)

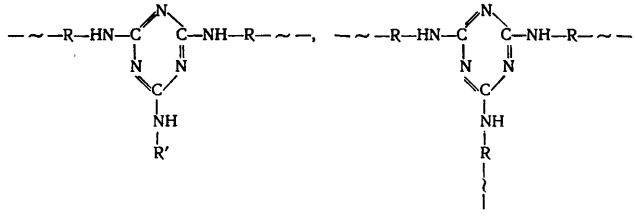
The characteristic features of substituted cyanamides and of the compounds formed on their cyclotrimerisation considered above must undoubtedly be taken into account in the synthesis and study of the properties of polymers based on cyanamides.

IV. Homopolymers of low-molecular-weight cyanamides

The first information about polymers obtained by the polycyclotrimerisation of substituted cyanamides appeared at the beginning of the 1960's and until the 1970's was limited mainly to patent data alone.[4,8,11,13,19,20,23–30,61–69,75]

The synthesis of polymers based on alkyldicyanamides, having the general formula $N \equiv C-NH-(CH_2)_n-NH-C \equiv N$, containing from 2 to 20 methylene groups, has also been described.[76–82] The polymerisation was carried out purely thermally or in the presence of alkaline catalysts by heating one alkyldicyanamide or a mixture of such compounds at the melting point of the monomers for 0.5–1 h.[76] The soluble oligomers thus formed were used as adhesives for the glueing of plastics, varnish coatings, etc. The final hardening was carried out by heating the oligomer to 100 °C. The structure of the polymers was not investigated.

The copolymerisation of bis(cyanamides) having the general formula $NC-NH-R-NH-CN$ with the monocyanamides $R'-NH-CN$ at 60–350 °C in the presence of acid or alkaline catalysts[83] yielded copolymers containing units with the following structure:



Depending on the ratio of the monocyanamide and the bis(cyanamide), both soluble and insoluble cross-linked polymers were obtained.[83]

The polycyclotrimerisation of cyanamides obtained from primary and secondary aromatic diamines was first achieved by Korshak, Pankratov, Vinogradova and co-workers.[61] The principal characteristics of this process were determined[11,58,60] and various properties of network heat-resistant and thermostable polymers based on a large set of bis(cyanamides)[4,8,11,13,20,22,29,58–61,71,72,84–108] were investigated in the studies by these workers.

Investigation of polymers based on bis(4-cyanamidophenyl)-methane, obtained at different temperatures, by IR spectroscopy and also by analysing the hydrolysis products has made it possible to discover[11,84] two types of reactions, as for the model compound phenylcyanamide. At reaction temperatures below the melting point of the initial primary bis(cyanamide), mainly a polymer containing isomelamine fragments is formed, whereas at high temperatures the reaction product is predominantly a polymer having the normal melamine structure.

The polycyclotrimerisation in bulk of secondary N-substituted bis(cyanamides)—bis(4-*N*-methylcyanamidophenyl)methane and bis(4-*N*-ethylcyanamidophenyl)methane—leads to the formation of substituted melamines with the normal structure only, as for the model compound *N*-ethyl-*N*-phenylcyanamide.[11,84] Aliphatic substituents in the α-position relative to the nitrile group diminish the reactivity of the cyanamide group compared with primary N-substituted cyanamides. The polycyclotrimerisation of such compounds takes place in the presence of catalysts of the type of Lewis acids. In contrast to patent data,[75–77,79–81,83,109–118] from which it is difficult to derive a general idea about the influence of the chemical structure of the initial bis(cyanamides) on the properties of the polymers, a number of workers[4,8,11,13,20,28,29,58–61,84–108] carried out a series of systematic investigations in which the influence of the nature of the bridging group between the phenylene moieties and the substituents in the cyanamide group on a number of properties of the polymers was traced under comparable conditions.

Table 1 compares certain properties of the polymers obtained. All the polymelamines investigated were infusible and insoluble close-network polymers, whose network nodes consisted of *sym*-triazine rings connected by the residues of the initial diamines. According to the results of dynamic thermogravimetric analysis of the polymelamines in air, the temperature of the onset of weight loss of these polymers lies within a fairly narrow range (400–420 °C). However, the subsequent course of the thermogravimetric curves of polymelamines with different structures is different. The highest thermal stability is characteristic of polymelamines containing the fluorene group between the phenylene moieties. The polymelamine based on 1,7-bis(4-cyanamidophenyl)carbaborane is characterised by a 5% weight loss on heating to 900 °C in an inert atmosphere.[11,86,87]

According to Hynds et al.,[109] the polymer based on 1,3-dicyanamidobenzene has a decomposition temperature of 464 °C [thermogravimetric analysis (TGA) at a rate of 6 K min^{-1}].

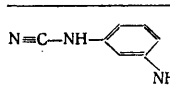
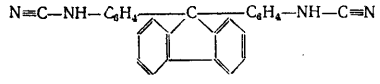
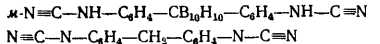
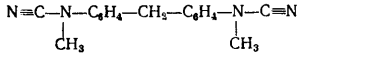
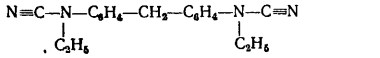
The polymer based on 4,4′-bis(*N*-methylcyanamido)diphenylmethane is characterised by a 50% reduction of weight after heating for 1200 h in air at 260 °C and has a modulus of elasticity equal to 28 800 of kgf cm^{-2}, which remains almost unchanged after 500 h at 260 °C.[111,112,116]

The study of the thermal stabilities of a series of polymers showed that in a helium atmosphere and in air the temperature of the onset of decrease in the weight of polymelamines is approximately the same. However, whereas polymelamines are degraded to the extent of 90% in air at 700 °C, in an inert atmosphere the coke residue at this temperature amounts to 60–80%.[8,11,84,86,87]

In order to deepen the understanding of the processes occurring in aromatic polymelamines on heating, a detailed study has been made also of the thermal degradation of the polymelamine based on bis-(4-cyanamidophenyl)methane and model compounds such as triphenylmelamine, triphenylisomelamine, and melamine.[11,20,88] The data obtained enabled the authors to postulate that the degradation of polymelamine proceeds not with the decomposition of the *sym*-triazine rings of the polymer but with formation of systems consisting of condensed *sym*-triazine rings.

The study of the character of the thermomechanical curves and of the regions corresponding to the useful employment of aromatic poly-

Table 1. The properties of bis(cyanamides) and the aromatic polymelamines based on them*.[94,99–102]

Initial bis(cyanamide) structure	T_m, °C	Network polymers: T_{def}, °C** 5%	T_{def}, °C** 15%	decrease in weight, %*** 400° C	500° C	700° C	Structure
	200—201	420	500	3	20	100	Amorphous
N≡C—NH—C_6H_4—O—C_6H_4—NH—C≡N	218—219	360	420	3	68	100	Amorphous
N≡C—NH—C_6H_4—CH_2—C_6H_4—NH—C≡N	162—163	410	520	1	13	100	Amorphous with signs of crystallinity
	$>T_{decomp}$	440	600	2 (3)	15 (13)	91 (22)	Ditto
	129—130	490	700	1.5 (1)	0 (5)	+3 (5)	»
	154—155	410	490	0.5	19	70	»
	76.5—77	390	460	2 (2)	30 (21)	86 (40)	Amorphous

*The degree of conversion of the cyanamide groups in all the polymers investigated was 90%.

**T_{def} is the temperature corresponding to deformations determined from thermomechanical curves (0.8 kgf cm^{-2} load, heating rate 80 K h^{-1}).

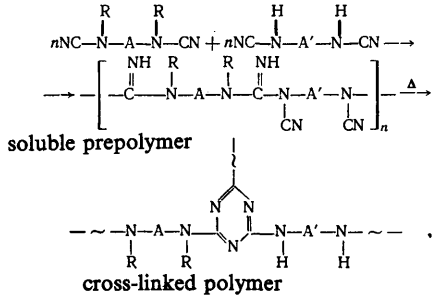
***According to TGA data in air (the values obtained in a helium atmosphere are given in brackets) on heating to the corresponding temperatures (heating rate 4.1 K min^{-1}).

melamines[11,84] showed that these polymers are characterised by a high heat resistance, which is limited by their thermal stability.

According to X-ray diffraction data, polymelamines have basically an amorphous structure, but a certain amount of order has been observed in some of them (Table 1), which is also characteristic of polycyanurates obtained by the polycyclotrimerisation of the dicyanoethers of bisphenols.[119,120] Thus the presence of a rigid three-dimensional network, formed during the synthesis, in these polymers is not an obstacle to the appearance of ordered structures. Bearing in mind that the ordering of the structure in close-network polmers after the formation of a network is unlikely, it has been suggested that the structures of such polymers are formed during their synthesis.[11,84]

It has been shown[8,11,59,84,85] (Table 2) that polymelamines are also characterised by good physicomechanical parameters. Some of the aromatic polymelamines obtained have been tested as binders for anti-friction materials. It has been demonstrated that these materials have a stable coefficient of friction in the temperature range 200–300 °C.[87]

The synthesis of copolymers based on primary and secondary aromatic bis(cyanamides) has also been achieved in accordance with the scheme



soluble prepolymer

cross-linked polymer

Di(4-aminophenyl)methane was chosen as the starting material for the synthesis of primary and secondary bis(cyanamides). The use of secondary bis(cyanamides) in combination with primary bis(cyanamides) enabled Kray[121] to reduce the rate of polymerisation and to obtain linear prepolymers which can be effectively processed in solution and in the melt. The prepolymers have been used as binders for glass and foam plastics and cast resins and as a base for honeycomb systems.

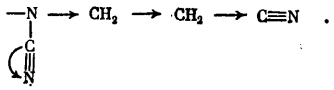
Table 2. Physicomechanical properties of aromatic network polymelamines.[99]

Initial arylbis(cyanamide)	σ_{comp}, kgf cm^{-2}	σ_i, kgf cm^{-2}	Ha_{Br}, kgf cm^{-2}	E_{comp} kgf cm^{-2}
4,4′-Bis(*N*-methylcyanamido)diphenylmethane	1300	1500	21	16 800
4,4′-Bis(*N*-methylcyanamido)diphenylmethane: 9,9′-bis(4-cyanamidophenyl)fluorene = 4:1 (molar ratio)	1600	1450	26	27 700
4,4′-Bis-(*N*-ethylcyanamido)diphenylmethane	1400	1350	23	17 600
4,4′-Bis(*N*-ethylcyanamido)diphenylmethane: 9,9′-bis(4-cyanamidophenyl)fluorene = 4:1 (molar ratio)	1900	1260	27	23 800

*Ha_{Br} is the Brinell hardness.

The characteristic features of the polycyclotrimerisation of cyanoethylated bis(cyanamides) of different chemical nature have been investigated.[72,91–94] The presence of the electron-accepting N ≡ C

group in the β-position relative to the nitrogen atom of the cyanamide group somewhat increases, compared with *N*-alkylcyanamides, the reactivity of the cyanoethylated bis(cyanamides):



The improvement of the thermal and physicomechanical properties of polymers based on cyanoethylated bis(cyanamides) has been explained by the possibility of additional cross-linking by virtue of the presence of nitrile groups. Thus the impact strength of these polymers is 4–9 kJ m^{-2}, the Brinell hardness is 310–320 MPa, and the density is 1230–1238 kg m^{-3}.[93]

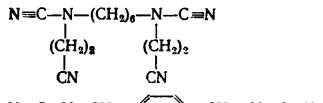
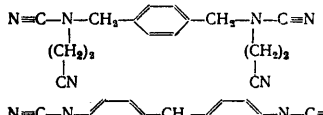
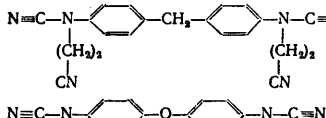
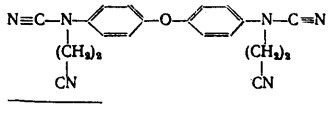
Bearing in mind the results of studies on model compounds, it has been suggested[91–94] that cyanoethylated bis(cyanamides) are polycyclotrimerised at 70–120 °C via the cyanamide groups, while the nitrile groups remain almost unchanged under these conditions. On raising the temperature (150–280 °C), the nitrile groups form polyconjugated



bonds.

Table 3 presents certain thermal characteristics of infusible and insoluble network polymers based on various cyanoethylated bis(cyanamides). The chemical nature of the internodal fragments has an appreciable influence on the properties of these polymers.[92–94]

Table 3. Cyanoethylated bis(cyanamides) and the thermal properties of the polymers based on them.[91–94]

Cyanoethylated bis(cyanamide)	Network polymers			
structure	T_m, °C	n_D^{20}	T_{def}, °C*	$T_{o.d.w.}$, °C**
	—	1.4625	264	200
	—	1.4338	324	200
	65—66	—	300	400
	81—82	—	220	390

*T_{def} is the temperature of the onset of deformation according to thermomechanical studies.

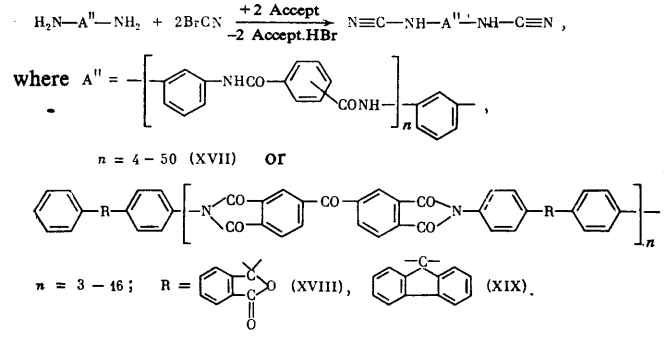
**$T_{o.d.w.}$ is the temperature of the onset of decrease in weight in air according to TGA data.

The high heat resistance and thermal stability as well as good physicomechanical parameters of the polymers obtained and the ability to polymerise without the evolution of volatile products have made it possible to use cyanoethylated bis(cyanamides) as adhesive compositions with heat resistance up to 250–300 °C.[92–94]

V. Polycyclotrimerisation of oligomers with N ≡ C–NH and N ≡ C–NR functional groups

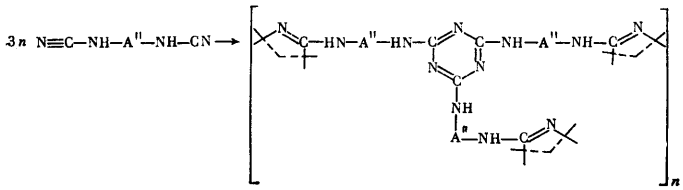
Some of the promising starting compounds for the synthesis of polymelamines by the polycyclotrimerisation reaction are oligomers containing cyanamide groups. Compared with monomeric unsubstituted bis(cyanamides) they have a lower concentration of functional groups and hence the rate of their polymerisation is lower. All these factors make it easy to monitor and to regulate their polycyclotrimerisation. The introduction of thermally stable fragments between the functional groups permits the synthesis of heat resistant and highly thermostable network polymers whose physicomechanical properties can be regulated by altering the length and nature of the oligomer chains.

The synthesis of the oligomers and their polycyclotrimerisation were first studied systematically and the properties of network polymers based on oligobis(cyanamides) were first investigated in Refs. 90, 95–108, 122, and 123. Korshak and co-workers[95–108] synthesised oligomeric bis(cyanamides) by the interaction of oligomers containing terminal NH_2 groups with bromocyanogen in *NN*-dimethylacetamide, which plays the role of both the solvent and the acceptor of the hydrogen bromide evolved, in accordance with the scheme



The properties and certain characteristics of the compounds obtained are presented in Table 4. It is seen from these data that oligomeric bis(cyanamides) have lower softening temperatures than their high-molecular-weight analogues.[124]

Polymelamines differing in the size and chemical nature of the internodal fragments have been synthesised by the polycyclotrimerisation of oligomeric bis(cyanamides) in accordance with the scheme



where A″ are oligomers having the structure shown in Table 4.[90,95–108]

The polycyclotrimerisation of oligoamidobis(cyanamides) was investigated by IR spectroscopy in relation to the oligomer with $n = 4$. The gradual decrease in the intensity of the absorption band of the N–C–NH groups was observed in the course of the polycyclotrimerisation of this compound and was accompanied by the appearance

of absorption bands in the region of 810 and 1560 – 1580 cm^{-1} referring to the vibrations of the *sym*-triazine ring.[105]

Since the concentration of the functional cyanamide groups per unit volume of the reaction system diminishes with increase in the molecular weight of the initial oligomeric bis(cyanamide), it is almost impossible to investigate in this way the cyclotrimerisation process by IR spectroscopy for oligomeric bis(cyanamides) with a higher molecular weight ($n > 10$). The influence of factors such as temperature, reaction time, pressure, and other conditions in processing by compression pressing on the polycyclotrimerisation of oligomeric bis(cyanamides) was therefore monitored from the yield of the gel-fraction of the polymers formed. The study was performed in relation to the oligoaminobis(cyanamide) with $n = 25$ (Table 4).[90,97,98,103,105] The authors recommend that the oligomeric bis(cyanamides) be processed by compression pressing at 320 °C and a pressure of 60 kgf cm^{-2}. The polymers based on other oligoamidobis(cyanamides), synthesised under the given conditions, contain between 93 and 99% of the gel-fraction depending on the length of the oligoamide chain between the cyanamide groups.

Table 4. The properties of oligomeric bis(cyanamides) and the polymelamines based on them.[90,95–108]

n	Initial oligomer		Network polymers		
	T_{soft}, °C*	M_n, found/calc.	content of gel fraction, %	$T_{o.d.w.}$** in air, °C	$T_{o.d.w.}$** in Ar, °C
			(XVII)		
4	280	1 000 / 1 110	99	410	410
7	280	2 000 / 1 828	98	405	—
12	280	3 000 / 3 014	98	400	400
17	280	4 000 / 4 205	98	400	—
25	290	6 000 / 6 108	97	400	—
50	290	12 000 / 12 034	93	400	400
			(XVIII)		
3	230	2 000 / 2 172	98	500	505
6	240	4 000 / 3 978	97	495	—
10	240	6 000 / 6 384	93	495	500
12	245	8 000 / 7 590	92	490	—
16	250	10 100 / 9 998	90	490	500
			(XIX)		
3	280	2000 / 2300	98	500	—

*T_{soft} is the softening temperature determined from thermomechanical curves.
**$T_{o.d.w.}$ is the temperature of the onset of decrease in weight according to TGA data.

The study of the rheological properties of oligoamidobis(cyanamide) melts subjected to a variable load on a capillary viscometer (Table 5) showed that these oligomers are promising materials, capable of being processed by casting under pressure.[98,99]

It has been found[97] that the deformational heat resistance of polymelamines based on oligoamidobis(cyanamides) depends on the size of the internodal network fragment, i.e. on the density of the network. For example, polymelamine based on oligoamidobis(cyanamide) with $n = 4$ softens in the same region as the high-molecular-weight aromatic polyamide with an analogous structure, while the cross-linked polymer has a softening temperature lying above the temperature of the onset of chemical decomposition.

Table 5. The properties of oligoamides with terminal NH_2 groups (a) and of oligoamidobis(cyanamides) (XVII) based on them (b).[98,99]

n	M_n^*	η_{eff}**, P	
		a	b
4	1 000	$0.16 \cdot 10^5$	$0.30 \cdot 10^5$
17	4 000	$0.32 \cdot 10^6$	$0.53 \cdot 10^6$
25	6 000	$0.45 \cdot 10^7$	$0.58 \cdot 10^7$
50	12 000	$0.16 \cdot 10^{10}$	$0.49 \cdot 10^6$

*From terminal NH_2 groups.
**η_{eff} is the effective viscosity of the melt at 320 °C and 6.7×10^7 dyn cm^{-2}.

For a more detailed investigation of the heat resistance of polymelamines, the regions corresponding to their useful employment have been determined for a number of them over a wide temperature range and over a wide range of mechanical stresses. It has been shown that the heat resistance of polymelamines depends on the molecular weight of the internodal network fragment, i.e. on the density of the network. Thus the polymelamine based on oligoamidobis(cyanamide) with $n = 4$ can be used at high mechanical stresses and temperatures in contrast to the other polymers investigated.[97]

Data obtained by dynamic thermogravimetric analysis in air (Table 4) show that the onset of the decrease in the weight of polymelamines based on oligoamidobis(cyanamides) is restricted to a fairly narrow range (400 – 410 °C). However, with increase in the density of the network, i.e. with decrease in the molecular weight of the internodal polymelamine fragments, the onset of the decrease in weight shifts towards higher temperatures.

A comparative study of the thermal stabilities of polymelamines in air and in an inert atmosphere has also been carried out. It has been shown that the temperature of the onset of the decrease in the weight of polymelamines in an inert atmosphere is in the same temperature range as in air. However, whereas in air polymelamine decomposes fully at 700 °C, in an inert atmosphere the amount of coke residue is 60 – 72%.[90,95–108]

The synthesis of polymelamines by the polycyclotrimerisation of bis(cyanamides) tends to form regularly cross-linked thermostable and heat resistant polymers. The polycyclotrimerisation of bis(cyanamides) is characterised by a high selectivity and a high degree of conversion of the cyanamide groups, which is nearly quantitative. The internodal fragments of these polymers are residues of the initial bis(cyanamides).[95–108]

The experimental and theoretically calculated structural parameters of polymelamines based on oligoaminobis(cyanamide) have been compared.[97] The method based on the statistical theory of high elasticity was used to calculate the parameters of the network structure of the polymelamine based on oligobis(cyanamide) with $n = 25$.[97] The experimental number-average molecular weight of the active chain (M_{ce}) and the concentration of the active chains per unit volume of the cross-linked polymer $(V_c/V)_{exp}$ were evaluated from the equilibrium modulus of elasticity E in extension.

Table 6. Parameters of the network structure of the polymelamine based on the oligoamidobis(cyanamide) (XVII).[97]

n	$M_{c\,exp}$, g mol^{-1}	$M_{c\,theor}$, g mol^{-1}	$10^{-4}(V_c/V)_{exp}$, mol cm^{-3}	$10^{-4}(V_c/V)_{theor}$, mol cm^{-3}	$\frac{(V_c/V)_{exp}}{(V_c/V)_{theor}}$
25	5260	6000	2	2.1	0.95

Table 7. Physicomechanical properties of the polymelamines based on oligoamidobis(cyanamides)[97] and oligoimidobis(cyanamides).[107]

n	M_c	Impact strength, kJ m^{-2}	Ha_{Br}*, MPa	σ_i, MPa
		(XVII)		
4	1 000	10	340	80
7	2 000	13	330	95
12	3 000	15	315	116
17	4 000	16	310	120
25	6 000	20	300	128
50	12 000	24	300	145
		(XVIII)		
3	2 000	3	290	80
6	4 000	3	280	82
10	6 000	5	275	85
12	8 000	8	270	92
16	10 000	11	260	110
		(XIX)		
3	2000	3	290	84

*Ha_{Br} is the Brinell hardness.

Table 6 shows, in relation to the polymelamine based on the oligoamidobis(cyanamide) with $n = 25$, that the experimental quantities are virtually identical with the theoretically calculated values, which shows that the degree of completion of the polycyclotrimerisation reaction is nearly quantitative and that the cross-linked polymer formed contains an oligoamide with $n = 25$ as the internodal fragments.[97]

The packing coefficients K have been calculated for certain polymelamines based on oligoamidobis(cyanamides). It was found that the polymelamines have a packing coefficient (0.680–0.690) close to the value determined earlier for linear amorphous polymers ($K = 0.681$).[125] Presumably the polymelamines based on oligoamidobis(cyanamides) are just as close-packed as linear amorphous polymers regardless of the value of M_c.[97]

In order to elucidate the possibility of synthesising polymelamines with specified properties by varying the length of the chain in the initial oligoamidobis(cyanamides) and oligoimidobis(cyanamides),[97,107] the influence of the molecular weights of the internodal fragments on certain physicomechanical characteristics of polymelamines has been studied (Table 7).

The dependence of the electrically insulating properties of the oligoamidobis(cyanamide)-based polymelamines on the effect of temperature, ageing time at different temperatures, and the influence of tropical moisture has been investigated.[100,106,107] Thus the electrically insulating properties of polymelamines based on the oligoamidobis(cyanamides) with $n = 50$ have been investigated as a function of the thermal ageing time at 200° and 250 °C.[100] The studies showed that, after the thermal ageing at 200° and 250 °C for 30 days, the electrically insulating properties of the polymelamines do not change signficantly (Table 8) and that various heat resistant and thermostable articles, used in the electrotechnical industry, can be manufactured from these polymers.

Table 8. Dependence of the electrically insulating properties of the polymelamine based on the oligobis(cyanamide) (XVII) ($n = 50$) on the ageing time.[100]

Conditions	T=200° C			T=250° C			E_{br}, kV mm^{-1}
	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm	
Initial state	0.004	3.3	3	0,004	3.3	3	30
After ageing for							
10 days	0.004	3.6	2	0.004	4.6	5	—
20 days	0.003	3.4	3	0.006	5.1	2	—
30 days	0.004	3.7	1	0.008	5.2	2	25

*At a frequency of 1 MHz.

Table 9. Dependence of the electrically insulating properties of polymelamine based on the oligoamidobis(cyanamide) (XVII) ($n = 50$) on the effect of tropical moisture (38 °C, 98% relative humidity).[107]

Duration of exposure	tan δ*	ε*	$10^{-15}\rho_V$, Ω cm
Initial state	0.004	3.2	3
After exposure to tropical moisture for 10 days	0.007	3.7	8
30 days	0.02	3.7	8

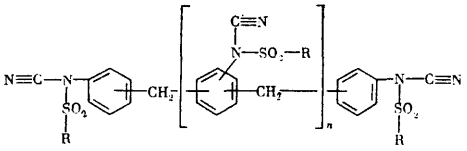
*At a frequency of 1 MHz.

It has been found[100] that the electrically insultating properties of polymelamines based on the oligoamidobis(cyanamide) with $n = 50$ do not change when the polymers are used under the conditions of a tropical climate. The results of these studies are presented in Table 9. Thus the authors[100,106,107] note that the polymelamines investigated exhibit a high heat resistance and thermal stability and have good physicomechanical and electrically insulating parameters at an elevated temperature and under the conditions of a tropical climate and are therefore promising materials for practical use.

Polymelamines, especially aromatic polymelamines, are in most cases highly heat resistant thermostable polymers obtained from a readily available raw material, exhibit an effective adhesion to various materials, and can be readily converted into articles without the evolution of volatile substances.

The preparation of oligomers containing cyanamide groups has been described in a number of studies.[126–128] The authors[126,128] achieved the synthesis of the oligomers by condensing an excess of various diamines with cyanuric chloride, phosphorus trichloride, and phosphoryl chloride. Next the terminal amino-groups were treated with chlorocyanogen in order to obtain cyanamides. The thermoreactive oligomers obtained were cyclotrimerised by the cyanamide groups to prepare heat resistant binders in composite materials.[126–128]

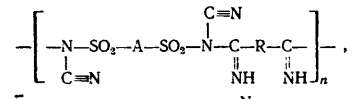
The preparation of α-cyanosulphonamide oligomers having the general formula



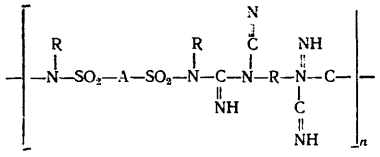
has been described in patents.[129–131] When these thermoreactive oligomers are hardened at 235 °C for 30 min, non-combustible heat resistant polytriazines with T_g = 275 °C are formed;[129] according to differential scanning calorimetric data, the heat of polymerisation is 60–63 cal g^{-1}.[130] The weight losses by the specimen of the composite material based on these oligomers (R = Ph, fillers—fused silica, glass fibre with a fibre length of 6 mm) are respectively 0.32, 0.57, and 4.38% after heating for 500 h at 200°, 225°, and 250 °C.[131]

Oligomeric aromatic polysulphones[132] and polyphosphazenes[133] containing cyanamide groups, and also copolymers of diallylcyanamide with vinyl monomers[134] have been described. Network polymers based on them are obtained by the cyclotrimerisation of the cyanamide groups.

Oligomers having the general formula



(Ref.135)

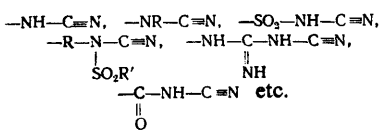


(Ref.136)

have been obtained by the copolymerisation of bis(*N*-cyanosulphonamides) with various bis(cyanamides).[135,136] These thermoreactive polymers, which can be effectively moulded in the melt, are hardened with formation of highly thermostable network polytriazines.

VI. Polymers based on cyanamides

Data are available, mainly of a patent character, for linear and network polymers based on various monomers with the following functional groups:



The polymers have been obtained by the copolymerisation of these monomers with bis(maleic amides),[137,138] diamines,[139–143] ε-caprolactone,[144] nitriles,[145] diamine salts,[146–148] triallyl cyanurate,[149] cyanates,[150–155] and phenols.[156]

There is also information in the patent literature about polymers obtained as a result of the interaction of cyanamides having different sructures with polyamidoacids, polybenzimidazoles, polyquinoxalines, polybenzothiazoles, polyamides, poly(aryl sulphones), and poly(phenylene sulphides), all containing terminal NH_2 groups,[157] and also as a result of reactions with unsaturated polyethers,[158] polybuta-1,2-diene with a molecular weight of 1000–200 000,[159] butadiene–acrylonitrile copolymers,[160] partly cyanomethylated polystyrene,[161] and polyethyleneimine.[162] Network polymers containing oxazolidine fragments are obtained by the reactions of cyanamides with various epoxides.[163–171]

Various cyanamide-based polymers have found applications as binders for filled plastics,[11,59,61,76,84–86,110,111,121,137,138,140,141,158–160,172,173] adhesives,[11,59,61,76,77,81,84–87,109–111] coatings,[11,26,59,61,76,77,81,84–86,109,113,154] films,[26,77,81,86,113,139] and fibres.[75,77,79,113] It has been suggested that polymers based on compounds containing cyanamide groups be used to prepare various thermostable materials—ion-exchange resins,[142,143] electrically insulating materials,[149,158–160,173] cast articles,[11,26,59,61,84,85,109,113,121] and materials for electronic engineering.[174]

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